

Article

Thermal Decomposition Properties of Epoxy Resin in SF₆/N₂ Mixture

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Abstract: As a promising alternative for pure SF₆, the mixture of SF₆/N₂ appears to be more economic and environment-friendly on the premise of maintaining similar dielectric properties with pure SF₆. But less attention has been paid to the thermal properties of an SF₆/N₂ mixture, especially with insulation materials overheating happening simultaneously. In this paper, thermal decomposition properties of epoxy resin in SF₆/N₂ mixture with different SF₆ volume rates were studied, and the concentrations of characteristic decomposition components were detected based on concentrations change of some characteristic gas components such as CO₂, SO₂, H₂S, SOF₂, and CF₄. The results showed that thermal properties of 20% SF₆/N₂ (volume fraction of SF₆ is 20%) mixture has faster degradation than 40% SF₆/N₂ mixture. As ratio of SF₆ content decreases, thermal stability of the system decreases, and the decomposition process of SF₆ is exacerbated. Moreover, a mathematical model was established to determine happening of partial overheating faults on the epoxy resin surface in SF₆/N₂ mixture. Also thermal decomposition process of epoxy resin was simulated by the ReaxFF force field to reveal basic chemical reactions in terms of bond-breaking order, which further verified that CO₂ and H₂O produced during thermal decomposition of epoxy resin can intensify degradation of SF₆ dielectric property.

Keywords: SF₆/N₂; thermal decomposition; epoxy resin; decomposition components

1. Introduction

SF₆ gas is colorless, odorless and nontoxic, and is widely used as power equipment's insulation material because of its excellent arc-extinguishing and insulating properties [1–7]. Its chemical property is so stable that it can stably remain in the atmosphere for 2300 years, and its global warming potential (GWP) is 2500 times that of CO₂. Hence, it was listed as one of the six greenhouse gases in Kyoto Protocol in 1997. To reduce the use of SF₆, researchers worldwide have developed new alternatives such as C₄F₇N, C₅F₁₀O, SF₆/CO₂, and SF₆/N₂ mixture as insulation gases and put them into practice [3,5,8–10]. Among these gases, an SF₆/N₂ mixture with low SF₆ volume fraction has been widely used in electric equipment such as gas insulated transmission lines (GIL) [6,11–14]. In the 1970s, 420/550 kV transmission lines of 20% SF₆/N₂ (volume fraction of SF₆ is 20%) were developed by SIMENS and put into use in Geneva, Switzerland, which proved to be of high economic benefits. The transmission lines of 10% SF₆/N₂ gases in Electricite De France (EDF) have been safely used up to the present.

When there happens to be an overloading problem in GIL, partial overheating failure is likely to occur at the insulation defects spots, especially in the poor contact surface, which would do harm to the dielectric properties of the insulation material, and the defects will aggravate partial overheating

failure in return. The deterioration of insulation material will lead to serious consequences, such as the failure of some key part, or even a blackout at worst [15–18]. As a widely used insulation material, epoxy resin is often used together with SF₆ in electrical equipment, such as supporting spacers in GIL. In order to detect partial overheating failure as early as possible, it has been proposed to detect the thermal decomposition components of SF₆ (such as SO₂, H₂S, SOF₂, SO₂F₂, CF₄, CO₂, and SOF₄) in the presence of organic solid insulation materials [2,16,19]. When partial overheating failure happens temperature also can be estimated approximately based on the concentration change of the components. N₂ molecules in the SF₆/N₂ mixture will make SF₆ molecules burden uneven stress distribution, causing increase in the bonding energy of S-F [20–24]. The increase of intramolecular energy hinders system stability, which intensifies the impact of partial overheating. As an organic insulating material, the decomposition products of epoxy resin will also affect the development of partial overheating. The method for detecting thermal decomposition components in SF₆/N₂ mixture in the presence of epoxy resin has not been reported yet. Hence, this issue has been investigated in this paper.

Thermogravimetric analysis instrument was used to investigate the decomposition of epoxy resin in SF₆/N₂ mixture with SF₆ ratio of 20%, 30%, and 40% respectively (20% SF₆/N₂, 30% SF₆/N₂, and 40% SF₆/N₂ in short). By analyzing TG/DSC curves and comparing them with those from epoxy resin decomposition under pure SF₆ or N₂, the effect of ratio of SF₆ on the decomposition of epoxy resin was obtained. The variation of SF₆ characteristic decomposition component concentration with temperature in three different proportions of mixed gases was observed by Shimadzu QP2010 Ultra GC/MS. Types of gases that could be used as the characteristic components to detect the partial overheating failure in the presence of epoxy resin have been determined. Also the criterion of sharp weight loss of epoxy resin is established based on the change of characteristic components ratio.

2. Materials and Methods

2.1. Materials

In the experiment, the bisphenol-A epoxy resin E51 was purchased from Wuxi Lan-Star Petrochemical Co., Ltd. (Wuxi, China). Epoxy resin was cured by an amine curing agent dubbed as type 593, supplied by Wuhan Shen Chemical Reagents and Equipments Co., Ltd. (Wuhan, China). High-precision SF₆/N₂ mixture gas was supplied by Wuhan Newradar Gas Co., Ltd. (Wuhan, China). The mixture gas was prepared according to the reference material number GBW(E)061516 in China, so the original percentage content of O₂ and H₂O in the mixture gas were too low to be taken into consideration. Therefore, the main resource of H₂O in the heating process may come from the thermal decomposition of epoxy resin.

2.2. Parameters in the Experiment

In order to obtain the TG/DSC curves of epoxy resin decomposition in SF₆/N₂ mixture, TGA/DSC 3+ thermogravimetric analyzer of Mettler Toledo company was used in the experiment. At first three parameters including thermal conductivity, density and specific heat capacity were calculated in order to keep the accuracy of experiments after filling them in the sheet of parameters of TG/DSC instrument.

2.2.1. Density of SF₆/N₂ Gas Mixture

The instrument uses gas density at 0 °C under standard atmospheric pressure. The density of SF₆/N₂ mixture is given by:

$$\rho_0 = \frac{\rho_1 \rho_2}{\rho_2 m_1 + \rho_1 m_2} \quad (1)$$

where ρ_1 is the density of SF₆; ρ_2 is the density of N₂, m_1 and m_2 are mass percentages of SF₆ and N₂ respectively in per mole of mixture. The calculation results are shown in Table 1.

Table 1. Experimental gas densities at 0 °C under standard atmospheric pressure.

Type of Gas	SF ₆	N ₂	20% SF ₆ /N ₂	30% SF ₆ /N ₂	40% SF ₆ /N ₂
Density/(kg/m ³)	6.5200	1.2506	2.3046	2.8316	3.3586

2.2.2. Specific Heat Capacity of SF₆/N₂ Gas Mixture

The instrument uses heat capacity at 25 °C under standard atmospheric pressure. The heat capacity of SF₆/N₂ gas mixture is calculated as follows:

$$C_P = C_{P1} * m_1 + C_{P2} * m_2 \quad (2)$$

where C_{P1} and C_{P2} represent the specific heat capacity of SF₆ and N₂ gas under constant pressure respectively; m_1 and m_2 are mass percentages of SF₆ and N₂ in per mole of mixture respectively. The calculation results are shown in Table 2.

Table 2. Specific heat capacity of experimental gases at constant pressure at 25 °C under standard atmospheric pressure.

Type of Gas	SF ₆	N ₂	20% SF ₆ /N ₂	30% SF ₆ /N ₂	40% SF ₆ /N ₂
Specific Heat Capacity/(J/kg·K)	665.180	1040.000	827.893	781.055	748.910

2.2.3. Thermal Conductivity of SF₆/N₂ Gas Mixture

The instrument uses thermal conductivity at 0 °C under standard atmospheric pressure. The thermal conductivity of SF₆/N₂ gas mixture λ is given by:

$$\lambda = \frac{\lambda_1 y_1}{y_1 + A_{12} y_2} + \frac{\lambda_2 y_2}{y_2 + A_{21} y_1} \quad (3)$$

where λ_1 and λ_2 represent the thermal conductivity of SF₆ and N₂ under atmospheric pressure, y_1 and y_2 are the molar fractions of SF₆ and N₂ in the mixture respectively, A_{12} and A_{21} are constants given by:

$$A_{12} = \frac{1}{4} \left\{ 1 + \left[\left(\frac{u_1}{u_2} \right) \left(\frac{M_2}{M_1} \right)^{\frac{3}{4}} \left(\frac{1 + \frac{1.5T_{b1}}{T}}{1 + \frac{1.5T_{b2}}{T}} \right) \right]^{\frac{1}{2}} \right\}^2 \frac{\left(1 + \frac{S_{12}}{T} \right)}{\left(1 + \frac{1.5T_{b1}}{T} \right)} \quad (4)$$

$$A_{12} = \frac{1}{4} \left\{ 1 + \left[\left(\frac{u_1}{u_2} \right) \left(\frac{M_2}{M_1} \right)^{\frac{3}{4}} \left(\frac{1 + \frac{1.5T_{b1}}{T}}{1 + \frac{1.5T_{b2}}{T}} \right) \right]^{\frac{1}{2}} \right\}^2 \frac{\left(1 + \frac{S_{12}}{T} \right)}{\left(1 + \frac{1.5T_{b1}}{T} \right)} \quad (5)$$

where u_1 and u_2 represent the viscosity of SF₆ and N₂ under atmospheric pressure (kg·s/m²), M_1 and M_2 are relative mass fractions of SF₆ and N₂, T_{b1} and T_{b2} are the boiling points of SF₆ and N₂ under atmospheric pressure (K), T is the constant of 273.15 (K), S_{12} and S_{21} are given by:

$$S_{12} = S_{21} = \sqrt{2.25T_{b1}T_{b2}} \quad (6)$$

The calculated values of thermal conductivities are shown in Table 3.

Table 3. The calculated values of thermal conductivities at 0 °C under standard atmospheric pressure.

Types of Gas	SF ₆	N ₂	20% SF ₆ /N ₂	30% SF ₆ /N ₂	40% SF ₆ /N ₂
Thermal Conductivity/(W/m·K)	0.01206	0.02598	0.02378	0.02256	0.02129

2.3. Experiment Process

In this paper, SF₆/N₂ mixture gas with the SF₆ volume ratio from 20% to 40% were used in experiment, and the results were compared with those from pure SF₆ and N₂. The sample mass of cured epoxy resin was 20 mg. The gas flow rate was set as 20 mL/min, the heating rate as 10 °C/min heating in the temperature range from 250 °C to 650 °C.

3. Results and Discussion

3.1. TG Curve Analysis of Epoxy Resin Decomposition

Figure 1 shows the TG curves of epoxy resin decomposed under different experimental gases. As can be seen that the main weight loss of epoxy resin happened in the temperature range from 330 °C to 470 °C, which are not affected by the type of gas in reaction. But it is noteworthy that the weight-loss ratio of epoxy resin varied with the type of gas in reaction, such as under N₂ condition, the decomposition of epoxy resin is most violent, with remaining mass of 1.59 mg, accounting for 7.97% of the total weight of experimental sample, while under SF₆ condition, the amount of remaining mass of decomposed epoxy resin was 4.53 mg, accounting for 22.73% of the total weight of experimental sample. The decomposition extent of epoxy resin in three mixed gases follows: 20% SF₆/N₂ > 30% SF₆/N₂ > 40% SF₆/N₂, that is to say, in the mixture of 20% SF₆/N₂, weight loss of epoxy resin was more severe than in the mixture of 40% SF₆/N₂.

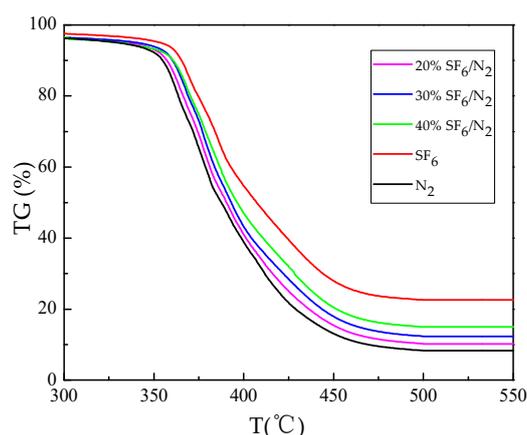


Figure 1. TG curve of epoxy resin decomposition under different experimental gases.

As the reaction gas, thermal conductivity of SF₆ is lower than that of N₂, therefore, the poor thermal conductivity of SF₆ is not conducive to the decomposition of epoxy resin. However, N₂ has higher thermal stability due to its large molecular bond energy of 946 kJ/mol. So N₂ will not decompose or react with epoxy resin in the experimental temperature range. In pure SF₆, SF₆ begins to decompose at about 260 °C, and reaction between SF₆ and epoxy resin would help add to the whole weight of the residue. The decrease of SF₆ content in gas mixture will reduce the thermal stability of the system, making epoxy resin easier to react with SF₆.

3.2. DSC Curve Analysis of Epoxy Resin Decomposition

In the DSC curve, the convex peak represents an increase in enthalpy(exothermic) and the concave peak represents a decrease in enthalpy(endotherm). Figure 2 is the DSC curves of epoxy resin decomposed under different experimental gas conditions. As can be seen from Figure 2, the decomposition process of epoxy resin is complicated. Within the main weight loss range of 340 °C–470 °C, there are obvious characteristic peaks of heat absorption and release. The process is divided into three reaction stages: melting, exothermic behavior (solidification, oxidation, reaction, crosslinking), decomposition, and gasification. The peak area of heat absorption indicates the

reaction energy level. By integrating the endothermic peak area in the main weight loss interval, the endothermic peak energy is obtained and shown in Table 4. The value arranged from big to small in the following order: 20% SF₆/N₂ > 30% SF₆/N₂ > 40% SF₆/N₂ > SF₆ > N₂.

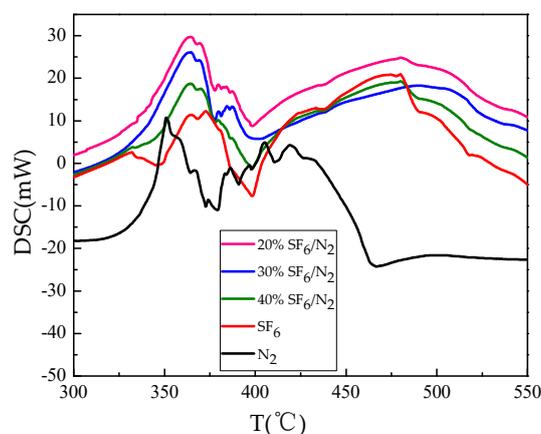


Figure 2. DSC curve of epoxy resin decomposed under different experimental gas conditions.

Table 4. Experimental gas exothermic peak energy at 330 °C–470 °C.

Types of Gas	SF ₆	N ₂	20% SF ₆ /N ₂	30% SF ₆ /N ₂	40% SF ₆ /N ₂
Exothermic Peak Energy/mJ	9359.28	6718.17	11,648.33	10,520.45	9587.56

During the exothermic behavior stage, the peak temperature at this stage is greatly affected by SF₆. In pure SF₆, the temperature at the exothermic peak is about 370 °C versus 350 °C in pure N₂. Besides, in the pure N₂, around 400 °C there are also existing some exothermic peaks representing the intrinsic thermal decomposition of epoxy resin. With the amount of SF₆ increasing, some consecutive small peaks showed up at about 385 °C. Thermal decomposition of epoxy resin is actually the process of breaking and regenerating chemical bonds. In epoxy resin, C–O bond and C–H bond account for the major chemical bonds, and they are easy to break due to low bond energy. After breaking, free C, H and O atoms are formed, and further combined to form small molecules such as H₂O and CO₂. As a highly thermal stable gas, chemical bonds in N₂ do not break to form N atoms under experimental temperature conditions, therefore, epoxy resin has intrinsic bond breakage in N₂. SF₆ decomposes at 260 °C in the presence of organic insulating solids [2]. And SF₆ decomposes continuously throughout the weight-losing temperature range, a continuous exothermic peaks were shown on the DSC curve, causing the peak values to shift to the high temperature zone compared with the results in N₂, indicating that the exothermic behavior is affected by SF₆ decomposition.

Decomposition of SF₆ is exacerbated with temperature increasing, and more free S and F atoms exist in the reaction gas to form a large amount of sulfides and fluorides resulting in increase of the exothermic peak area. It also confirms the conclusion that the smaller volume fraction of SF₆ in the mixture would result in lower thermal stability, although it proved that 20% SF₆/N₂ has better dielectric property than 40% SF₆/N₂ [16]. Better dielectric property of 20% SF₆/N₂ cannot guarantee a better thermal property.

3.3. Effect of Epoxy Resin on the Decomposition Components of SF₆/N₂ Gas Mixture

In this study, 20% SF₆/N₂, 30% SF₆/N₂, and 40% SF₆/N₂ gas mixtures were selected as experimental gases and the heating temperature was in the range of 200 °C–650 °C. In order to detect the formation temperature of characteristic components as accurately as possible, small heating increment of 2 °C/min was selected, and time interval for continuous gas collection was 15 min, meaning that temperature rose by 30 °C. The volume of collected gas was about 0.3 L and the gas

component concentration was detected by GC/MS instrument quickly. The average component concentration in 15 min reflects the component formation rate.

3.3.1. Variation of Characteristic Decomposition Components with Temperature

Seven SF₆ decomposition characteristic gases including CO₂, SO₂, H₂S, SOF₂, SO₂F₂, CF₄, and CS₂ were detected in our study. If the measured characteristic gas concentration is less than 0.05 ppm, it is considered to be below the detection limit of the instrument, meaning the gas is not generated. Judging by the above principle, in the entire temperature range of the experiment, no CS₂ or SO₂F₂ was detected. Therefore, five gases including CO₂, SO₂, H₂S, SOF₂, and CF₄ were selected as the characteristic decomposition components of overheating failure on epoxy resin surface.

Figure 3 shows the formation of CO₂ with temperature. It can be seen that the initial temperature of CO₂ formation was always 275 °C under three gas mixtures with different proportions and the rate of CO₂ formation increased before 450 °C and the generation rate of CO₂ was fastest in the 20% SF₆/N₂. The formation rate of CO₂ tended to become constant during a small temperature range after 450 °C. Finally, the CO₂ formation rates of all three gases began to decrease from 515 °C.

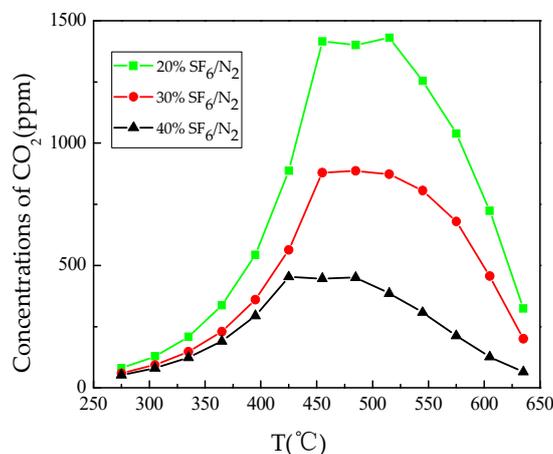


Figure 3. Formation of CO₂ with temperature.

Figure 4 shows the pattern of CF₄ generation with temperature. The initial temperature of CF₄ formation was 455 °C under three different ratios of gas mixtures, and the formation rate of CF₄ increased exponentially with the increase of temperature. The relationship of the initial formation concentration shows in the order: 20% SF₆/N₂ > 30% SF₆/N₂ > 40% SF₆/N₂, that is to say, CF₄ has fastest formation rate in the 20% SF₆/N₂ mixture.

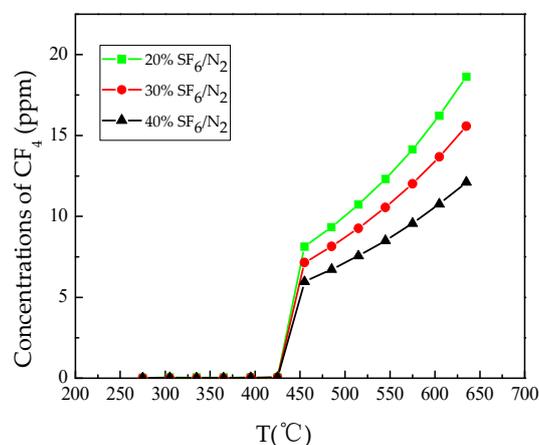


Figure 4. Formation of CF₄ with temperature.

The initial formation temperature of CO_2 and CF_4 in the presence of epoxy resin in mixed gas is the same as the results in pure SF_6 [2]. By observing the gas formation of CO_2 and CF_4 , it can be concluded that the formation rate of CO_2 became constant when CF_4 started to be generated, and the rate of CO_2 formation started to decrease versus the increase of CF_4 generation rate, which is likely to be caused by the fact that C atom preferentially binds with F atom above $450\text{ }^\circ\text{C}$, which affects the formation rate of CO_2 .

Figure 5 shows the formation of SO_2 and SOF_2 with temperature respectively. The initial formation temperature of SO_2 and SOF_2 was $275\text{ }^\circ\text{C}$ under three gas mixtures with different ratios. The formation rates of SO_2 and SOF_2 increased exponentially with the increase of temperature, and the relationship of the initial formation concentration shows in the order: $20\% \text{SF}_6/\text{N}_2 > 30\% \text{SF}_6/\text{N}_2 > 40\% \text{SF}_6/\text{N}_2$. With temperature increasing, the formation rate of SO_2 was bigger than that of SOF_2 .

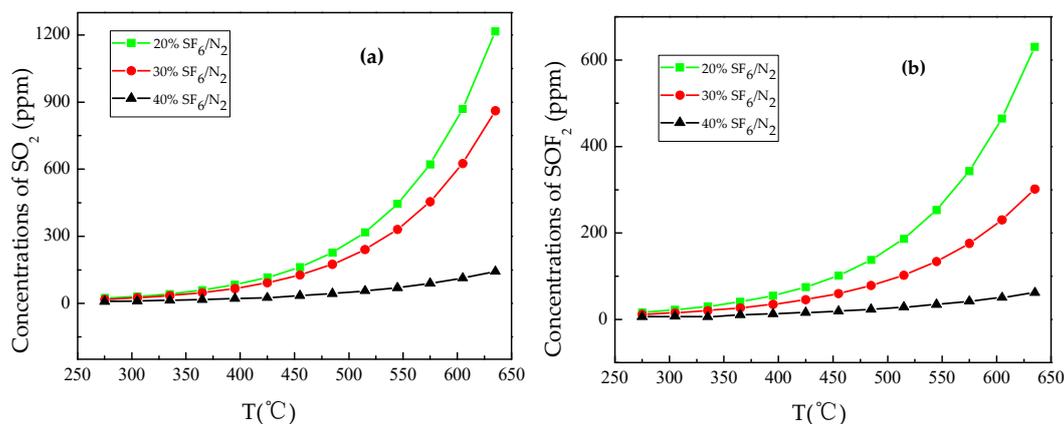


Figure 5. Formation of SO_2 and SOF_2 with temperature (a) SO_2 ; (b) SOF_2 .

Compared with the decomposition of epoxy resin in SF_6 atmosphere, the formation temperature of SO_2 and SOF_2 in the presence of epoxy resin is lower [2]. SOF_2 reacts with H_2O to form SO_2 . Therefore, it can be seen that the formation of SO_2 is greatly affected by H_2O . During the decomposition of epoxy resin, more H_2O is produced because of the dehydration condensation during elimination reaction within the molecule, which objectively enhances the hydrolysis of SOF_2 and the formation of SO_2 .

Figure 6 shows the formation of H_2S with temperature. The initial formation temperature of H_2S in three gas mixtures with different ratios was about $335\text{ }^\circ\text{C}$. The H_2S formation rate tended to be constant between $335\text{ }^\circ\text{C}$ and $395\text{ }^\circ\text{C}$, and started to decrease above $425\text{ }^\circ\text{C}$. The formation of H_2S and CF_4 indicates that epoxy resin has entered the stage of rapid decomposition and weight loss. Early detection of this stage can effectively help avoid the serious consequences of further aggravation of overheating fault.

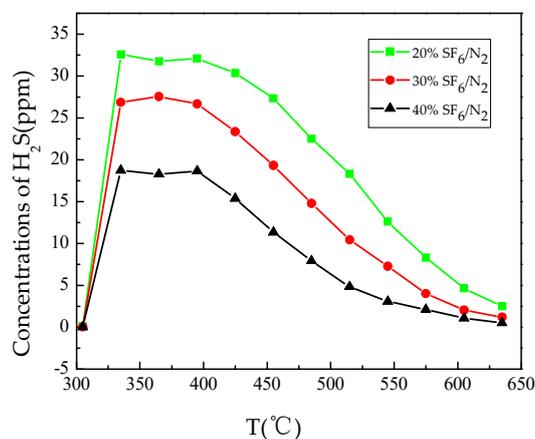


Figure 6. Formation of H_2S with temperature.

3.3.2. Main Criteria for Determining Weight Loss of Epoxy Resins

It can be seen from the TG curves that the main weight loss temperature range of epoxy resin was 330 °C–470 °C. In this range, under SF₆/N₂ gas mixture conditions, main criteria for determining weight loss of epoxy resins can be concluded based on the concentration change of the characteristic components, such as H₂S mainly generated in the range of 320 °C–350 °C while CF₄ generated in the range of 440 °C–470 °C, the initial concentrations of H₂S and CF₄ had an obvious difference.

In order to obtain the standard for detecting the occurrence of an overheating fault, during heating samples of epoxy resin, concentrations of five characteristic components of CO₂, SO₂, H₂S, SOF₂, and CF₄ were measured in the interval of 15 °C. Statistically the proportion of H₂S and CF₄ was used to determine whether the epoxy resin began to lose weight rapidly. When CF₄ was not detected, the variation of H₂S ratio was used as the criterion. Table 5 shows that the concentrations of H₂S at different temperature range during the decomposition of epoxy resin under three gas mixtures. By the way, the concentrations represent the measured value at every interval rather than a cumulative value, reflecting formation rate of H₂S. The formation rate of H₂S decreased with temperature.

Table 5. Concentrations of H₂S at different temperature range in the interval of 15 °C (ppm).

Unit/%	320 °C	335 °C	350 °C	365 °C	380 °C	395 °C	410 °C	425 °C	440 °C
20% SF ₆ /N ₂	9.44	10.12	9.01	7.63	5.38	4.97	3.94	2.80	1.24
30% SF ₆ /N ₂	0	9.32	8.96	7.82	5.01	4.11	2.88	2.63	0.99
40% SF ₆ /N ₂	0	10.10	9.22	7.77	5.89	4.82	4.12	3.62	2.09

To obtain a mathematical principle for detecting the sharp weight-losing of epoxy resin, the concentrations of H₂S in Table 5 should sum up. Because heating rate was 2 °C/min, the sum of concentrations from 320 °C to 440 °C was concentration in one hour. The total concentration of the five characteristic components generated in an hour is set as C(T), as shown in Table 6. C(H₂S) represents the concentration of H₂S. Before the occurrence of the CF₄, the following criteria for determining the weight loss of epoxy resin can be obtained:

$$C(\text{H}_2\text{S})/C(\text{T}) > 0.01 \quad (7)$$

Table 6. Total concentration of five characteristic gases at different temperature range in the interval of 15 °C (ppm).

Unit/%	350 °C	365 °C	380 °C	395 °C	410 °C	425 °C	440 °C	455 °C	470 °C
20% SF ₆ /N ₂	1037.81	1440.82	1673.29	2152.99	2435.98	3367.67	4359.82	5167.27	5557.31
30% SF ₆ /N ₂	733.95	908.33	1023.89	1332.36	1241.07	1996.00	2112.52	2985.67	3811.16
40% SF ₆ /N ₂	527.16	727.37	772.42	1051.19	1113.77	1554.41	1493.30	1596.54	2095.89

On the other hand, CF₄ began to form from 440 °C. Table 7 shows concentrations of CF₄ formed at different temperature range during the decomposition of epoxy resin under three gas mixtures. The formation rate of CF₄ increases exponentially with the increase of temperature.

Table 7. Concentrations of CF₄ at different temperature range in the interval of 15 °C (ppm).

Unit/%	440 °C	455 °C	470 °C
20% SF ₆ /N ₂	0.10	0.10	0.11
30% SF ₆ /N ₂	0.18	0.23	0.24
40% SF ₆ /N ₂	0.28	0.31	0.32

The appearance of CF_4 indicates that the rapid weight loss of epoxy resin has come to the late stage, and serious overheating fault has occurred. Setting the total concentration of five characteristic components as $C(T)$, and $C(\text{CF}_4)$ as the concentration of CF_4 , the following criteria can be obtained for determining the weight loss range of epoxy resin.

$$C(\text{CF}_4)/C(T) > 0.001 \quad (8)$$

Epoxy resin in SF_6 -infused electrical equipment are designed to have high thermal and dielectric properties. To assess the operating condition of the sealed equipment based on the concentration of characteristic gases change would help find the overheating fault at an early stage. Equation (7) reflects the decomposition of epoxy resin at an early stage and Equation (8) represents the severe condition that epoxy resin enters sharp weight-losing stage. Once partial overheating faults happen on the surface of insulating material, usually it would be a lasting process to cumulate heat slowly so carbonization of epoxy resin in a small defect spot need to be analyzed both by Equations (7) and (8).

3.4. XPS Analysis

Figure 7 shows XPS spectrum of burnt residue of epoxy resin in air and in SF_6 atmosphere. Figure 7a shows the XPS spectrum of the epoxy resin in air. It can be seen that the peak intensity of the oxygen element and the carbon element are relatively high.

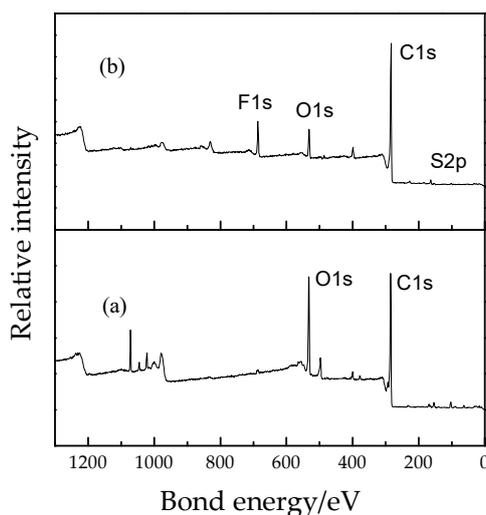


Figure 7. XPS spectra of residues of pure epoxy after decomposition (a) in air (b) in SF_6 heated after $500\text{ }^\circ\text{C}$.

In Figure 7b, the elemental peaks of F1s and S2p are found in the residue of the epoxy resin after pyrolysis in SF_6 , indicating that some of the fluoride and sulfide are present in the residue. It is highly probable that fluorine is adsorbed in the form of CF_4 by strong hydrogen bonds formed by carbonization of epoxy resin and the specific molecular structure deserves further study. The content of sulfur element is lower than that of fluorine element, indicating that the sulfur element interacts with the epoxy resin as long as it is released as SO_2 gas. The chemical reaction mechanism of epoxy resin and SF_6 gas also deserves further study.

3.5. Simulation of Decomposition Mechanism of Epoxy Resin

As to the intrinsic decomposition mechanism of epoxy resin at high temperature, the simulation analysis was carried out by using ReacFF force field in Materials Studio software to study the formation of small molecular gases such as CO_2 and H_2O . Firstly, the molecular model of the bisphenol A epoxy resin after curing was constructed as shown in Figure 8. In the figure, ①, ②, ③, ④, ⑤, ⑥, and

⑦ represent C-O bonds at different positions respectively. The unit cell models of 15 epoxy resin molecules were created by using the Construction function in the tool of Amorphous Cell.

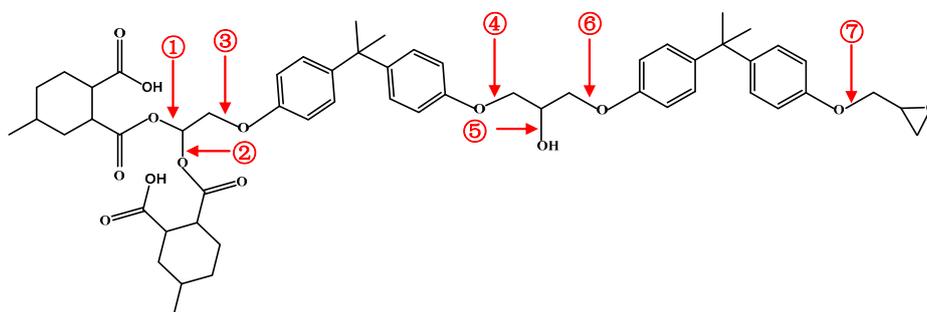


Figure 8. Single cured epoxy resin molecule.

The steps are summarized as follows: Single epoxy resin molecule shown in Figure 8 was constructed, and an initial density of 0.5 g/cm^3 was applied. After 300 ps NPT ensemble simulation followed by 1000 ps structural optimization, the final unit cell model with the density of 1.14 g/cm^3 was obtained, which is shown in Figure 9. After that, the ReaxFF force field was employed to simulate the decomposition process of the unit cell model at a maximum temperature of 1300 K during local discharge.

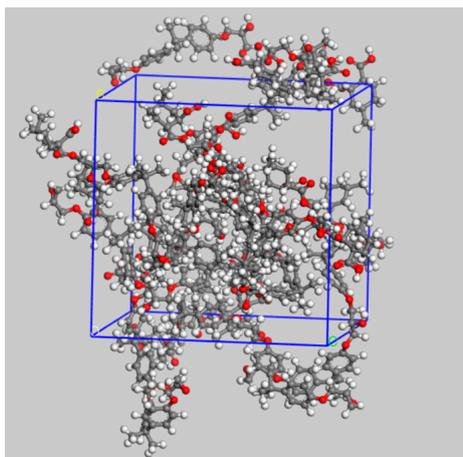


Figure 9. A unit cell model for epoxy resin.

Figure 10 is a schematic diagram of the simulated bond breaking process. Figure 10a represents an epoxy resin molecule with the chemical formula of $\text{C}_{57}\text{H}_{70}\text{O}_{14}$. The decomposition of epoxy resin starts with the cleavage of the C-O bond at locations ① and ② in Figure 8, which have the lowest activation energy, as shown in Figure 10b. After the cleavage the CO_2 molecule is directly generated, as shown in Figure 10c. Following that, the C-O bond at location ⑦ in Figure 8 is cleaved, and ethylene radicals and CH_2O are formed, as shown in Figure 10d. The C-O bonds at locations ⑤ and ⑥ in Figure 8 are cleaved to form free hydroxyl groups, which generate H_2O when encountering highly active H ions, as shown in Figure 10e. Finally, propylene radicals and active bisphenol ions appear in Figure 10f.

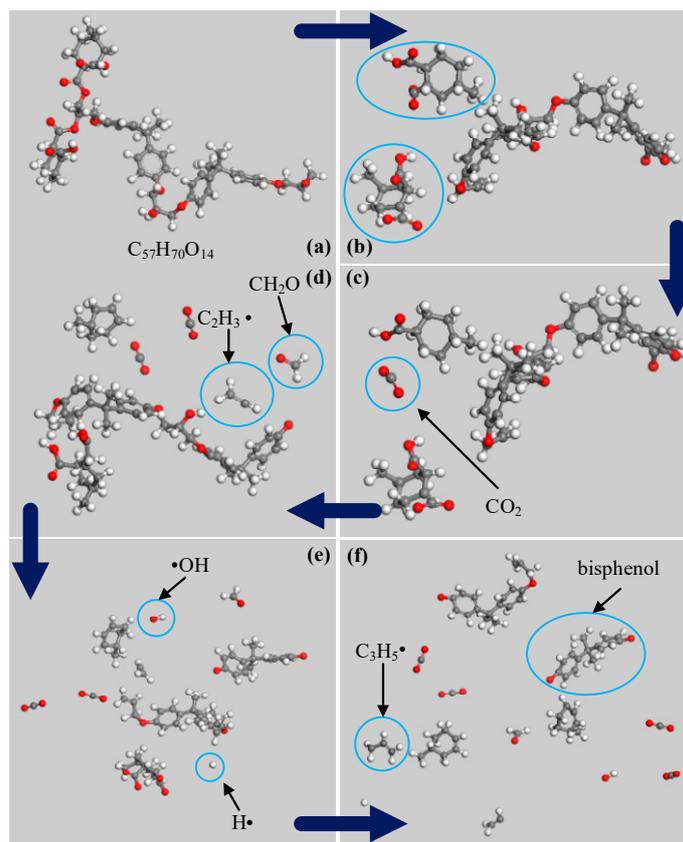


Figure 10. Schematic diagram of simulated bond-breaking process.

Figure 11 shows the decomposition products of the epoxy resin unit cell model as a function of time. It can be seen that CO_2 appears around 70 ps, followed by CH_2O , and finally H_2O . The concentration of CO_2 is higher than that of H_2O . CO_2 mainly comes from the cleavage of the ester bond connecting the epoxy group, and H_2O mainly comes from the elimination reaction of macromolecular ions and the dehydration condensation reaction between molecules.

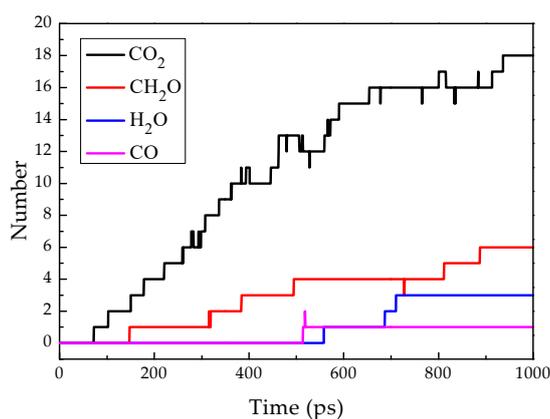
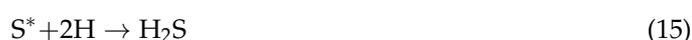


Figure 11. Theoretical byproduct numbers change during decomposition of epoxy resin cell over time.

It is conventionally stipulated that the maximum concentration of H_2O in the main air chamber of the SF_6 gas-insulated equipment to be put into operation should not exceed 500 ppm and the air content should not exceed 1%. Therefore, when there is an early latent insulation fault inside the equipment, the content of each component produced by the decomposition of SF_6 will increase with the duration of discharge and overheating, and then the rate of increase will gradually slow down,

and finally will reach a state of dynamic equilibrium until further increase happens due to aggravated fault. The presence of organic insulating material is one of the factors that accelerate the deterioration. At high temperature, SF₆ is decomposed into low fluorides such as SF₄ and SF₅, which then react with H₂O and O₂ molecules. The decomposition process is shown in Equations 9–15.



The H₂O molecules generated by epoxy resin due to heating will react with SF₆ to form SO₂F₂, SOF₂, SO₂ and other gases, which greatly affects the concentrations of decomposition components of SF₆. By detecting the changes in concentration of each type of gas and comparing that with the thermal decomposition components of pure SF₆, the rule of concentration change of the characteristic gases of the SF₆ thermal decomposition components in the presence of epoxy resin can be summarized, and a basic method for judging whether there is a thermal decomposition fault of the epoxy resin in the electrical equipment can be proposed.

4. Conclusions

The thermal decomposition characteristics of epoxy resin in SF₆/N₂ mixture were studied. The concentration of characteristic decomposition components was detected. The following conclusions are drawn:

1. The TG curve shows that the main weight loss range of epoxy resin is 330 °C–470 °C. The degree of weight loss follows: N₂ > 20% SF₆/N₂ > 30% SF₆/N₂ > 40% SF₆/N₂ > SF₆. The DSC curves show that the decomposition of epoxy resin under SF₆ condition is a series of complex chemical reactions. Epoxy resin decomposition in the 20% SF₆/N₂ is more severe than in 40% SF₆/N₂.
2. During heating from 200 °C to 650 °C, the five gases of CO₂, SO₂, H₂S, SOF₂, and CF₄ are selected as the characteristic decomposition components of SF₆. CO₂, SO₂ and SOF₂ are all formed at 275 °C and the formation rate increases exponentially, but the formation rate of CO₂ gradually decreases after CF₄ has been generated. The formation rate of SO₂ is higher than that of SOF₂. The reason is that the decomposition of epoxy resin produces H₂O, promoting hydrolysis of SOF₂.
3. When epoxy resin was heated in the gas mixture, the initial generation temperature of H₂S was lower than in the pure SF₆, and CF₄ generation rate also relatively increased. Concentration change of H₂S and CF₄ can be used as the criteria for judging the sudden weight loss caused by overheating fault happening on the surface of epoxy resin. 20% SF₆/N₂, 30% SF₆/N₂, and 40% SF₆/N₂ share the same judging standard: When there is no CF₄ generation, H₂S is used as the criterion depicted as follow: C(H₂S)/C(T) > 0.01; when CF₄ is generated, CF₄ is used as the criterion depicted as follow: C(CF₄)/C(T) > 0.001, among which C(T) represents the total decomposition gas concentration.
4. Thermal decomposition process of epoxy resin was simulated by the ReaxFF force field to reveal basic chemical reactions in terms of bond-breaking order, which further verified that CO₂ and H₂O produced during thermal decomposition of epoxy resin can intensify degradation of SF₆ dielectric property. To judge the operation situation of SF₆-infused electrical equipment, the problem of overheating faults involving epoxy resin decomposition should draw more attention.

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References

1. Chu, F.Y. SF₆ Decomposition in Gas-Insulated Equipment. *IEEE Trans. Electr. Insul.* **1986**, *21*, 693–725. [[CrossRef](#)]
2. Tang, J.; Liu, F.; Zhang, X.; Ren, X.; Fan, M. Characteristics of the Concentration Ratio of SO₂F₂ to SOF₂ as the Decomposition Products of SF₆ Under Corona Discharge. *IEEE Trans. Plasma. Sci.* **2012**, *40*, 56–62. [[CrossRef](#)]
3. Stoller, P.C.; Doiron, C.B.; Tehlar, D.; Simka, P.; Ranjan, N. Mixtures of CO₂ and C₅F₁₀O perfluoroketone for high voltage applications. *IEEE Trans. Dielectr. Electr. Insul.* **2017**, *24*, 2712–2721. [[CrossRef](#)]
4. Resnik, M.; Zaplotnik, R.; Mozetic, M.; Vesel, A. Comparison of SF₆ and CF₄ Plasma Treatment for Surface Hydrophobization of PET Polymer. *Materials* **2018**, *11*, 311. [[CrossRef](#)] [[PubMed](#)]
5. Zhang, X.; Li, Y.; Chen, D.; Xiao, S.; Tian, S.; Tang, J.; Zhuo, R. Reactive molecular dynamics study of the decomposition mechanism of the environmentally friendly insulating medium C₃F₇CN. *Rsc. Adv.* **2017**, *7*, 50663–50671. [[CrossRef](#)]
6. Qu, B.; Yang, Q.; Li, Y.; Malekian, R.; Li, Z. A New Concentration Detection System for SF₆/N₂ Mixture Gas in Extra/Ultra High Voltage Power Transmission Systems. *IEEE Sens. J.* **2018**, *99*. [[CrossRef](#)]
7. Albano, M.; Haddad, A.; Griffiths, H.; Coventry, P. Environmentally Friendly Compact Air-Insulated High-Voltage Substations. *Energies* **2018**, *11*, 2492. [[CrossRef](#)]
8. Chen, K.S.; Yeh, R.Z.; Wu, C.H. Kinetics of Thermal Decomposition of Epoxy Resin in Nitrogen-Oxygen Atmosphere. *J. Environ. Eng.* **1997**, *123*, 1041–1046. [[CrossRef](#)]
9. Sun, W.; Li, Y.; Zheng, D.S.; Guo, R.Y.; Du, X.H. Insulation characteristics of SF₆/N₂ gas mixtures and applied researches. *Electr. Insul. Dielectr. Phenom.* **2014**. [[CrossRef](#)]
10. Guo, C.; Zhang, Q.; You, H.; Ma, J.; Li, Y.; Wen, T.; Qin, Y. Influence of electric field non-uniformity on breakdown characteristics in SF₆/N₂ gas mixtures under lightning impulse. *IEEE Trans. Dielectr. Electr. Insul.* **2017**, *24*, 2248–2258. [[CrossRef](#)]
11. Han, S.U.; Yong, S.B.; Song, K.B.; Choi, E.H.; Ryu, H.Y.; Lee, J. Analytical investigation of electrical breakdown properties in a nitrogen-SF₆ mixture gas. *Phys. Plasmas.* **2010**, *17*, 1291. [[CrossRef](#)]
12. Hoshina, Y.; Sato, M.; Murase, H.; Toyada, M.; Kobayashi, A. Dielectric properties of SF₆/N₂ gas mixtures on a full scale model of the gas-insulated busbar. *IEEE Power Eng. Soc. Winter Meet.* **2000**. [[CrossRef](#)]
13. Piemontesi, M.; Koenig, F.; Niemeyer, L.; Heitz, C. Insulation performance of 10% SF₆/90% N₂ mixture. In Proceedings of the 1999 Annual Report Conference on Electrical Insulation and Dielectric Phenomena (Cat. No.99CH36319), Austin, TX, USA, 17–20 October 1999. [[CrossRef](#)]
14. Rokunohe, T.; Yagihashi, Y.; Endo, F.; Oomori, T. Fundamental insulation characteristics of air; N₂, CO₂, N₂/O₂, and SF₆/N₂ mixed gases. *Electr. Eng. Jpn.* **2010**, *155*, 9–17. [[CrossRef](#)]
15. Vial, L.; Casanovas, A.M.; Diaz, J.; Coll, I.; Casanovas, J. Decomposition of high-pressure (400 kPa) SF₆ and SF₆/N₂ (10:90) mixtures submitted to negative or 50 Hz ac corona discharges in the presence of water vapour and/or oxygen. *J. Phys. D Appl. Phys.* **2001**, *34*, 2037. [[CrossRef](#)]
16. Casanovas, A.-M.; Vial, L.; Coll, I.; Storer, M.; Casanovas, J.; Clavreul, R. Decomposition of SF₆ Under AC and DC Corona Discharges in High-Pressure SF₆ and SF₆/N₂ (10–90%) Mixtures. *Gaseous Dielectr.* **1998**. [[CrossRef](#)]
17. Kamath, B.R.; Sundararajan, J. Study of metallic particle induced partial discharge activity in 10:90 SF₆-N₂ gas mixtures. In Proceedings of the IEEE International Conference on the Properties and Applications of Dielectric Materials, Icpadm 2009, Harbin, China, 19–23 July 2009. [[CrossRef](#)]
18. Imano, A.M.; Feser, K. Flashover behavior of conducting particle on the spacer surface in compressed N₂, 90%N₂+10%SF₆ and SF₆ under lightning impulse stress. In Proceedings of the Conference Record of the 2000 IEEE International Symposium on Electrical Insulation (Cat. No.00CH37075), Anaheim, CA, USA, 5 April 2000. [[CrossRef](#)]

19. Gong, G.; Zhang, P.; Dong, G.Y.; Dong, Z. The influence of SF₆ and SF₆/N₂ dissociating products on the electrical performance of several insulating varnishes. In Proceedings of the International Symposium on Electrical Insulating Materials, Tokyo, Japan, 17–20 September 1995. [[CrossRef](#)]
20. Stankovic, K.; Alimpijevic, M.; Vujisic, M.; Osmokrovic, P. Numerical Generation of a Statistic Sample of the Pulse Breakdown Voltage Random Variable in SF₆ Gas with Homogenous and Nonhomogenous Electric Field. *IEEE Trans. Plasma. Sci.* **2014**, *42*, 3508–3519. [[CrossRef](#)]
21. Osmokrovic, P.; Vujisic, M.; Stankovic, K.; Vasic, A.; Loncar, B. Mechanism of electrical breakdown of gases for pressures from 10^{−9} to 1 bar and inter-electrode gaps from 0.1 to 0.5 mm. *Plasma. Sources. Sci. Technol.* **2007**, *16*, 643. [[CrossRef](#)]
22. Wang, C.; Tu, Y.; Li, X.; Tan, R. Performance of flashover on the resin spacer surface in N₂/SF₆ and SF₆/air gas mixture under AC power frequency. In Proceedings of the Conference Record of the 2012 IEEE International Symposium on Electrical Insulation, San Juan, PR, USA, 10–13 June 2012. [[CrossRef](#)]
23. Rajan, J.S.; Dwarakanath, K.; Srinivasan, N. Surface flashover strength of different insulating materials in N₂-SF₆ gas mixtures under combined AC/DC voltages. In Proceedings of the International Symposium on Electrical Insulating Materials, Himeji, Japan, 22 November 2001. [[CrossRef](#)]
24. Zheng, Y.; Zhou, W.; Yang, S.; Qiao, S.; Huang, J.; Qin, Z. Temperature effect on the insulation performance of SF₆/N₂ gas mixture at a constant volume. In Proceedings of the IEEE International Conference on High Voltage Engineering and Application, Chengdu, China, 19–22 September 2016. [[CrossRef](#)]



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