Calculation of Thermodynamic Properties and Transport Coefficients of C_4F_7N–PTFE Mixtures

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Abstract The thermodynamic properties and transport coefficients of C_4F_7N–PTFE gas mixtures in the temperature range from 300 to 30,000 K and the pressure range from 0.1 to 1.6 MPa are calculated. Special attention is paid to the effects of different PTFE ratios and gas pressures on the physical properties of C_4F_7N–PTFE mixed gases. The composition of arc plasma particles was determined based on the principle of minimizing Gibbs free energy, and the thermodynamic parameters and transport coefficients were determined by standard thermodynamic equations and Chapman-Enskog theory. It can be concluded that the addition of PTFE will have a certain degree of impact on the specific heat at constant pressure and thermal conductivity of the mixture. However, due to the compositional similarity between C_4F_7N and PTFE elements, a small amount of PTFE is not expected to result in significant changes to the performance of the plasma. Elevating the gas pressure can lead to an augmentation of the transport coefficients, particularly within the domain of elevated temperatures. The calculation results provide basic data for the simulation of plasmas using magnetohydrodynamics arc models, also provide a reference for the design of environmentally-friendly high-voltage circuit breakers; some examples are presented.

Keywords Thermodynamic properties · Transport coefficients · C_4F_7N · PTFE · Environmentally-friendly circuit breakers · Arc

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1 Introduction

C_4F_7N is under investigation as a promising SF_6 environmentally friendly substitute gas and is widely utilized in high-voltage circuit breakers owing to its excellent insulation and arc-extinguishing properties. C_4F_7N has a significantly lower global warming potential (GWP) than SF_6 and a suitable liquefaction temperature [1], making it an excellent choice for environmentally friendly substitute gases. In addition, compared with CO_2 and N_2, C_4F_7N has better arc interruption characteristics. In the low temperature and pressure range, the presence of C_4F_7N can increase the dielectric strength of CO_2 by more than half [2]. Therefore, studying the thermodynamic parameters and transport coefficients of C_4F_7N in the arc combustion process is essential.

When the self-powered circuit breaker is opened, PTFE vapor inevitably generated from the ablating nozzle material will alter the composition [3], thermodynamic properties, and transport coefficients of the arc plasma to a certain extent. To accurately evaluate the properties of gas mixtures and understand plasma behavior, it is essential to calculate the thermodynamic parameters and transport coefficients of C_4F_7N -PTFE mixed gases. In addition, plasma thermophysical parameters are essential input parameters for macroscopic magnetohydrodynamic (MHD) simulations of arc plasmas, which will also provide guidance for the design and manufacturing of environmentally friendly self-energizing expanding circuit breaker.

Previous research on the parameters of C_4F_7N gas has mostly focused on pure C_4F_7N and C_4F_7N-CO_2 binary mixtures. Chen et al. [4] used the Gibbs free energy minimization method to calculate the composition of C_4F_7N arc plasma under the assumptions of local thermodynamic equilibrium (LTE) and non-local chemical equilibrium (NLCE), and established a complete chemical decomposition pathway. Zhang et al. [5] derived the saturated vapor pressure of C_4F_7N-CO_2 mixture gas using the gas–liquid equilibrium law, and calculated the physical properties of the mixture such as compressibility factor, specific heat at constant pressure, and viscosity based on the Peng Robinson (P-R) equation of state, Joback group contribution method, and Thodos method. Zhang et al. [6] also calculated the equilibrium composition, thermodynamic properties, and transport coefficients of C_4F_7N-CO_2 thermal plasma at 300K-30kK, and analyzed the effect of pressure and CO_2 mixing ratio on the results, providing basic parameters for the magnetohydrodynamic (MHD) simulation of arc plasma.

In fact, the conditions in practical applications are highly complex. For example, in high-voltage circuit breakers, vapors generated from the arcing erosion of contacts and nozzles will mix with the arc extinguishing medium to form more complex gas mixtures. We have already calculated the thermodynamic properties and transport characteristics of the SF_6-PTFE-Cu ternary mixture generated from the nozzle erosion [7]. The results show that the addition of PTFE has a significant impact on the physical property parameters of SF_6, while a small amount of Cu vapor has little effect except for the electrical conductivity in the low-temperature region. However, research on environmentally friendly gas insulation media is still insufficient, and the properties of such mixtures are not fully understood. To address this issue, we studied the thermodynamic properties and transport coefficients of C_4F_7N-PTFE mixtures in this paper.

2 Calculation Principle and Method

The composition of thermal plasmas under local thermodynamic equilibrium (LTE) was calculated by the method of minimizing Gibbs free energy. The effect of solid phase on the calculation of transport coefficients and thermodynamic parameters in the low-temperature range was not considered in our calculations, due to the restrictions imposed by the MHD simulation modeling. The mass conservation law, Dalton's law of partial pressures, and the quasi-neutrality condition were used as constraints to determine the particle composition that minimizes the Gibbs free energy of the system. The system's Gibbs free energy can be expressed as follows:

$$G = \sum_{i=1}^{N} n_i \mu_i \tag{1}$$

$$\mu_i = \mu_i^0 + RT \ln(n_i / \sum_{j=1}^{N} n_j) + RT \ln(p/p^0) \tag{2}$$

In the equation, n_i represents the particle number density of species i, μ_i represents the chemical potential of species i, μ_i^0 represents the standard chemical potential of species i, R is the ideal gas constant, T is the plasma temperature, p is the gas pressure and p^0 is the reference pressure, and N is the total number of particle species.

Due to the additional effect of the electrostatic interaction between charged particles, it is assumed that the average electrostatic energy of electrons is much smaller than their thermal energy. It is also assumed that there are many of charged particles in the Debye sphere. According to the Debye–Huckel correction, the Gibbs free energy will be correspondingly reduced [8]:

$$g_h = -\sum_{j=1}^{N} N_j \left(eZ_j\right)^2 / (8\pi\varepsilon_0\lambda_D) \tag{3}$$

Dalton's law of partial pressures should be corrected to:

$$P + kT/\left(24\pi\lambda_D^3\right) = \sum_{i=1}^{w_{max}^g} n_i kT \tag{4}$$

The charge number of ion j is denoted as Z_j, ε_0 is the vacuum permittivity, λ_D is the Debye length, and k is the Boltzmann constant. The thermodynamic functions used to calculate the standard chemical potentials of the particles are often theoretically calculated using standard statistical mechanics methods for thermodynamic data such as particle rotational constants, fundamental vibrational frequencies, electron excitation energies, and formation enthalpies. These functions are then fitted to temperature-dependent standard functions using the least-squares method in the NASA chemical equilibrium code CEA. Upon determining the particle composition of the plasma, the thermodynamic properties such as density, enthalpy, and specific heat can be computed using established thermodynamic functions [9]. Specifically, they can be expressed as:

$$\rho = \sum_{i=1}^{N} n_i m_i \tag{5}$$

$$h = \frac{1}{\rho} \sum_{i=1}^{N} n_i m_i h_i \tag{6}$$

$$C_p = \frac{\partial h}{\partial T}|_{p=const} \tag{7}$$

3 Comparison and Analysis of Calculation Results

3.1 Plasma Composition

This section mainly calculates the plasma composition of C_4F_7N-PTFE mixed gas within the temperature range spanning from 300 K to 30,000 K. The main species considered in the calculation are shown in Table 1.

Figure 1 illustrates the variation of mole fraction of each species in 70% C_4F_7N-30% PTFE thermal plasma at 0.8 MPa with temperature from 300 to 30,000 K. In the lower temperature range of 300 to 5000 K, ionization reactions are weak, and the dissociation of C_4F_7N and PTFE molecules is the dominant process, resulting in a low concentration of charged ions in the plasma. The primary ionization strength significantly increases above 5000, and at about 9000 K, carbon atoms undergo

Table 1 Particle components of C_4F_7N-PTFE mixture

Particle type	Main species considered in plasma
Neutral	CF, CF_2, CF_3, CF_4, CN, C_2N, C_4N_2, C, F, N, C_2, C_3, N_2
Charged	C^+, C^{2+}, F^+, F^{2+}, N^+, N^{2+}, e

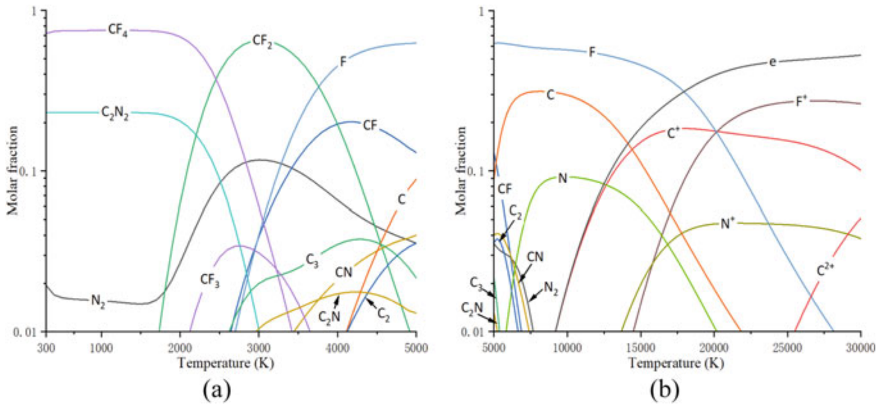

Fig. 1 Composition of C_4F_7N-PTFE mixture (C_4F_7N: PTFE = 7:3) as a function of temperature at 0.8 MPa, within the temperature ranges **a** from 300 to 5000 K, and **b** 5000 K to 30,000 K

intense ionization, resulting in a rapid increase in the number density of C^+ ions in the space. The significant ionization of nitrogen and fluorine atoms occurs at about 13,700 K and 14,500 K, respectively, due to the difference in their first ionization energies. At approximately 25,000 K, carbon atoms undergo intense second-order ionization, and the number of C^{2+} ions in the space significantly increases. With increasing temperature, molecular thermal motion and ionization reaction intensity become stronger, thus the behavior of electrons becomes evident at about 9000 K, and their number density continues to increase with increasing temperature.

The calculation results of the mole fraction of each species in the plasma do not correspond to the standard 70% C_4F_7N-30%PTFE mixture at 300K, which is due to the limitation of the algorithm principle. When calculating the plasma composition based on the principle of minimizing Gibbs free energy, only the possible particles in the system and their combinations that can exist in the specified temperature and pressure with the minimum Gibbs free energy are considered. Therefore, the calculation results in the low-temperature region correspond to the composition of the substance after the arc combustion, which is the result of the recombination of the high-temperature decomposition products of C_4F_7N-PTFE, and matches the post-arc analysis process.

3.2 Thermodynamic Properties

Effects caused by gas pressure. The partial thermodynamic properties of the C_4F_7N-PTFE mixture at different pressures are shown in Fig. 2. According to the gas state equation, an elevation in pressure results in an augmentation of the particle number per unit volume, resulting in an increase in the mass density of the plasma at all temperatures. In addition, according to the Le Chatelier's principle, ionization

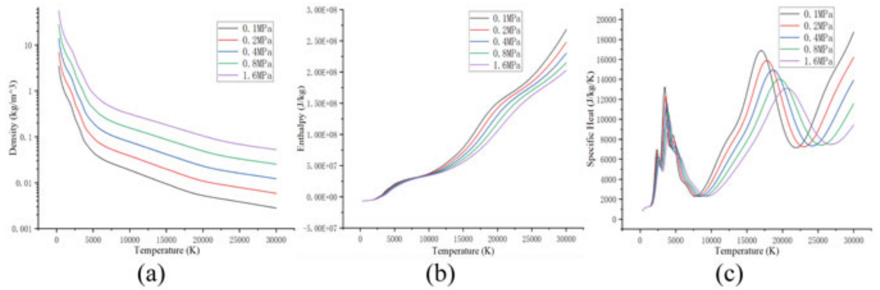

Fig. 2 Thermodynamic properties of C_4F_7N-PTFE mixture (C_4F_7N: PTFE = 7:3) as a function of temperature at 0.1–1.6 MPa, **a** Density **b** Enthalpy **c** Specific Heat

and dissociation reactions are suppressed as pressure increases, and heavy particles appear at higher temperatures. Figure 2 further illustrates the specific heat and enthalpy at constant pressure of the C4F7N-PTFE mixture under varying pressures. As the gas pressure increases, the peak of the specific heat related to ionization and dissociation reactions moves to higher temperatures and the peak value gradually decreases. This further corroborates that raising the gas pressure at a specific temperature can mitigate ionization and dissociation reactions.

Effects caused by PTFE. The partial thermodynamic properties of C_4F_7N-PTFE mixtures at 8 atm under different mixing ratios are shown in Fig. 3. Since the atomic composition of C_4F_7N is similar to that of PTFE, the proportion of PTFE has little effect on the density and enthalpy of the mixture. In the mixture, the peak values of the specific heat at constant pressure are observed approximately around 2600, 3900, and 5200 K, corresponding to the decomposition of CF4, CF2, and CF molecules, respectively. The differences in the specific heat at constant pressure of the mixture at different PTFE contents around 3900, 5200, and 8000 K are mainly related to the decomposition and recombination of CN, C_2N, and N_2 molecules. The physical and chemical reactions in the mixture are dominated by the ionization and recombination of C and F atoms, so the trends in the thermodynamic properties of the plasma under different mixing ratios are roughly the same.

3.3 Transport Properties

Effects caused by gas pressure. The partial transport coefficients of the C_4F_7N-PTFE mixture at different pressures are shown in Fig. 4. Within the high-temperature range, an elevation in pressure leads to an augmentation of the plasma conductivity. This phenomenon arises due to the positive correlation between the conductivity of the mixture and the electron number density. At high temperatures, the C_4F_7N-PTFE mixture is intensely ionized, and higher pressure results in a greater electron number

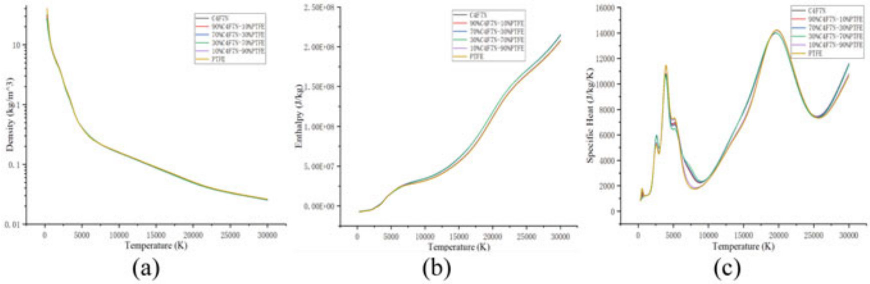

Fig. 3 Thermodynamic properties of C_4F_7N-PTFE mixture with different mixing ratios at 0.8 MPa, **a** Density **b** Enthalpy **c** Specific Heat

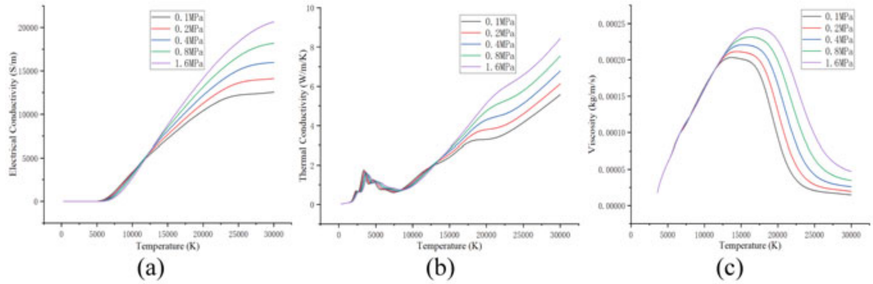

Fig. 4 Transport properties of C_4F_7N-PTFE mixture (C_4F_7N: PTFE = 7:3) as a function of temperature at 0.1–1.6 MPa, **a** Electrical Conductivity **b** Thermal Conductivity **c** Viscosity

density, which in turn increases the plasma conductivity. However, at low temperatures, increasing pressure suppresses the ionization reaction, leading to a decrease in the corresponding electron number density. Therefore, at low temperatures, the conductivity of the mixture decreases with increasing pressure.

Regarding the thermal conductivity of the C4F7N-PTFE mixture, an increase in pressure results in a shift of the thermal conductivity peak towards higher temperatures, accompanied by a decrease in the absolute value of the peak. This is consistent with the variation pattern of the mixture's specific heat capacity at constant pressure and is related to the effect of pressure on ionization and dissociation reactions. Additionally, Fig. 4 also shows the viscosity coefficient of the mixture at different pressures. At temperatures above approximately 12,000 K, the viscosity coefficient exhibits a significant increase with rising pressure. This phenomenon is attributed to the reduction in particle ionization degree caused by the elevated pressure, which subsequently impacts the Coulomb collisions among charged particles. The cross section of Coulomb collisions is significantly greater than that of collisions between neutral particles. Therefore, the viscosity increases with decreasing ionization degree, i.e., it increases with increasing pressure.

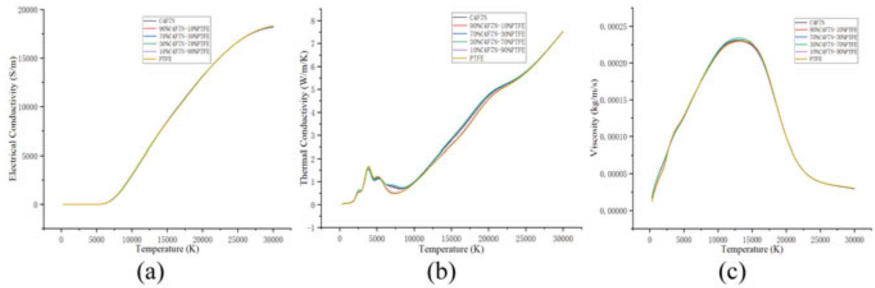

Fig. 5 Transport properties of C_4F_7N-PTFE mixture with different mixing ratios at 0.1–1.6 MPa, **a** Electrical Conductivity **b** Thermal Conductivity **c** Viscosity

Effects caused by PTFE. The partial transport coefficients of C_4F_7N-PTFE mixtures at 8 atm for various mixing ratios are presented in Fig. 5. The electrical conductivity of the plasma mainly depends on the electron number density. Since the ionization energy of C atoms is relatively low and the N content in the mixture is relatively low, the ionization reaction of the mixture is mainly dominated by C and F atoms, and the PTFE content has little effect on the electrical conductivity of the C_4F_7N-PTFE mixture. The differences in thermal conductivity around 8000 K correspond to the decomposition of CN and N_2 and the generation of N atoms. Meanwhile, due to the similarity in the number density of charged particles, the collision integral results of Coulomb interactions are also similar, and the viscosity coefficient of the mixture is also less affected by the PTFE content.

4 Discussion

The computational accuracy of thermodynamic properties and transport coefficients for low-temperature plasmas is currently insufficient. At low plasma temperatures, the inter-particle collisions are insufficient, and the efficiency of energy transfer between electrons and heavy particles is low, leading to the breakdown of the assumption of thermodynamic equilibrium (LTE). In situations where the collisions between electrons and heavy particles are insufficient, they acquire different temperatures, and the principle of minimum Gibbs free energy no longer applies. In future work, we will consider non-equilibrium thermodynamics and double-temperature plasma models to obtain more accurate results.

In addition, some researchers have shown that solid deposition can affect certain properties of low-temperature plasmas [10]. Although the theoretical calculation of transport coefficients is not significantly affected by solid particles, this is still an area that can be improved for obtaining more accurate theoretical calculations.

5 Conclusion

This paper calculates the thermodynamic properties and transport coefficients of C_4F_7N-PTFE mixtures, and studies the effects of different pressures and PTFE mixing ratios on these parameters. The results show that due to the similarity in atomic composition between C_4F_7N and PTFE, the PTFE mixing ratio has a small influence on the physical properties parameters, except for specific heat and thermal conductivity. The thermal conductivity and specific heat of the plasma are mainly related to the dissociation and ionization reactions of the mixture, and are affected to some extent by the presence of N-containing particles. Furthermore, the gas pressure exerts a notable influence on the transport coefficients and thermodynamic parameters of the mixture, particularly at elevated temperatures. At lower temperatures, the electrical conductivity of the plasma decreases with increasing pressure, indicating that higher gas pressure is beneficial for extinguishing the arc in high-voltage circuit breakers.

The thermodynamic properties and transport coefficients of the plasma are essential input parameters for the macroscopic magnetohydrodynamic (MHD) model of the arc. The calculated results of this study will provide basic data for MHD simulations of the arc, and further guide the design and manufacture of C_4F_7N environmentally friendly gas circuit breakers.

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