Numerical Analysis on the Nonequilibrium Phenomena of the Electronic Excitation Process behind Hypersonic Shock Waves

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In this study, the nonequilibrium phenomena of the electronic excitation process behind hypersonic shock waves have been investigated through numerical analysis. In the analysis, the three-temperature model is employed and temperature profiles are computed along the distance from the shock front. In the three-temperature model, the translational–rotational, vibrational and electron-electronic excitation temperatures are separately described and the relaxation processes for each energy mode are considered. Numerical calculations are conducted under the conditions corresponding to the shock tube experiments conducted in our previous study and the results are compared with the experimental data. It is found that the calculated and measured vibrational temperature profiles are in good agreement. In contrast, the calculated electronic excitation temperature is much lower than the measured one, revealing the discrepancy in the modeling of the electronic excitation temperature. To investigate the effect of electron behavior, parametric studies are conducted using the three-temperature model. The calculated temperatures agree well with the measured temperatures by considering the electrons in the region ahead of the shock wave. This result suggests that the effect of electron behavior is significant for hypersonic shock waves and a detailed model to describe the nonequilibrium phenomena is needed.

Key Words: Three-Temperature Model, Re-Entry, Shock Wave, Thermochemical Nonequilibrium, Precursor Heating

Nomenclature

\[ \begin{align*}
    C & : \text{reaction rate constant, m}^3/(\text{mol} \cdot \text{s}) \\
    D_0 & : \text{dissociation energy, J/kg} \\
    E & : \text{total energy per unit volume, J/m}^3 \\
    E_v & : \text{vibrational energy per unit volume, J/m}^3 \\
    E_e & : \text{electronic energy per unit volume, J/m}^3 \\
    e & : \text{electronic charge, } 1.9 \times 10^{-19}, \text{C} \\
    e_{v,s} & : \text{vibrational energy per unit mass of species } s, \text{J/kg} \\
    e_{e,s} & : \text{electronic energy per unit mass of species } s \text{ evaluated at temperature } T_e, \text{J/kg} \\
    e_{v,s}^{**} & : \text{vibrational energy per unit mass of species } s \text{ evaluated at temperature } T_v, \text{J/kg} \\
    e_{e,s} & : \text{electronic energy per unit mass of species } s, \text{J/kg} \\
    h & : \text{mixture enthalpy per unit mass of species } s, \text{J/kg} \\
    M & : \text{molecular weight, kg/mol} \\
    n & : \text{number density, m}^{-3} \\
    P_0 & : \text{ambient pressure ahead of the shock wave, Pa} \\
    \rho & : \text{density, kg/m}^3 \\
    \rho_0 & : \text{ambient pressure ahead of the shock wave, Pa} \\
    \bar{R} & : \text{universal gas constant, 8.314 J/(mol} \cdot \text{K}) \\
    T & : \text{translational temperature, K} \\
    T_{\text{shock}} & : \text{post-shock translational–rotational temperature, K} \\
    T_v & : \text{vibrational temperature, K} \\
    T_{v,\text{shock}} & : \text{post-shock vibrational temperature, K} \\
    T_e & : \text{electron-electronic excitation temperature, K} \\
    u & : \text{velocity, km/s} \\
    V & : \text{shock velocity, km/s} \\
    q_v & : \text{vibrational heat conduction, W/m}^2 \\
    q_e & : \text{electronic heat conduction, W/m}^2 \\
    q_r & : \text{translational–rotational heat conduction, W/m}^2 \\
    \alpha & : \text{mole fraction of electrons} \\
    \varepsilon_0 & : \text{vacuum permittivity, F/m} \\
    \kappa & : \text{Boltzmann constant, } 1.380622 \times 10^{-23}, \text{J/K} \\
    \lambda & : \text{thermal conductivity, W/(m} \cdot \text{K}) \\
    \theta_v & : \text{characteristic temperature, K} \\
    \rho & : \text{density, kg/m}^3 \\
    v & : \text{vibration} \\
    e & : \text{electron} \\
    s & : \text{species} \\
    t & : \text{translation} \\
\end{align*} \]

Subscripts

0: initial condition

1. Introduction

The thermochemical nonequilibrium phenomena behind hypersonic shock waves play a pivotal role in the development of re-entry vehicles because they have a significant influence on the aerodynamic characteristics and heating rates of these vehicles. Much research has been conducted to both theoretically and experimentally investigate these phenomena.1–4) As a result, several thermochemical models for re-entry calculations have been developed and applied to the design of re-entry vehicles.5–8) Recently, a series of shock tube experiments were conducted by Yamada et al.9,10) to validate the two-temperature model for the super-orbital re-entry flight conditions encountered by the Hayabusa re-entry capsule.11) In these experiments, the gas radiation behind a shock wave was...
observed by spectroscopic measurements and rotational, vibrational and electronic excitation temperatures were deduced from the measured spectra. The results show that the electronic excitation temperature is higher than the vibrational temperature immediately behind a shock wave. This contradicts the assumption of the two-temperature model. This is because the electron translational and electronic excitation temperatures are assumed to be equal to the vibrational temperature in the model. Therefore, the electronic excitation temperature should be separated from the vibrational temperature in thermochemical models.

In the present study, the three-temperature model formulated by Fujita and Abe^{12} is applied and numerical analysis is conducted to investigate the thermochemical nonequilibrium phenomena of the electronic excitation process behind a shock wave. The numerical conditions correspond to those of the shock tube experiments in our previous study^{10} and the results are compared with the experimental data.

2. Numerical Model

2.1. Governing equations

The following assumptions are made:
(1) The flow is one-dimensional.
(2) The free-stream gas is \( N_2 \) and five species components \( (N_2, \text{N, e, N}^+, \text{N}_2^+) \) in the shock layer are considered.
(3) The translational and rotational temperatures are in equilibrium and are denoted as the translational–rotational temperature \( T_t \). The electron translational and electronic excitation temperatures are also in equilibrium and are uniquely defined as the electronic temperature \( T_e \). The translational–rotational temperature \( T_t \) and the vibrational temperature \( T_v \) are common among the chemical components.
(4) Radiative processes are not considered.
(5) The ionized gas is electrically quasi-neutral.

In this study, one-dimensional Navier-Stokes equations with thermochemical nonequilibrium model are solved. The governing equations are given as follows

\[
\frac{\partial Q}{\partial t} + \frac{\partial F}{\partial x} = \frac{\partial F_v}{\partial x} + W. \tag{1}
\]

Here, the vector \( Q \) comprises conservative variables, \( F \) is the inviscid flux vector, \( F_v \) is the viscous flux vector and \( W \) is the source vector. These vectors are given by the following expressions

\[
Q = \begin{pmatrix}
\rho_v \\
\rho_v u \\
\rho_v u^2 + p \\
E_v \\
E_v \\
E_v \\
E_v \\
\end{pmatrix}, \quad F = \begin{pmatrix}
\rho_v u \\
\rho_v u^2 + p \\
(E + p)u \\
E_v u \\
E_v u \\
E_v u \\
\end{pmatrix}, \quad F_v = \begin{pmatrix}
-\rho_v u \\
\tau_{xx} u - q_t - \sum_{s} \rho_v h_s u_s \\
-\rho_v q_t - \sum_{s} \rho_v e_{ts,vs} u_s \\
-\rho_v q_t - \sum_{s} \rho_v e_{ts,vs} u_s \\
\end{pmatrix}, \quad W = \begin{pmatrix}
W_t \\
W_e \\
0 \\
W_e \\
\end{pmatrix}. \tag{2}
\]

The shear stress \( \tau_{xx} \) is assumed to be proportional to the first derivative of the velocity, and the Stokes assumption for the bulk viscosity is made. Therefore, the shear stress is given by the following equation

\[
\tau_{xx} = 4 \mu \frac{\partial u}{\partial x}. \tag{3}
\]

The heat conduction fluxes are given by the Fourier heat law as follows

\[
q_t = -\lambda \frac{\partial T}{\partial x}, \quad q_e = -\lambda_e \frac{\partial T_e}{\partial x}, \tag{4}
\]

The transport properties formulated by Gupta et al.\(^{7}\) are widely used to perform CFD calculations. However, it has been reported that the accuracy of this model deteriorates when the gas temperature is extremely high. To eliminate the uncertainties in the mass and heat transfer processes, the viscosity, heat conductivity and diffusion flux are computed in a manner similar to Fertig et al.\(^{13}\) on the basis of the Chapman-Cowling first approximation.\(^{14}\) The effect of an ambipolar electric field is incorporated into the diffusion flux.\(^{15}\) Most collision integrals used for the evaluation of the transport properties are taken from the latest curve fitting of Capitelli et al.\(^{16}\) and those for the shielded Coulomb collisions between charged particles are calculated by fitting to the result from Ref. 17.

2.2. Energy exchanges among different modes

In this study, translational–vibrational (T–V), translational–electronic (T–E) and vibrational–electronic (V–E) energy transfers are considered.

2.2.1. Translational–vibrational energy exchange

The vibrational energy source term \( W_v \) in Eq. (2) is described as

\[
W_v = Q_{T-V} + Q_{E-V} + Q_{P-V}. \tag{5}
\]

The first term of Eq. (5) is the rate of the energy exchange between the translational and vibrational modes. This is described by the Landau-Teller formula\(^{18}\) modified by Park

\[
Q_{T-V} = \sum_{s=\text{molecule}} \rho_v s \left[ \frac{E_{ts} - E_{vs}}{T_{\text{shock}} - T_v} \right] \frac{T_{\text{shock}} - T_v}{T_{\text{shock}} - T_{v,\text{shock}}}^{5/2} \tag{6}
\]

where

\[
S = 3.5 \exp(-5000/T_{\text{shock}}), \tag{7}
\]

and \( t_{\text{shock}} \) is the translational–vibrational energy relaxation time for species \( s \) from the correlation of Millikan-White\(^{19}\) given by

\[
\frac{1}{\rho^*_{e,\text{electron}}} = \sum_{s=\text{molecule}} \frac{n_s \exp[A_s \left( T^{-1/3} - B_s \right) - 18.42]}{\sum_{s=\text{molecule}} n_s}. \tag{8}
\]

The constants \( A \) and \( B \) are listed in Ref. 8). \( t_{\text{shock}}^p \) is the translational and vibrational energy relaxation time for species \( s \) (the limiting form at high temperatures) as proposed by Park and is given by
where the average molecular speed of species \( s \), \( c_s \), and the limiting collision cross-section \( \sigma_{s} \), are given by

\[
c_s = \sqrt{8kT/\pi M_s}, \quad \sigma_s = 10^{-20}(50,000/T)^2.
\]

\( Q_{E-V} \) in Eq. (5) is the rate of the energy exchange between the vibrational and electronic excitation modes. It is described by the Landau-Teller formula as

\[
Q_{E-V} = \sum_{s=molecule} \rho_s e^{v_s^+}_e - e^{v_s}_e \ \tau_e.
\]

\( Q_{D-V} \) in Eq. (5) is the change in the vibrational energy at dissociation and recombination and given by Eq. (12). \( \bar{T}_i \) is the average vibrational energy which is created or destroyed by the Landau-Teller formula as

\[
Q_{D-V} = \sum_{s=molecule} \bar{T}_i, W_s.
\]

2.2.2. Translational electron energy exchange

The electron and electronic excitation source term \( W_e \) in Eq. (2) is described by

\[
W_e = Q_{T-E} - Q_{E-V} + Q_{L-E}.
\]

The first term of Eq. (13) is the energy exchange due to the elastic collisions between the electrons and heavy particles. It is given in terms of the electronic collision frequency as

\[
Q_{T-E} = 2n_e \frac{k(T_i - T_e)}{\tau_e} \sum_{s=electron} \frac{v_{es}}{M_s}
\]

where \( v_{es} \) is the collision frequency given by

\[
v_{es} = n_e \sigma_s \sqrt{8kT_e/\pi M_e}
\]

and \( \sigma_s \) is the energy transfer cross-section between the electrons and heavy particles of species \( s \). If species \( s \) is an ion, the energy transfer cross-section is much larger than that of a neutral species. This is owing to the effect of the Coulomb force. For an ion species, the energy transfer cross-section is given by

\[
\sigma_s = \frac{4}{3} \frac{2\pi e^4}{(3kT_e)^2} \ln \left( 1 + \frac{d^2(3kT_e)^2}{e^2} \right).
\]

Here, \( d \) is the Debye cutoff length defined as

\[
d = \sqrt{\frac{8\pi kT_e}{n_e e^2}}.
\]

For a neutral species, the energy transfer cross-section is given as

\[
\sigma_s = \bar{a}_n + \bar{b}_n + \bar{c}_n.
\]

Here \( \bar{a}_n, \bar{b}_n, \bar{c}_n \) are constants and are listed in Ref. 6.

\( Q_{E-V} \) in Eq. (13) is the rate of the energy exchange between the vibrational and electron-electronic excitation modes and is given by Eq. (11).

\( Q_{L-E} \) in Eq. (13) is the change in the electron-electronic excitation energy at ionization. In this study, the electron-electronic excitation energy lost at ionization is assumed to be equivalent to the ionization energy measured from the electronic ground state and is given as

\[
Q_{L-E} = -\sum_{s=ion} n_s I_s
\]

where \( I_s \) is the first ionization energy of species \( s \).

2.3. Chemical reaction model

In this study, five species related to nitrogen are considered. These include \( N_2, N, e, N_2^+ \), and \( N_2^{++} \). Following Park et al., the six types of chemical reactions shown in Table 1 are taken into account for the chemical composition under consideration. In these reactions, the forward chemical reaction rate coefficient \( kf \) is defined as

\[
k_f = CT_e^{aa} \exp(-\theta_d/T_e)
\]

where \( T_e \) is the control temperature of the reaction. In the three-temperature model, the control temperature of reactions (i) and (ii) is given as

\[
T_e = \frac{T_i + T_a}{2}
\]

This control temperature is identical to that in the two-temperature model. \( T_i \) is used instead of \( T_a \) for reactions (iii) and (v), and \( T_i \) is used instead of \( T_a \) for reactions (iv) and (vi). The reverse chemical reaction rate coefficient \( kr \) is expressed in terms of \( k_f \) and the equilibrium constant \( Keq \) given as

\[
Keq = \exp \left( a'_i/Z + a'_2 + a'_3 \ln Z + a'_4 Z + a'_5 Z^2 \right)
\]

where \( a'_n \) is a constant listed in Ref. 5, and \( Z \) is defined as

\[
Z = 10,000/T.
\]

The reactions of the five species related to nitrogen and the corresponding values of \( C, n, \theta_d, \) and \( T_a \) are listed in Table 1.

3. Numerical Method and Conditions

In the present method, a shock wave is generated by imposing a hypersonic flow to a wall instead of solving the shock tube problem. This method is suitable to investigate the thermochemical nonequilibrium phenomena behind the shock front because the effect of expansion waves can be reduced. Figure 1 shows the computational region used for the calculation: 600 grid points corresponding to a grid spac-
ing of 83.5 µm. After the hypersonic flow impinges the wall, a shock wave is generated and then the computation is started. The generated shock wave propagates leftward and calculations are conducted until the shock wave arrives at 5 mm. The governing equations are integrated by a cell-centered finite volume scheme. The inviscid fluxes are evaluated using the AUSM-DV scheme whose special accuracy is extended to second-order using the MUSCL approach with the minmod limiter. The viscous fluxes are evaluated by central differencing. Time integration is performed with a CFL number of 0.1, which is combined with the diagonal point implicit method for maintaining the stability of the source term.

Calculations are conducted for the free-stream conditions corresponding to the shock tube experiments in our previous study. That is, the shock velocity is 10.4 km/s, and the pressure ahead of the shock wave is 40 Pa.

4. Results and Discussion

4.1. Calculated temperature profile

Figures 2 and 3 show the calculated temperature profiles and mole fractions as a function of the distance from the shock front. In Fig. 2, the calculated electronic excitation temperature increases and plateaus in the region ahead of the shock wave. This is caused by the diffusion of electrons. Electrons produced behind a shock wave diffuse to the region ahead of the shock wave because the mass of the electrons is too light. The existence of electrons can be seen in Fig. 3. In the region ahead of the shock wave, nitrogen atoms are produced first by the electron impact dissociation process and then ions and electrons are produced by the electron impact ionization process. Therefore, the calculated electronic excitation temperature increases in the region ahead of the shock wave. The calculated electronic excitation temperature equilibrates with the vibrational temperature at 6 mm from the shock front. However, the vibrational and electronic excitation temperatures are in significant nonequilibrium with the translational temperature behind the shock wave. Furthermore, the measured electronic excitation temperature is much higher than the calculated electronic excitation temperature and decreases slowly with increasing distance from the shock front. Therefore, there exists a discrepancy in the present model. On the other hand, the measured vibrational temperature agrees well with the calculated vibrational temperature.

4.2. Parametric study

To reproduce the measured electronic excitation temperatures, parametric studies are conducted. The numerical calculation fails to reproduce the high electronic excitation temperature behind the shock wave observed in the shock tube experiments. This high electronic excitation temperature is considered to be caused by precursor heating. The precursor is the region ahead of the shock wave in which radiation, primarily ultraviolet, emitted by the hot shock layer is reabsorbed by the gas. This absorption of radia-
tion causes a heating of the gas in the precursor region and the production of atoms, ions and electrons through the photo-dissociation and photo-ionization reactions.\(^{25,26}\) Electrons are also produced by the electron diffusion from the shock front.\(^{27,28}\) The presence of electrons ahead of shock waves might affect the relaxation process behind the shock front. Radiative processes are important mechanisms for precursor heating. However, the phenomena are still unknown and a suitable model does not exist. For this reason, radiative processes are not considered in this study. Instead, the effects of thermochemical states of electrons ahead of shock waves on the temperature profiles behind the shock wave are investigated. Calculations are conducted by changing the electronic excitation temperature and mole fractions of chemical species for the free-stream conditions of a hypersonic flow. In the present calculation, electrons in the precursor region are assumed to be produced by the photo-ionization reaction of molecular nitrogen. Therefore, the mole fraction of \(N_2^+\) is set to be equal to that of electrons in the precursor region.

First, the mole fractions of electrons and \(N_2^+\) are set to 0.02 and calculations are conducted by increasing only the electronic excitation temperature. The calculated temperature profile for the electronic excitation temperature is shown in Fig. 4. The measured electronic excitation temperatures are also shown. The calculated temperatures come close to the measured temperatures with increasing electronic excitation temperature. When the electronic excitation temperature is assumed to be 15,000 K, the calculated temperatures are close to the measured ones. However, the relaxation process for the measured electronic excitation temperatures is slightly slower than that for the calculated ones. In a previous study, the electron temperatures in the precursor region were measured by the shock tube experiments using the triple-probe method.\(^{29}\) The result shows that the electron temperature ahead of shock waves is in the order of 10,000 K, which is quite similar to the assumed temperature of 15,000 K in this calculation.

Second, the electronic excitation temperature is kept at 15,000 K, and then calculations are conducted by increasing only the mole fractions of electrons and \(N_2^+\). The calculated temperature profile for the electronic excitation temperature is shown in Fig. 5. The measured electronic excitation temperature is also shown. The temperature profile comes close to the measured temperature with increasing mole fractions. When the mole fractions of electrons and \(N_2^+\) are assumed to be 0.06, the calculated temperatures agree well with the measured ones.

Figures 6 and 7 show the temperature profiles and mole fractions of chemical species when the electronic excitation temperature and mole fractions are set to be 15,000 K and 0.06, respectively. The measured vibrational and electronic excitation temperatures are also shown. The measured electronic excitation temperature agrees well with the calculated electronic excitation temperature. The measured vibrational temperature is also reproduced well by the numerical calculation. In Fig. 7, many nitrogen atoms are produced ahead of shock waves. This is because the electrons and \(N_2^+\) are recombined and nitrogen molecules are ionized by the electron impact dissociation process. The present result shows that the thermochemical states of electrons ahead of shock waves affect the temperature profiles behind the shock wave. Further investigations on precursor heating are necessary, and a detailed model should be developed in the future.

### 4.3 Grid convergence study

A grid convergence study is conducted by comparing the temperature profiles calculated using the standard grid (600 grid points) and a fine grid (1,200 grid points). Figure 8
shows the temperature profiles when the electronic excitation temperature and mole fractions of electrons and N\textsubscript{2}\textsuperscript{+} in the precursor region are 15,000 K and 0.06, respectively. It can be observed that there are no significant differences between the results obtained using the two grid sizes. This result shows that the standard grid yields sufficiently converged results.

\section{Conclusions}

In the present study, the nonequilibrium phenomena of the electronic excitation process behind hypersonic shock waves have been investigated via numerical analysis. The three-temperature model was employed and the temperature profile behind the shock wave was computed for the conditions corresponding to shock tube experiments. The calculated vibrational temperature agreed well with the measured vibrational temperature. On the other hand, the calculated electronic excitation temperature is lower than the measured one, revealing the discrepancy in the present model.

To investigate the effects of thermochemical states of electrons on the temperature profiles behind the shock wave, parametric studies were conducted using the three-temperature model. Calculations were conducted by changing the electronic excitation temperature and mole fractions of electrons and N\textsubscript{2}\textsuperscript{+} for the free-stream conditions of a hypersonic flow. The calculated temperatures reproduced the measured temperatures well when the electronic excitation temperature and mole fractions were assumed to be 15,000 K and 0.06, respectively. The result shows that the thermochemical states of electrons ahead of shock waves affect the temperature profiles behind the shock wave. However, radiative processes were not considered in the analysis. This warrants future investigations on the mechanism of the precursor heating. Nonetheless, the present analysis will be useful to understand the mechanism of precursor heating.

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