Thermodynamic and Transport Properties of N$_2$/O$_2$ Mixtures at Different Admixture Ratios

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Thermodynamic and transport properties such as mass density, enthalpy, specific heat, electrical and thermal conductivities and radiation power of N$_2$/O$_2$ mixture plasmas at different admixture ratios were calculated in pressure range from 0.1 to 2 MPa on the assumption of thermal equilibrium condition. The first order approximation of Chapman-Enskog method was adopted to derive the transport properties. The thermodynamic and the transport properties thus derived were used to predict the temperature distributions and electric field strength of wall-stabilized N$_2$/O$_2$ arcs in steady state at a current of 20 A$_{dc}$ in order to investigate fundamental feature of N$_2$/O$_2$ mixture arcs before current zero. The calculation revealed that the temperature at the center of the arcs had a local minimum value of 8800 K at an admixture ratio around 80%N$_2$-20%O$_2$ and whilst the conductance of the arc has a minimum at an admixture ratio of 100%N$_2$ for pressure of 0.5 MPa in steady state.

Keywords: thermodynamic and transport properties, N$_2$/O$_2$ mixture plasma, admixture ratio, temperature distribution

1. Introduction

In high-voltage circuit breakers, SF$_6$ gas is widely adopted as the arc quenching medium since it has an attractive arc quenching capability. The capability is considered to arise not only from the electronegative properties of SF$_6$ gas and its products, but also from the high thermal conductivity at low temperature around 2000 K (29). The use of SF$_6$ gas as the arc quenching medium has led to the high interruption capability and the downsizing of a circuit breaker.

Recently, however, emission of SF$_6$ gas and its products to the atmosphere has been an environmental issue because of its remarkable greenhouse effect. In order to compare the greenhouse effect of different gases, a method has been developed of estimating their global warming potentials (GWP). The GWP is the cumulative enhancement occurring between now and a chosen later time, in relation to a reference gas, CO$_2$. Pure SF$_6$ gas has an extremely high GWP of 23 900 over 100 years. Thereby, in the third Conference of Parties to the U.N. Framework Convention on Climate Change (COP3) held in Kyoto, Japan in 1997, developed countries were required to reduce the generation of six greenhouse gases like CO$_2$ as well as SF$_6$ gas by on average 5.2 percent by the period 2008-2012 (29). Much effort have been made to find out an alternative gas of SF$_6$ gas for arc quenching medium until now. However, none of gases with small GWP and attractive arc quenching property has been able to be found yet. Gas mixtures such as SF$_6$/N$_2$, SF$_6$/CF$_4$ and SF$_6$/C$_2$F$_4$ have been developed to utilize for the arc quenching medium (39)-(79). These SF$_6$ gas mixtures are expected to be used for the moment, however, the use of these mixtures is not an essential resolution of the environmental issue.

The atmosphere, that is air, is composed mainly of 78%-nitrogen and 22%-oxygen, which are, of course, environmental-friendly gases. The air has so far been used in an air-blast circuit breaker as the arc quenching medium, although it has much weaker arc quenching capability than SF$_6$ gas. However, few engineers tried to find the optimum admixture ratio of N$_2$/O$_2$ for the purpose of arc interruption.

The present research aims to find an N$_2$/O$_2$ admixture ratio adequate to the arc quenching in a circuit breaker from the view point of thermodynamics. For this purpose, it is greatly required to obtain the thermodynamic and transport properties of N$_2$/O$_2$ mixtures. In this paper, therefore, numerical calculations were performed to derive thermodynamic and transport properties such as mass density, enthalpy, specific heat, electrical and thermal conductivities and radiation power of N$_2$/O$_2$ mixture plasmas at different admixture ratios on the assumption of thermal equilibrium. First, equilibrium compositions of N$_2$/O$_2$ plasma at different admixture ratios were calculated. Secondly, their thermodynamic and transport properties were theoretically derived. Finally, using the properties thus derived, temperature distributions of a wall-stabilized arc in steady state were predicted for different admixture ratios of N$_2$/O$_2$ in order to investigate fundamental feature of the arc before current zero.
2. Equilibrium composition of N₂/O₂ mixture

In this calculation, we took account of the following 16 species: N₂, O₂, NO, N, O, N⁺, N₂⁺, O⁺, O₂⁺, N⁻, O⁻, N₂⁻, O₂⁻, NO⁺, N⁻, O⁻, and the electron. For these species, a system of equations was set up including Saha's equations for ionization reactions, Gulberg-Waage's equations for dissociation reactions, the charge neutrality equation, the equation of state and the conservation equation of N₂/O₂ ratio, i.e.:

\[ \frac{X_{N_2}}{X_{O_2}} = \frac{N_N}{N_O} \]  

\[ N_N = 2(n_{N_2} + n_{N_2^+} + n_{N_2^-}) + n_N + n_{N_2}^+ + n_{N_2^-} + n_{N_2O^+} \]

\[ N_O = 2(n_{O_2} + n_{O_2^+} + n_{O_2^-}^+ + n_{O_2^-}) + n_{O_2^-} + n_{N_2O}^+ + n_{N_2O^-} \]

\[ X_{O_2} = 100 - X_{N_2} \]

where \( X_{N_2} \) and \( X_{O_2} \) are the concentrations of nitrogen and oxygen, respectively, \( n_j \) is the number density of species \( j \). These equations were simultaneously solved using Newton-Raphson method in temperature range of \( T=300-30000 \) K, for \( X_{N_2} \) from 0 to 100% and pressure \( P \) from 0.1 to 2 MPa. The case of \( X_{N_2}=78\% \) corresponds to the pure dry air.

Figure 1 indicates the equilibrium composition of N₂/O₂ plasma at an admixture ratio of 80% N₂-20% O₂ and at a pressure of 0.1 MPa as an example. As seen in Fig. 1, N₂ and O₂ dissociate with temperature \( T \) to be N and O atoms. At the same time, N and O combine to produce NO. The molecule NO mainly emits electrons at temperatures up to 8000 K because of its lowest ionization potential of 9.26 eV among all species in N₂/O₂ plasmas (11).
on pressure \( P \). The mass density \( \rho \) proves to be almost in proportion to pressure.

3.2 Enthalpy  Enthalpy \( h \) of thermal plasma is given by the following expression:

\[
  h = \frac{1}{\rho} \sum_j n_j \left( \frac{5}{2} k T + k T^2 \frac{\partial \ln Z_j}{\partial T} + \Delta H_f^j \right)
\]

where \( k \) is the Boltzmann’s constant, \( Z_j \) and \( \Delta H_f^j \) are the internal partition function and the standard enthalpy of formation, respectively. Figure 4 represents variations in \( h \) versus \( T \) at \( P=0.5 \) MPa. Sharp variations are found in \( h \) around 4200 and 7500 K. Each of them arises from the energy necessary for dissociations of \( \text{O}_2 \) and \( \text{N}_2 \), respectively.

3.3 Specific heat at constant pressure  Specific heat \( C_p \) is one of the important properties for transient plasma. The value \( C_p \) can be computed by

\[
  C_p = \frac{\partial h}{\partial T} \bigg|_{P=\text{const.}}
\]

Figure 5 shows \( C_p \) for \( \text{N}_2/\text{O}_2 \) plasma at \( P=0.5 \) MPa. We can notice two remarkable peaks in \( C_p \) around \( T=4200 \) and 7500 K. They result from the requirement of energy for dissociating \( \text{O}_2 \) and \( \text{N}_2 \), respectively, as discussed in the previous section of \( h \). The peak around \( T=17 200 \) K is due to ionizations of \( \text{N} \) and \( \text{O} \). In Fig.6 pressure dependence of \( C_p \) is demonstrated for 50% \( \text{N}_2-50\% \text{O}_2 \) plasma. At higher pressure, the \( \text{O}_2 \) and \( \text{N}_2 \) dissociation peaks and the \( \text{O} \) and \( \text{N} \) ionization peaks are shifted to higher temperatures, and lower maximum values are obtained. This is due to the fact that the fraction of dissociated and ionized particles in the gas decreases with rising pressure according to Guldberg-Waage’s and Saha’s equations (8).

4. Transport properties

4.1 Collision integrals  The Chapman-Enskog formula for calculating electrical and thermal conductivities requires data on the collision integrals classified into momentum transfer cross sections \( \pi_{ij}^{(1,1)} \) and viscosity cross sections \( \pi_{ij}^{(2,2)} \) between all couples of particles in \( \text{N}_2/\text{O}_2 \) plasma. These data were obtained as follows:

(i) Neutral-neutral interaction. The cross sections \( \pi_{ij}^{(1,1)} \) and \( \pi_{ij}^{(2,2)} \) among \( \text{N}_2, \text{O}_2, \text{NO}, \text{N}, \text{and O} \) have been given by Yos (9). These data were directly used in this calculation.

(ii) Ion-neutral interaction. For the interactions between neutral species \( \text{N}_2, \text{O}_2, \text{NO}, \text{N}, \text{and O} \), and ionized species \( \text{NO}^+, \text{N}^+, \text{O}^+, \text{N}_2^+, \text{and O}_2^+ \), the cross sections were given by Yos (9). The cross sections \( \pi_{ij}^{(1,1)} \) and \( \pi_{ij}^{(2,2)} \) of the other couples were assumed to be equal to the ones for neutral-neutral interactions.

(iii) Electron-neutral interaction. The cross sections \( \pi_{ij}^{(1,1)} \) and \( \pi_{ij}^{(2,2)} \) of electron-\( \text{N}_2, \text{O}_2, \text{NO}, \text{N}, \text{and O} \) were also derived by Yos (9).
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(iv) Interaction between charged particles. The cross sections between charged particles were calculated by Gvosdover cross section for Coulomb potential \(^9\).

4.2 Electrical conductivity The data on the compositions and the collision integrals derived in the previous sections enable us to calculate the electrical conductivity \(\sigma\) of N₂/O₂ plasma in accordance with the first order approximation of the Chapman-Enskog method:

\[
\sigma = \frac{e^2}{4\pi \varepsilon_0 kT} \sum_{j} \sum_{i} n_i \Delta_{ej}^{(1)}
\]

where \(e\) is the electronic charge, \(k\) the Boltzmann’s constant and \(\varepsilon_0\) the dielectric constant of vacuum.

Figure 7 plots \(\sigma\) versus \(X_{N_2}\) at \(P=0.5\) MPa. It should be noted that \(\sigma\) has a local maximum value around \(X_{N_2}\) of 10% at 3000-8000 K. For example, at \(T=5000\) K, \(\sigma\) is 45.6 S/m. Whereas, \(\sigma\) drops drastically with \(X_{N_2}\) from 95 to 100%. This is because NO which has lower ionization potential than the other species markedly diminishes with \(X_{N_2}\) from 95 to 100 %.

The effect of pressure on \(\sigma\) can be seen in Fig.8. Pressure rise leads to a decline of \(\sigma\) at lower temperatures than 12 500 K. The reason is more frequent collisions occurring at higher pressures. On the other hand rising pressure enhances \(\sigma\) at higher temperatures than 12 500 K. This is due to the augment of electron number density resulting from pressure rise.

4.3 Thermal conductivity Thermal conductivity \(\kappa\) is expressed by the sum of three contributions:

\[
\kappa = \kappa_{tr} + \kappa_{in} + \kappa_{re}
\]

\[
\kappa_{tr} = \frac{15}{4} k \sum_i \sum_j n_i \alpha_{ij} n_j \Delta_{ij}^{(2)}
\]

where \(\kappa_{tr}, \kappa_{in}\) and \(\kappa_{re}\) are translational, internal and reactional thermal conductivities, respectively, \(C_p\) is the specific heat of species \(i\), \(\Delta H_l\) is the reaction heat for a reaction \(l\).

Figure 9 shows the variations of \(\kappa\) of N₂/O₂ mixtures for different admixture ratios. For pure O₂ the peak centered at about 4200 K can be remarked. Rising \(X_{N_2}\) brings a decrease in this peak value, and whilst forms another peak around 7500 K. These means that the peak at 4200 K originates from the dissociation of O₂ and the peak at 7500 K from that of N₂. Figure 10 includes the effect of pressure on \(\kappa\). As found in the section of \(C_p\) two peaks at 4200 and 7500 K are shifted to the higher temperature with an increase in pressure. At temperatures between 15 000–30 000 K, pressure rise results in elevating \(\kappa\), which is ascribable to rising translational thermal conductivity of the electron by the increase in electron number density.

5. Radiation power In this paper, we calculated radiation power \(P_{rad}\) taking account of contributions of continuous spectra due...
6. Temperature distribution in a wall-stabilized arc in steady state

For the purpose of investigating the arc interruption characteristics, it is useful to understand features of the wall-stabilized arcs. A wall-stabilized arc in steady state was assumed to be governed by the following relationship:

$$E = \frac{I}{G}$$

where $$E$$ is the electric field strength, $$I$$ is the current, $$r_{\text{wall}}$$ is the radius of the wall and $$G$$ is the conductance for a 1-m long arc. The above equations were solved by iterative method to find the effect of admixture ratio of N$_2$/O$_2$ on the temperature distribution of a wall-stabilized arc in steady state. The wall radius $$r_{\text{wall}}$$ and the temperature at the wall boundary were set to be 2.5 mm and 300 K, respectively. The value of current $$I$$ was fixed to 20 A$_{\text{dc}}$ as an example, because it is important to investigate the important and fundamental characteristics of the arc at several micro-seconds before current zero in the high current interruption. In this calculation, any self-absorption was neglected for the quantity $$P_{\text{rad}}$$ for pure N$_2$ plasma at a pressure of 0.1 MPa derived in this paper was confirmed to have similar value to that calculated by Gleizes in the case that no self-absorption was taken into account$^{(5)}$. From Fig.11, we can find that $$P_{\text{rad}}$$ increases with $$X_{N_2}$$ in the temperature range above 7000 K since emission coefficients of N and N$^+$ spectral lines in the ultraviolet wavelength region, which are dominant components of $$P_{\text{rad}}$$, rises with $$X_{N_2}$$.

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simplicity and $P_{\text{rad}}$ derived in the previous section was directly used. Thereby, note that the arc temperature and the arc conductance $G$ were under-estimated.

Figure 12 presents the temperature distributions of $N_2/O_2$ plasmas at a pressure of 0.5 MPa in steady state. As the concentration of $O_2$ increases, the temperature distribution shrinks in the radial direction and further the temperature at the center of the arc is generally elevated. This is attributed to the higher thermal conductivity at $T=4200$ K caused by the dissociation of $O_2$.

The effect of pressure on the temperature distribution of a wall-stabilized arc can be seen in Fig.13. Pressure rise makes temperature distribution plainer shape because of high $P_{\text{rad}}$ at the center of the arc and of high thermal conductivity.

In addition, Fig.14 (a)(b)(c) and (d) demonstrate $T$, $\sigma$ at the center of the arc and $E$ as well as $G$ for different $P$ as a function of $X_{N_2}$. It should be noted from Fig.14 (a) and (b) that $T$ and $\sigma$ at the center of the arc have local minimum values 8800 K and 1240 S/m at 0.5 MPa, respectively, in the case of admixture ratio 80$\%$ $N_2$-20$\%$ $O_2$, which is almost the air composition. Further, $T$ at the center of the arc decreases with $P$ resulting mainly from high thermal conductivity and high radiation loss as mentioned above. However, as seen in Fig.14 (c), $E$ increases with $X_{N_2}$ except in the case of $P=2.0$ MPa. At the same time, the whole conductance $G$ of the arc decreases with $X_{N_2}$ and has a minimum value at $X_{N_2}=100$ $\%$ as illustrated in Fig.14 (d). For example, $G$ has a minimum value of 0.0045 S m at 0.5 MPa. This means that pure $N_2$ requires more input power than any other $N_2/O_2$ mixtures to sustain 20 A$_{dc}$ arcs. This result might imply that pure $N_2$ is better medium than air from the viewpoints of arc interruption.

7. Conclusions

Thermodynamic and transport properties such as mass density, enthalpy, specific heat and electrical and thermal conductivities as well as radiation power were computed for $N_2/O_2$ mixture plasmas at different admixture ratios. The calculation was based on the thermal equilibrium. The first order approximation of Chapman-Enskog method was adopted to get the transport properties. In addition, using the thermodynamic and transport properties thus derived, the temperature distributions of a wall-stabilized arc in steady state were calculated to find the effect of admixture ratio on fundamental characteristics of the arc. It was found that the temperature and electrical conductivity have local minimum values at an admixture ratio of 80$\%$ $N_2$-20$\%$ $O_2$ which is almost the air composition, and while that the electric field strength has a maximum at $X_{N_2}=100$. For example, $E$ is 4500 V/m at $X_{N_2}=100$ $\%$ at a pressure of 0.5 MPa. This result indicates $X_{N_2}=100$ $\%$ causes lowest conductance of the arc for a current of 20 A$_{dc}$.

The above results give us an important and fundamental information about high current arc around current zero region.

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![Figure 14](image.png)

Fig. 14. Dependence of temperature, electrical conductivity at the center of the arc, electric field strength and conductance in N<sub>2</sub>/O<sub>2</sub> arcs at different pressures. The current is 20 A<sub>dc</sub>.