Study on the Mechanism of the Effect of Temperature on the Decomposition Reaction of SF$_n$ (n=1-6) under Discharge Conditions

Minghao Yang, Jing Yan*, Mengyuan Xu, Yingsan Geng, Zhiyuan Liu and Jianhua Wang

Author to whom correspondence should be addressed: yanjing@mail.xjtu.edu.cn

State Key Laboratory of Electrical Insulation and Power Equipment
Xi’an Jiaotong University
Xi’an, P. R. China

ABSTRACT

The study on the mechanism of the effect of temperature on the decomposition reaction of SF$_n$ (n=1-6) under discharge conditions is very important in studying the potential fault of SF$_6$ high voltage switch equipment and perfecting the chemical kinetic model of SF$_6$ discharge. In this paper, structural optimizations, vibrational frequency calculations, and zero-point energy calculations for the reactants and products were performed at the B3LYP/6-311++G(d,p) theory level. The single-point energies of all species were collected at the CCSD(T)/aug-cc-PVTZ level. The electric and thermal decomposition mechanism of SF$_n$ under discharge conditions of 298K–10000K were studied, respectively. The conclusion drawn was that in the temperature range of 298–10000K, the thermal decomposition homolytic reaction $\Delta G$ began to decline from 200 kJ/mol, while the $\Delta G$ of the other two heterogenous reactions began to decrease from 1000 kJ/mol and 2000 kJ/mol, showing a downward trend of an almost similar slope. The electrolysis of SF$_n$ is related to the electron energy. When the electron energy is low, SF$_n$ + e→SF$_n^-$ series reactions occur, and $\Delta G$ of R12, R20, R28, R36, R44 increases with temperature rise, while $\Delta G$ of R4 decreases with temperature. When the electron energy is high, one of SF$_n^-$→SF$_{n-1}^- + F$, SF$_n^-→$SF$_{n-1}^- + F$ and SF$_n^-→$SF$_{n-1}^- + F + e$ will occur, and the reactions that occur at various temperature ranges as the temperature rises vary. When the second electron hits the SF$_n^-$, the SF$_n^- + e→$SF$_{n-1}^- + F$ reaction will occur. The $\Delta G$ of this reaction slowly decreases with an increase in temperature. This study in clearer terms explains the decomposition process and mechanism of SF$_n$ at different temperatures.

Keywords: gibbs free energy change, electronic impact, quantum chemistry, reaction mechanism

INTRODUCTION

SF$_6$ high voltage switch equipment has a number of advantages. These include small size, high safety, and long maintenance period. With the improvement of power system voltage level, SF$_6$ high voltage switch equipment use has drastically grown. SF$_6$ is a colorless, tasteless, non-toxic, non-flammable stable gas. Because of its good electron affinity, thermodynamic stability and good dielectric property, it is commonly used as insulating medium and arc extinguishing medium for gas insulated equipment. However, when partial discharge or arc discharge occurs in the equipment, SF$_6$ gas will decompose on reacting with heat and electricity and form neutral low-flourine fluorsulfur species, such as SF$_5$, SF$_4$, SF$_3$, SF$_2$, SF, and anions SF$_6^-$, SF$_5^-$, SF$_4^-$, SF$_3^-$, etc. Most of the low-fluorine sulfides (99.9%) will react with F atoms to regenerate SF$_6$ in a very short period of time. But a small part will
react with trace amount of water and oxygen inside the equipment in a series of complex chemical reactions, and finally produce SOFs, SOF₂, SO₂F₂, HF, SO₂, CF₄, CO₂, CS₂ and other by-products. As much as these products reduce the purity of SF₆ gas and affect its insulation and arc extinguishing performance, they also corrode the metal parts and solid insulating materials in the equipment, lowering the durability of the equipment. On the other hand, the components and contents of some characteristic products can be utilized in evaluating the deterioration of the metal and solid insulating materials in the equipment, and to identify the discharge defects in the equipment.

Many scholars have done a lot of research on the decomposition products of SF₆ under discharge conditions. Local overheating is an important cause of decomposition of SF₆ molecule. Wilkins found through experimental research that at a temperature 1500K, the main decomposition product of SF₆ gas is SF₄. W·Frie used the counter ion concentration calculation method to roughly estimate the number of equilibrium particles in SF₆ plasma at various temperatures. It was found that when the temperature of SF₆ gas was higher than 1500K, its concentration was significantly minimal, and the SF₄ concentration and F atoms would rise rapidly. At temperatures higher than 4000K, most of the SF₆ molecules would be completely decomposed, but the decomposition mechanism has not been further studied. Under arc discharge, electron collision is another key factor affecting the decomposition of SF₆ molecules. As early as 1953, AJ Ahearn et al. discovered that the main products of SF₆ molecules ionized by electron impact in vacuum are SF₆⁻, SF₅⁻ and F plasma. Wiggart N and Wang Y et al. believed that SF₆ was a strongly electronegative gas, which if combined with electrons would form metastable molecular group (SF₆)*. After a very short time, the molecular group will further generate SF₅⁻, SF₄⁻, F and other anions. On further increase to the electron energy, SF₃⁻, SF₂⁻ and other anion low-fluoride sulfide may be formed. Ziegler et al. theoretically studied the decomposition process of anion low-fluoride sulfide, and found that further decomposition of SF₅⁻, SF₄⁻, SF₃⁻, SF₂⁻, SF⁻ and other anions would lead to a formation of a lower level of neutral low-fluoride sulfide molecule and an F⁻ anion, but he did not take a keen note on the process in which electrons participate in the reaction. Fifen found that the thermodynamic data of electrons would vary greatly with temperature change, and he corrected the thermodynamic data of 0–10000K through algorithm iteration. Wang et al. studied the particle compositions of an SF₆ arc using a two-temperature chemical kinetics model. The chemical reaction system consists of 18 particles, and 63 chemical reactions are taken into consideration. But they did not consider the effect of temperature change on the reaction, and did not include reactions involving SF₂⁻ and SF₃⁻. The chemical reaction equation was incomplete.

Early research mainly focused on the qualitative analysis of the types of SF₆ gas decomposition products. The thermal decomposition mechanism and electron impact decomposition mechanism of SF₆ at different temperatures has not been systematically studied. This paper systematically combs the decomposition process of SF₆ discharge decomposition products in different temperature ranges, and gives a detailed explanation of the decomposition process of SF₆ at different temperatures. In addition, it has certain guiding significance for a further study on the reaction of SF₆ with micro water and micro oxygen at different temperatures. This paper
uses quantum chemistry theory to systematically comb the decomposition products and processes of SF$_n$ at a temperature of 298–10000K. The second part describes the calculation method, and the third part provides the results and discussion. In addition, this article also has certain reference significance for establishing a complete arc plasma model.

2 CALCULATION METHOD

In this paper, quantum chemistry method is used to find out the reaction mechanism of SF$_n$ ($n = 1–6$) under overheating and electron impact conditions under discharge conditions. Table 1 lists all the reaction equations in this paper. It is divided into two types of processes: overheating decomposition and electron impact decomposition. Taking the decomposition of SF$_6$ as an example, R1 is the process of covalent bond homolysis resulting from overheating, R2 and R3 are the process of covalent bond heterolysis, R4 and R8 are electron capture process while R5, R6, and R7 are decomposition processes resulting from R4.

Table 1. All reaction equations in this paper

| Serial number | Chemical reaction |
|---------------|-------------------|
| R1            | SF$_6$→SF$_3$ + F |
| R2            | SF$_6$→SF$_5^+$ + F$^+$ |
| R3            | SF$_6$→SF$_4$ + F$^+$ |
| R4            | SF$_6$ + e→SF$_6^-$ |
| R5            | SF$_6$→SF$_5$ + F |
| R6            | SF$_6$→SF$_3$ + F |
| R7            | SF$_6$→SF$_3$ + F + e |
| R8            | SF$_6^-$ + e→SF$_5^-$ + F$^-$ |
| R9            | SF$_3$→SF$_4$ + F |
| R10           | SF$_3$→SF$_4^+$ + F$^+$ |
| R11           | SF$_3$→SF$_4$ + F$^+$ |
| R12           | SF$_3$ + e→SF$_3^-$ |
| R13           | SF$_3$→SF$_4$ + F |
| R14           | SF$_3$→SF$_4$ + F |
| R15           | SF$_3$→SF$_4$ + F + e |

R16 SF$_5^-$ + e→SF$_4^-$ + F$^-$
R17 SF$_4$→SF$_3$ + F
R18 SF$_4$→SF$_3^+$ + F$^+$
R19 SF$_4$→SF$_3$ + F$^+$
R20 SF$_4$ + e→SF$_4^-$
R21 SF$_4$→SF$_3$ + F
R22 SF$_4$→SF$_3$ + F
R23 SF$_4$→SF$_3$ + F + e
R24 SF$_4$ + e→SF$_3^+$ + F$^+$
R25 SF$_3$→SF$_2$ + F
R26 SF$_3$→SF$_2^+$ + F$^+$
R27 SF$_3$→SF$_2$ + F$^+$
R28 SF$_3$ + e→SF$_3^-$
R29 SF$_3$→SF$_2$ + F
R30 SF$_3^-$→SF$_2$ + F
R31 SF$_3$→SF$_2$ + F + e
R32 SF$_3$ + e→SF$_2$ + F$^+$
R33 SF$_2$→SF + F
R34 SF$_2$→SF$^+$ + F$^+$
R35 SF$_2$→SF$^+$ + F$^+$
R36 SF$_2$ + e→SF$_2^-$
R37 SF$_2$→SF + F
R38 SF$_2$→SF + F
R39 SF$_2$→SF + F + e
R40 SF$_2^-$ + e→SF + F$^-$
R41 SF→S + F
R42 SF→S$^+$ + F$^+$
R43 SF→S$^+$ + F$^+$
R44 SF + e→SF$^-$
R45 SF→S + F
R46 SF→S + F
R47 SF→S + F + e
R48 SF$^+$ + e→S$^-$ + F$^-$

Table 2. Entropy, enthalpy and Gibbs free energy of gaseous electrons

| T (K) | S (J/mol) | H (kJ/mol) | G (kJ/mol) |
|-------|-----------|------------|------------|
| 298.15 | 22.6432  | 3.1351     | -3.616     |
| 300    | 22.7491  | 3.1659     | -3.6588    |
| 350    | 25.4629  | 4.0467     | -4.8653    |
| 400    | 27.9153  | 4.9654     | -6.2008    |
| 450    | 30.1427  | 5.9111     | -7.6531    |
All the calculations of quantum chemistry in this study are completed in Gaussian 09. Gaussian 09 is currently the most popular and powerful quantum chemical calculation software. So as to predict the accuracy of the outcome, the article uses M06-2X/def2-TZVP level and B3LYP/6-31G(d) level and B3LYP/6-311++G(d, P) level for verification and comparison. The above levels were used to optimize the structure of reactants and products, and calculate the vibration frequency and zero-point energy. Thermodynamic data consists of the sum of single point energy and thermal correction. Because the calculation of the thermal correction does not require a high level of calculation to get a very accurate result. The thermal correction was obtained at the B3LYP/6-311++G(d, p) level. Single point energy requires a high level of calculation to get accurate results, so single-point energy calculation was done at the CCSD(T)/aug-cc-PVTZ level. To ensure accuracy in the calculated outcome, the frequency vibration factor is considered. When using the B3LYP/6-311++G(d, p) level, the frequency vibration factor is 0.967.

Because of some limitations of Gaussian 09 in obtaining thermodynamic data, this paper used the KisTheIP to obtain thermodynamic data of all structures at 298–10000K. KisTheIP is a program renown for calculating chemical reaction rates and thermodynamic data. It has many functions which include calculating thermodynamic data, calculating reaction equilibrium constants, calculating the reaction rate constants of single or bimolecular reactions by TST or VTST methods, and some more. For the record, KisTheIP cannot get the thermodynamic data of electrons. The thermodynamic data of electrons used in this paper uses the thermodynamic data mentioned in the Fifen’s article as shown in Table 2, and is derived to by fitting the cubic spline difference. The Gibbs free energy of gas phase electrons changes with temperature as shown in Figure 1. After obtaining the thermodynamic data of all the structures, ΔG of all the reactions in this paper was got by subtracting G of the reactants from G of the products. For example, at 298K, for the reaction SF$_6$→SF$_5$ + F in Table 3, the G of the reactant SF$_6$ is -996.1496484Hartree, the G of the product SF$_5$ is -896.3641003Hartree, the G of F is -99.64262951Hartree, the ΔG of this reaction is:

$$
\Delta G = (-996.3641 - 99.6426 + 996.1496484) \times 2625.5 = 375.2 \text{kJ/mmol}
$$

Calculate the ΔG of all reactions in the temperature range of 298-10000K, and get the curve in Figure 3-10.
3 RESULTS AND DISCUSSION

3.1 STRUCTURAL OPTIMIZATIONS AND ENERGIES

The optimized structure of reactants and products in reaction R1-R48 is displayed in Figure 2. In this paper, structural optimization was performed at the B3LYP/6-311++G(d,p) level of theory. The optimized structure of all neutral reactants and products was compared with the experimental geometric data in the NIST database and the outcomes of other theoretical calculations (B3LYP/6-31g (d)) \(^{18}\). The structural parameters of all reactants and products coincide with the literature of Tom Ziegler and Cheung \(^{2,16}\). The key structural parameters are shown in Figures 2. The B3LYP/6-311++G(d, p) level not only provides excellent computing accuracy, but also significantly saves computing resources. In comparison to the experimental data, the bond angle error of all structures was <0.1 Å, and the bond length error of all structures was <2.6°. The error mainly results from the difference of theoretical level.

Table 3. \(\Delta G\) of reactions at 298, 5000, and 10000K temperatures

| Chemical reaction | 298K | 5000K | 10000K |
|-------------------|------|-------|---------|
| \(\text{SF}_6\rightarrow\text{SF}_5 + F\) | 375.2 | -434.3 | -1274.0 |
| \(\text{SF}_6\rightarrow\text{SF}_5^+ + F\) | 1004.3 | 334.5 | -353.0 |
| \(\text{SF}_6\rightarrow\text{SF}_5^+ + F^+\) | 1913.5 | 1010.7 | 70.0 |
| \(\text{SF}_6 + e\rightarrow\text{SF}_6^-\) | -126.1 | -246.5 | -255.5 |
| \(\text{SF}_6\rightarrow\text{SF}_5^- + F\) | 105.2 | -410.4 | -933.3 |
| \(\text{SF}_6\rightarrow\text{SF}_5^- + F^-\) | 187.1 | -181.1 | -545.4 |
| \(\text{SF}_6\rightarrow\text{SF}_5 + F + e\) | 501.3 | -187.8 | -1018.5 |
| \(\text{SF}_6^- + e\rightarrow\text{SF}_5^- + F\) | -209.0 | -403.6 | -460.3 |
Table 3, we can roughly see the trend of the $\Delta G$ of reactions with the change of temperature, which is more clearly compared with Figure 3-10. The $\Delta G$ is in kJ/mol in Table 3.

### 3.2 REACTION MECHANISMS

During the installation and operation of SF$_6$ high voltage switchgear, electrode surface burrs, free conducting particles and suspension potential may exist in the equipment, leading to partial discharge or overheating in the equipment, making the gas temperature near the fault center higher compared to the ambient temperature. Under the parameters of arc and spark discharge, the decomposition of SF$_6$ mostly results from electron impact or high temperature. Under partial discharge and corona discharge, SF$_6$ dissociation is as a result of electron collisions in the discharge area due to low temperature. In this paper, the influence of different temperature on SF$_6$ decomposition reaction is considered, and Gibbs free energy is utilized in the analysis of each reaction.

#### 3.2.1 Thermal decomposition of SF$_6$ (n = 1–6) under overheating conditions

The SF$_6$ discharge decomposition reaction equation of SF$_6$ high voltage switchgear is shown in Table 1. As Table 1 displays, the decomposition of SF$_6$ is the process of S-F bond breaking in its molecular structure to form free radicals. The thermal decomposition process of SF$_6$ may be directly decomposed into SF$_3$ and F atoms, or heterocracking of covalent bonds may lead to formation of SF$_3^+$, F, or SF$_3^-$, F$^-$. Figure 3 shows the change of $\Delta G$ of R1, R2, and R3 at the temperature of 298–10000K. Figure 3 shows that the $\Delta G$ of R1-R3 decreases linearly with the increase of temperature. The $\Delta G$ of R1 at 298K is 375.2kJ/mol. When the

| Reaction | $\Delta G$ (kJ/mol) |
|----------|---------------------|
| SF$_3$→SF$_4$ + F | -53.4 | -867.5 | -1712.1 |
| SF$_3$→SF$_4^+$ + F | 936.2 | 309.1 | -333.3 |
| SF$_3$→SF$_4^+$ + F$^+$ | 1884.6 | 1097.6 | 281.8 |
| SF$_3$ + e→SF$_3^-$ | -396.1 | -222.5 | 85.2 |
| SF$_3$→SF$_4$ + F | 346.4 | -347.5 | -162.2 |
| SF$_3$→SF$_4$ + F | 215.9 | -267.7 | -756.0 |
| SF$_3$→SF$_4$ + F + e | 530.1 | -274.4 | -1229.1 |
| SF$_3$ + e→SF$_3^-$ | 32.2 | -340.7 | -589.2 |
| SF$_4$→SF$_3$ + F | 372.6 | -300.6 | -993.6 |
| SF$_3$→SF$_4$ + F | 1120.3 | 590.6 | 52.6 |
| SF$_4$→SF$_3$ + F | 203.3 | -291.2 | -792.3 |
| SF$_3$→SF$_3$ + F | 242.1 | -220.8 | -687.4 |
| SF$_4$→SF$_3$ + F + e | 556.3 | -227.6 | -1160.4 |
| SF$_4$ + e→SF$_3$ + F | -110.9 | -284.4 | -319.3 |
| SF$_3$→SF$_2$ + F | 819.6 | 329.8 | -165.8 |
| SF$_3$→SF$_2$ + F | 1445.5 | -371.7 | -896.4 |
| SF$_3$→SF$_3^+$ + F | 2007.5 | 1568.5 | 1149.4 |
| SF$_3$ + e→SF$_3^+$ | -353.0 | -63.6 | 368.1 |
| SF$_3$→SF$_2$ + F | 426.1 | -35.5 | -477.6 |
| SF$_3$→SF$_2$ + F | 183.3 | -301.4 | -791.4 |
| SF$_3$→SF$_2$ + F + e | 497.5 | -308.1 | -1264.5 |
| SF$_3$ + e→SF$_3$ + F | 1119.9 | -28.8 | -4.5 |
| SF$_2$→SF + F | 303.5 | -223.3 | -784.7 |
| SF$_2$→SF$_3$ + F | 1117.2 | 657.3 | 167.5 |
| SF$_2$→SF$_3$ + F | 2033.3 | 1544.5 | 1023.0 |
| SF$_2$ + e→SF$_3$ | -71.4 | 272.6 | 786.9 |
| SF$_2$→SF + F | 1703.9 | -395.7 | -1022.8 |
| SF$_2$→SF + F | 60.7 | -489.1 | -1098.5 |
| SF$_2$→SF + F + e | 374.9 | -495.9 | -1571.6 |
| SF$_2$ + e→SF + F$^-$ | 64.3 | -191.6 | -363.6 |
| SF→S + F | 302.9 | -173.1 | -705.6 |
| SF→S$^+$ + F$^-$ | 1172.5 | 739.5 | 252.7 |
| SF→S + F$^+$ | 2053.8 | 1620.8 | 1134.0 |
| SF + e→SF$^-$ | -204.6 | 100.2 | 548.8 |
| SF→S$^+$ + F | 324.1 | -147.0 | -673.7 |
| SF→S$^+$ + F | 193.2 | -266.6 | -781.3 |
| SF→S + F + e | 507.4 | -273.3 | -1254.4 |
| SF + e→S$^+$ + F | 9.9 | -140.2 | -200.6 |

Table 3 shows the $\Delta G$ of all reactions at 298K, 5000K, and 10000K. From the data in
temperature reaches about 2450K, $\Delta G$ falls below 0kJ/mol, and the reaction can proceed spontaneously. When the temperature reaches 10000K, $\Delta G$ drops to $-1274$kJ/mol. The $\Delta G$ of R2 at 298K is 1004.3kJ/mol, when the temperature reaches about 7400K, the $\Delta G$ of reaction can drop below 0kJ/mol, when the temperature reaches 10000K, $\Delta G$ is 70kJ/mol, and it does not drop below 0kJ/mol. Therefore, for the thermal decomposition process of SF$_6$, R1 is most likely to occur within the temperature range of 298–10000K.

The thermal decomposition process of SF$_5$ may directly decompose SF$_4$ and F atoms, or the covalent bond may heterocrack to produce SF$_4^+$, F$^-$, or SF$_4^-$, F$^+$. The SF$_5$ thermal decomposition $\Delta G$ changes with temperature as Figure 4 shows. It can be seen from Figure 4 that $\Delta G$ of R9-R11 also decreases linearly with the temperature rise. During the thermal decomposition of SF$_5$, the $\Delta G$ of R9 at 298K is $-53.4$kJ/mol, when the temperature reaches 10000K, the $\Delta G$ decreases to $-1712.1$kJ/mol. The $\Delta G$ of R10 at 298K is 936.2kJ/mol, when the temperature reaches about 7400K, $\Delta G$ drops below 0kJ/mol, and the reaction can be spontaneous. When the temperature reaches 10000K, $\Delta G$ drops to $-333.3$kJ/mol. The $\Delta G$ of R11 at 298K is 1884.6kJ/mol, when the temperature reaches 10000K, $\Delta G$ decreases to 281.8kJ/mol. Therefore, for the thermal decomposition process of SF$_5$, R9 will most probably occur within the temperature range of 298–10000K.

From the above analysis, it can be seen that $\Delta G$ of SF$_n$ displayed similar thermal decomposition rules within the temperature range of 298–10000K, and there was a decrease in energy required for the reaction as the temperature increased. Moreover, the energy required for the homolytic reaction is far less than the other two heterolytic reactions, so the homolytic reaction is most probable to take place. This is because SF$_n$ and F are both highly electronegative molecules. It is very hard for each molecule to lose electron and need to absorb a lot of energy. In addition, the same is the heterolytic dissociation, the reactions R2 and R10 can proceed spontaneously as the temperature increases, but the reactions R3 and R11 still cannot proceed spontaneously at very high temperatures. This is because the electronegativity of F is greater than that of SF$_n$ (n=1-5), so the stability of SF$_n^+$ in the product is better than F$^+$ 19. The reaction process curve and mechanism of other reactants SF$_m$ (m=1-4) are similar to that of SF$_5$ and SF$_6$. Please refer to the supplementary materials for details.
3.2.2 The electron impact decomposition process of SF₆ (n = 1-6)

SF₆ in gas insulation equipment will be decomposed by energy because of electron impact in addition to simple thermal decomposition. Figure 5 shows the change of ΔG of R4-R8 reaction at 298–10000K. From Figure 5 we realize that ΔG of R4-R8 showed a decreasing trend with the increase of temperature. SF₆ is a highly electronegative gas. When the energy of electrons in space is low, SF₆ can be combined with electrons in space to form a metastable molecular group (SF₆)*. In a short while, this molecular group can further generate anion SF₆⁻. That is, R4: SF₆ + e→SF₆⁻. When the temperature is 298K, ΔG is 126.1kJ/mol, when the temperature rises to 5000K, ΔG is −246.5kJ/mol, when the temperature reaches 10000K, ΔG is −255.5kJ/mol. With the temperature rise, the ΔG of this reaction was less than zero, so it could proceed spontaneously.

When electrons continue to hit SF₆⁻, R8: SF₆⁻ + e→SF₅⁻ + F⁻ occurs. When the temperature is 298K, ΔG is 209kJ/mol, when the temperature rises to 5000K, ΔG is −403.6kJ/mol, when the temperature reaches 10000K, ΔG is −460.3kJ/mol. The ΔG of this reaction is also less than zero, and goes on spontaneously.

When the energy of electrons hitting SF₆ is high, SF₆ + e→SF₅⁻ reaction will occur first, and then SF₆⁻ will be decomposed because of the huge energy of electrons, and three reactions of R5-R7 may occur: SF₆⁻→SF₅⁻ + F, SF₆→SF₅ + F, SF₆⁻→SF₅ + F⁻ + e. At a temperature 298K, the ΔG of R5 is 105.2 kJ/mol, with a rise to about 1200K, it decreases to 0 kJ/mol, when the temperature reaches 10000K, the ΔG is −933.3 kJ/mol. The ΔG of R6 at 298K is 105.2 kJ/mol, when the temperature increases to about 2600K, it drops to 0 kJ/mol, when the temperature reaches 10000K, ΔG is −545.4 kJ/mol. The ΔG of R7 at 298K is 501.3kJ/mol, when the temperature rises to about 3800K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1018.5 kJ/mol. Since the curve of reaction R5-7 has an intersection point in the temperature range of 298–10000K, the reaction that takes place with temperature rise varies. At 298–8700K, R5 has the lowest ΔG, so it is most likely to occur. The reaction produces SF⁵⁻ and F. The ΔG of R7 is the lowest at 8700–10000K, and the probability of R7 is greater in this temperature range.

When electrons continue to hit SF₅⁻, R16: SF₅⁻ + e→SF₄⁻ + F⁻ occurs. When the temperature of R16 is 298K, ΔG is 32.2kJ/mol, when the temperature is increased to 3800K, ΔG is 85.2kJ/mol, showing an upward trend with increased temperature.
to 5000K, $\Delta G$ is $-340.7$ kJ/mol, when the temperature reaches 10000K, $\Delta G$ is $-589.2$ kJ/mol. At 298K, the $\Delta G$ of this reaction is very low and it is likely to take place. With increase in temperature, the reaction can proceed spontaneously.

When the energy of electrons hitting SF$_5$ is high, SF$_5$ + e→SF$_5^-$ reaction will occur first, and then SF$_5^-$ will be decomposed as a result of the huge energy of electrons, and three reactions R13-R15 may occur: SF$_5^-$→SF$_4$ + F, SF$_5^-$→SF$_4$ + F$^-$, SF$_5^-$→SF$_4$ + F + e. When the temperature is 298K, the $\Delta G$ of R13 is 346.4 kJ/mol, when the temperature rises to about 2600K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the $\Delta G$ is $-1062.2$ kJ/mol. The $\Delta G$ of R14 at 298K is 215.9 kJ/mol, when the temperature rises to about 2300K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the $\Delta G$ is $-756$ kJ/mol. The $\Delta G$ of R15 at 298K is 530.1 kJ/mol, when the temperature rises to about 3500K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the $\Delta G$ is $-1229.1$ kJ/mol. In the temperature range of 298–3250K, the $\Delta G$ of R14 is the lowest, so there is a high likelihood of occurrence. The reaction produces SF$_4$ and F$^-$. At 3250–6700K, the $\Delta G$ of R13 is the lowest, so there is a high likelihood of occurrence. The reaction produces SF$_4$ and F$^-$. At 6700–10000K, the probability of R13 is higher in this temperature range. When the temperature continues to rise to 6700–10000K, the probability of R15 is greatest.

$\Delta G$ changes with temperature

Figure 7 shows the change of $\Delta G$ of the R20-R24 reaction at a temperature of 298–10000K. It can be seen from Figure 7 that the $\Delta G$ of R21-R24 displays a downward trend with increasing temperature, but the $\Delta G$ of R20 rises with increasing temperature. When the electron energy in the space is low, the R20 reaction will occur: SF$_4$ + e→SF$_4^-$.

When the temperature is 298K, the $\Delta G$ is $-183.7$ kJ/mol, when the temperature is increased to 5000K, the $\Delta G$ is $-73$ kJ/mol, when the temperature reaches 10000K, the $\Delta G$ is $-1062.2$ kJ/mol. When electrons continue to hit SF$_4^-$, R24 will occur: SF$_4^-$ + e→SF$_3$ + F$^-$. When the temperature of R24 is 298K, the $\Delta G$ is $-110.9$ kJ/mol, when the temperature is increased to 5000K, the $\Delta G$ is $-284.4$ kJ/mol, when the temperature reaches 10000K, the $\Delta G$ is $-319.3$ kJ/mol. The $\Delta G$ of this reaction is less than zero, so it can carry on spontaneously.

When the energy of electrons hitting SF$_4^-$ is high, the SF$_4^-$ + e→SF$_4$ reaction will take place first, and then SF$_4^-$ will be decomposed due to the huge energy of the electrons, and three reactions R21-R23 may occur: SF$_4^-$→SF$_3$ + F, SF$_4^-$→SF$_3$ + F$^-$, SF$_4^-$→SF$_3$ + F + e. When the temperature of R21 is 298K, the $\Delta G$ is 203.3 kJ/mol, with a rise to about 2200K, it drops to 0 kJ/mol, when the temperature reaches 10000K, the $\Delta G$ is $-792.3$ kJ/mol. The $\Delta G$ of R22 at 298K is 242.1 kJ/mol, when the temperature rises to about 2700K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the $\Delta G$ is $-687.4$ kJ/mol. The $\Delta G$ of R23 at 298K is 556.3 kJ/mol, with the temperature rise to about 3700K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the $\Delta G$ is $-1160.4$ kJ/mol. In the temperature range of 298–5800K, the $\Delta G$ of R21 is the lowest, so it
has the highest likelihood to take place. The reaction produces SF3- and F. The ΔG of R23 is the lowest at 5800–10000K, and the probability of occurrence of R23 is the highest in this temperature range.

Figure 7. SF4 electron impact decomposition process
ΔG changes with temperature

Figure 8 shows the change of the ΔG of the R28-R32 reaction at a temperature of 298–10000K. It can be seen from Figure 8 that the ΔG of R29-R32 shows a downward trend with temperature rise, but the ΔG of R28 increases with increasing temperature. When the electron energy in the space is low, the R28 reaction will occur: SF3 + e→SF3-. When the temperature is 298K, ΔG is −353 kJ/mol, when the temperature rises to 5000K, ΔG is −63.6kJ/mol, when the temperature reaches 10000K, ΔG is 368.1kJ/mol, showing an upward trend as the temperature rises. When electrons continue to hit SF3-, R32 will occur: SF3- + e→SF2- + F. When the temperature of R32 is 298K, ΔG is −111.9kJ/mol, on increasing it to 5000K, ΔG is −28.8kJ/mol, when the temperature reaches 10000K, ΔG is −4.5 kJ/mol. The ΔG of this reaction is less than zero, so it can proceed spontaneously.

When the energy of electrons hitting SF3 is high, the SF3 + e→SF3 reaction will occur first, and then SF3- will decompose as a result of the huge energy of the electrons, and three reactions R29-R31 may occur: SF3→SF2- + F, SF3→SF2 + F, SF3→SF2 + F + e. The ΔG of R29 at 298K is 426.1kJ/mol, when the temperature rises to about 4600K, it drops to 0 kJ/mol, and with the temperatures at 10000K, the ΔG is −477.6 kJ/mol. The ΔG of R30 at 298K is 183.3kJ/mol, when the temperature rises to about 2000K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −791.4 kJ/mol. The ΔG of R31 at 298K is 497.5 kJ/mol, when the temperature rises to about 3300K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1264.5 kJ/mol. In the temperature range of 298–5000K, R30 has the lowest ΔG, so it has the highest occurrence likelihood. The reaction produces SF2 and F. The G of R31 is the lowest at 5000–10000K, and the probability of occurrence of R31 is the highest in this temperature range.

Figure 9 shows the change of ΔG of the R36-R40 reaction at a temperature of 298–10000K. It can be seen from Figure 9 that the ΔG of R37-R40 shows a downward trend with increasing temperature, but the ΔG of R36 increases with increasing temperature. With a low electron energy in the space, the R36 reaction will occur: SF2 + e→SF2-. When the temperature is 298K, the ΔG is −71.4 kJ/mol, when the temperature is increased to 5000K, the ΔG is −28.8kJ/mol, when the temperature reaches 10000K, the ΔG is −4.5 kJ/mol. The ΔG of this reaction is less than zero, so it can proceed spontaneously.

When the electron energy in the space is low, the R36 reaction will occur: SF2 + e→SF2-. When the temperature is 298K, the ΔG is −71.4 kJ/mol, when the temperature is increased to 5000K, the ΔG is 272.6kJ/mol, when the temperature reaches 10000K, the ΔG is 786.9kJ/mol, showing an upward trend with
the increase of temperature.

When electrons continue to hit SF₂, R40 will occur: SF₂⁻ + e→SF⁻ + F. When the temperature of R40 is 298K, ΔG is 64.3kJ/mol, when the temperature is increased to 5000K, ΔG is −191.6kJ/mol, and when the temperature reaches 10000K, ΔG is −363.6 kJ/mol. When the temperature is 298K, the ΔG of the reaction is high, when the temperature increases, the ΔG decreases, and the reaction can proceed spontaneously.

When the energy of electrons hitting SF₂ is high, the SF₂ + e→SF₂⁻ reaction will occur first, and then SF₂⁻ will be decomposed because of the huge electrons’ energy, and three reactions R37-R39 may occur: SF₂⁻→SF⁻ + F, SF₂⁻→SF + F, SF₂⁻→SF + F + e. The ΔG of R37 at 298K is 170.3kJ/mol, when the temperature rises to about 1750K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1072.8kJ/mol. The ΔG of R38 at 298K is 60.7kJ/mol, when the temperature rises to about 850K, it is reduced to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1098.5 kJ/mol. The ΔG of R39 at 298K is 374.9 kJ/mol, when the temperature rises to about 2500K, it reduces to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1571.6 kJ/mol. The temperature is in the range of 298–4900K, and R38 has the lowest ΔG, so it has the highest occurrence likelihood. The reaction produces SF and F-. The ΔG of R39 is the lowest at 4900–10000K, and the probability of occurrence of R39 is the highest in this temperature range.

When electrons continue to hit SF⁻, R48 will occur: SF⁻ + e→S⁻ + F. When the temperature of R48 is 298K, ΔG is 9.9kJ/mol, when the temperature is increased to 5000K, ΔG is −204.6 kJ/mol, when the temperature reaches 10000K, ΔG is 548.8kJ/mol, showing an upward trend with increasing temperature.

When the energy of the electrons hitting SF is high, the SF + e→SF⁻ reaction will occur first, and then the SF⁻ will decompose because of the huge energy of the electrons, and three reactions R37-R39 may occur: SF→S⁻ + F, SF→S + F, SF→S + F + e. The ΔG of R45 at 298K is 324.1kJ/mol, when the temperature rises to about 3600K, it is...
minimized to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −673.6 kJ/mol. The ΔG of R46 at 298K is 193.2 kJ/mol, when the temperature rises to about 2300K, it goes down to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −781.3 kJ/mol. The ΔG of R47 at 298K is 507.4 kJ/mol, when the temperature rises to about 3500K, it drops to 0 kJ/mol, and when the temperature reaches 10000K, the ΔG is −1254.4 kJ/mol. In the temperature range of 298–4900K, R46 has the lowest ΔG, so it is most probable to take place. The reaction produces S and F-. The ΔG of R47 is the lowest at 4900–10000K, and the probability of occurrence of R47 is the highest in this temperature range.

From Figure 11, it can be found that the ΔH of these six reactions decreases with the increase of temperature, and the rate of decrease is almost the same, and they are all less than zero. From Figure 12, it can be found that the entropy changes of these six reactions all decrease with the increase of temperature. The difference is that the entropy change of R4 is always greater than 0 in the temperature range of 298–10000K, while the entropy change of SFₙ₊ₑ→SFₙ⁻ (n<6) is less than 0 with increasing temperature. It can also be seen from Figure 13 that the rate of decrease of ΔT*S product of R4 is much lower than that of the other five reactions, and the decrease rate of the ΔT*S is lower than that of ΔH. It can be seen from the definition of free energy that the ΔG of R4 increases with increasing temperature. In the other five reactions, the ΔT*S decrease rate is greater than the decrease rate of ΔH, that is, the increase rate of −ΔT*S is greater than the decrease rate of ΔH. Therefore, the ΔG of SFₙ₊ₑ→SFₙ⁻(n<6) increases with increasing temperature.

Figure 10. SF electron impact decomposition process

We have noticed, The ΔG of R4(SF₆₊ₑ→SF₆⁻) gradually decreases with the increase of temperature, but the ΔG of SFₙ₊ₑ→SFₙ⁻ (n<6) increases with increasing temperature. The ΔG of a chemical reaction is defined as

$$\Delta G = \Delta H - \Delta TS$$

Among them, ΔH is the enthalpy change, T is the temperature, and ΔS is the entropy change.

Through the previous calculations, we obtained the ΔH and ΔS of all reaction processes at the same time, and the entropy of electrons was obtained in Fifen's article. Figure 11-13 is obtained by calculating other thermodynamic data of these six reactions.
4. CONCLUSION

This paper uses quantum chemistry theory to study the reaction mechanism of SF₈ thermal decomposition and electrical decomposition at 298–10000 K, including a total of 17 particles and 48 chemical reactions. The Gibbs free energy data of electrons are acquired by cubic spline difference fitting, and the electrons are taken into account in the reaction equation. Structural optimizations, vibrational frequency calculations, and zero-point energy calculations for the reactants and products were performed at the B3LYP/6-311++G(d,p) level of theory. The single-point energies of all species were obtained at the CCSD(T)/aug-cc-PVTZ level. The frequency vibration factor (0.967) is taken into consideration. The main conclusions drawn are:

(1) In the temperature range of 298–10000K, the ΔG of SF₈ thermal decomposition and homocracking reaction starts to decrease from 200kJ/mol, while the ΔG of the other two heterocracking reactions starts to decrease from 1000kJ/mol and 2000kJ/mol respectively. Both show a downward trend with an almost similar slope, and homolytic reaction is more likely to occur.

(2) In the temperature range of 298–10000K, the SF₈ electron impact decomposition process can be divided into three possibilities based on the size of the electron energy. When the electron energy is low, SF₈ + e→SF₇ occurs, and the ΔG of SF₅, SF₄, SF₃, SF₂, SF decomposition reaction increases with the rise in temperature, while the ΔG of SF₆ decomposition decreases with increasing temperature.

(3) When the electron energy is high, the electrons hitting SF₈ will not generate SF₇⁻ but directly decompose SF₈⁻: In the temperature range of 298–8700K, ΔG of R5 is lowest, so it has the highest probable occurrence. SF₅⁻ decomposition produces SF₄⁻ and F. In the temperature range of 8700–10000K, ΔG of R7 is the lowest, and R7 has a greater probability of occurrence in this temperature range.

(4) In the temperature range of 298–3250K, the ΔG of R14 is the lowest, so it will most likely occur. SF₅⁻ decomposes to produce SF₄ and F. In the temperature range of 3250–6700K, the ΔG of R13 is the lowest, and the probability of occurrence of R13 is greater in this temperature range. SF₅⁻ decomposes to produce SF₄⁻ and F. When the temperature continues to rise to 6700–10000K, the probability of occurrence of R15 is greatest.
In the temperature range of 298–5800K, the $\Delta G$ of R21 is the lowest, so it has the highest occurrence likelihood. SF$_3^-$ decomposes to produce SF$_3^-$ and F. In the temperature range of 5800–10000K, the $\Delta G$ of R23 is the lowest, and the probability of occurrence of R23 is the highest in this temperature range.

In the temperature range of 298–5000K, R30 has the lowest $\Delta G$, so it is most probable to occur. SF$_2^-$ decomposition produces SF$_2^-$ and F. In the temperature range of 5000–10000K, the $\Delta G$ of R31 is the lowest, and the probability of occurrence of R31 is the highest in this temperature range.

In the temperature range of 298–4900K, R38 has the lowest $\Delta G$, so it is most likely to occur. SF$_2^-$ generates SF and F. In the temperature range of 4900–10000K, the $\Delta G$ of R39 is the lowest, and the probability of occurrence of R39 is the highest in this temperature range.

In the temperature range of 298–4900K, R46 has the lowest $\Delta G$, thus it has the highest occurrence likelihood. The decomposition of SF$_6^-$ produces S and F. In the temperature range of 4900–10000K, the $\Delta G$ of R47 is the lowest, and the probability of occurrence of R47 is the highest in this temperature range.

When the second electron hits SF$_n^-$, the SF$_n^-$ + e$\rightarrow$SF$_{n-1}^-$ + F occurs. And the $\Delta G$ of the reaction gradually decreases with the increase of temperature. The $\Delta G$ of this series of reactions is lower and more likely to occur. This work provides a reference for studying the by-products of the reaction of SF$_6$ with micro water or micro oxygen.

SUPPLEMENTARY MATERIAL
See the supplementary material for the thermal decomposition reaction of SF$_4$, SF$_3$, SF$_2$, and SF in detail.

Declarations

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material
The data that support the findings of this study are available within the article.

Code availability
The author’s organization owns the copyright of the software program used in the article, and there is no custom code in this article.

Authors' contributions
There were equal contributions of the authors to the completion of this work.

REFERENCES
1. H. D. Lin Tao, Zhong Haifeng, Qi Yao, and Zhang Guoqiang, Transactions of China Electrotechnical Society 29 (2), 219-225 (2014).
2. T. Ziegler and G. L. Gutsev, The Journal of Chemical Physics 96 (10), 7623-7632 (1992).
3. L. N. M. Piemontesi, in 1996 IEEE International Symposium on Electrical Insulation (IEEE, MONTREAL, CANADA, 1996), pp. 828-838.
4. Y. Qiu and E. Kuffel, IEEE Transactions on Dielectrics and Electrical Insulation 6 (6), 892-895 (1999).
5. B. Belmadani, J. Casanovas and A. M. Casanovas, IEEE Transactions on Electrical Insulation 26 (6), 1177-1182 (1991).
6. R. L. Wilkins, The Journal of Chemical Physics 51 (2), 853-854 (1969).
7. W. Frie, Zeitschrift für Physik 201 (3), 269-294 (1967).
8. A. J. Ahearn and N. B. Hannay, The Journal of Chemical Physics 21 (1), 119-124 (1953).
9. N. Wiegart, L. Niemeyer, F. Pinnekamp, J. Kindersberger, R. Morrow, W. Zaengl, M. Zwicky, I. Gallimberti and S. A. Boggs, IEEE Transactions on Power Delivery 3 (3), 923-930 (1988).
10. Y. Wang, R. L. Champion, L. D. Doverspike, J. K. Olthoff and R. J. Van Brunt, The Journal of Chemical Physics 91 (4), 2254-2260 (1989).
11. J. J. Fifen, J Chem Theory Comput 9 (7), 3165-3169 (2013).
12. X. Wang, Q. Gao, Y. Fu, A. Yang, M. Rong, Y. Wu, C. Niu and A. B. Murphy, Journal of Physics D: Applied Physics 49 (10) (2016).
13. A. D. Becke, Phys Rev A Gen Phys 38 (6), 3098-3100 (1988).
14. F. C. Pickard, D. R. Griffith, S. J. Ferrara, M. D. Liptak, K. N. Kirschner and G. C. Shields, International Journal of Quantum Chemistry 106 (15), 3122-3128 (2006).
15. S. Canneaux, F. Bohr and E. Henon, J Comput Chem 35 (1), 82-93 (2014).
16. Y. S. Cheung, Y. J. Chen, C. Y. Ng, S.-W. Chiu and W.-K. Li, Journal of the American Chemical Society 117 (38), 9725-9733 (1995).
17. M. J. Frisch, G. W. Trucks, et al. Gaussian 09, Revision A.02, Gaussian, Inc. Wallingford CT, 2009.
18. National Institute of Standards and Technology 2018 NIST chemistry webbook. https://webbook.nist.gov/chemistry
19. S. Y. Ye, F. Z. Deng, Journal of Huai Bei Coal Teachers College (Natural Science Edition),(01):71-74, 1992.