

Thermochemistry of strong air plasmas for hypervelocity Earth entry of asteroids

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I. Introduction

Meteors entering the atmosphere from beyond Earth's orbit can have entry velocities greater than 15 km/s. Under these conditions the air in the bow shock layer will be dissociated and ionized, creating a strong plasma with temperatures greater than 15,000 K. The Chelyabinsk meteor (1) that exploded over central Russia in February 2013 was a 20 m diameter superbolide. It exploded at an altitude of 29.7 km with a force equivalent to 0.5 megatons of TNT. This object was determined to be a chondrite, which is comprised mostly of silica (SiO_2) and significant amounts of calcium, magnesium and iron. At NASA Ames Research Center an exercise is under way to simulate the aerothermodynamics of these events using computational fluid dynamic (CFD) models developed for atmospheric entry of spacecraft with ablating heat shields. For our nominal test case we are considering a 20 m silica object entering the atmosphere at 20-40 km/s. Initial calculations for 20 km/s entry speed indicated the equilibrium temperature in the bow shock layer is $\sim 20,000\text{K}$ with stagnation point pressures of 10-30 bar (2). The overall goal of the project to study the atmospheric entry of asteroids is to validate computational models for Chelyabinsk type meteors using the observed light curve (i.e., radiance vs. time) and the altitude at which the object exploded. We expect the shock layer temperature and pressure for 40 km/s entry will be greater than 60,000 K and 100 bar. At 20,000 K, air in the shock layer is completely dissociated and

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ionized. Only neutral and singly ionized species (N^+ and O^+) are included in these calculations. At 60,000 K multiply ionized species (e.g., N^{++} and N^{+++}) must be considered as well. It is not clear from previous work on high-temperature air plasmas whether doubly ionized species will have significant mole fraction at 30,000 K (3,4). The objective of the proposed paper is to determine accurate thermochemical functions (C_p , H , S and G) as functions of temperature and pressure so we can characterize the extent of multiple ionization.

In order to carry out the CFD simulation, thermochemical functions for enthalpy, entropy and free energy of all species are needed. The enthalpy is computed from the standard formation enthalpy $\Delta_f H^\circ$ at standard temperature and pressure ($T = 298.15$ K and $P = 1$ bar) with $N_2(g)$ and $O_2(g)$ defined as elemental reference states with $\Delta_f H^\circ = 0$. For N and O and their singly charged ions, accurate tabulations of these thermochemical functions are only available for temperatures up to 20,000 K, because the contributions from high-lying electronic states are not complete (e.g., JANAF(5), CEA(6) and Gurvich(7)). Recently, Capitelli et al. (8-10) have published thermochemical tables for Earth and Mars atmospheric species for temperatures up to 50,000 K. These tables include quadruply charged ions of C, N and O. However, these authors made certain decisions that are not appropriate to the higher bow shock pressures expected for high-speed entries of large objects, such as the Chelyabinsk meteor. One such example is their treatment of the so-called “pressure ionization” effect, i.e., the lowering of the ionization energy and the subsequent truncation of the atomic and ion energy levels.

For each species, the calculation of H , S and G is carried out in a sequence of steps. First the thermodynamic partition function (5-11) $Q(T)$ is computed as the product of translational and internal components $Q^{tr}(T)$ and $Q^{int}(T)$, respectively, with

$$Q^{tr}(T) = \left(\frac{2\pi M}{Nh^2}\right)^{3/2} \frac{(k_B T)^{5/2}}{P}, \text{ and} \quad (1)$$

$$Q^{int}(T) = \sum_i g_i \exp\left(-\frac{E_i^{int}}{k_B T}\right). \quad (2)$$

M is the atomic weight of the species in kg, N is Avogadro's number, h is Planck's constant and k_B is Boltzmann's constant. E_i^{int} and g_i are the energy and degeneracy of the i th electronic level of the atom or atomic ion. The summation in $Q^{int}(T)$ is over all the electronic levels of that species up to the next ionization energy. The second step is the calculation of the specific heat at constant pressure $C_p(T)$, that is the amount of heat required to raise the temperature of one mole of that species by one degree. For this definition, of the internal contribution to the specific heat can be written as (11)

$$C_p^{int}(T) = \frac{d\langle E^{int} \rangle}{dT}, \quad (3)$$

where $\langle E^{int}(T) \rangle$ is the internal energy for a Boltzmann distribution of energy levels,

$$\langle E^{int}(T) \rangle = (Q^{int})^{-1} \sum_i g_i E_i^{int} \exp\left(-\frac{E_i^{int}}{k_B T}\right). \quad (4)$$

$C_p^{int}(T)$ is more commonly written in terms of the partition function(5-10)

$$C_p^{int}(T) = RT^2 \frac{d^2 \ln [Q^{int}]}{dT^2} + 2RT \frac{d \ln [Q^{int}]}{dT}, \quad (5)$$

where R is the gas constant. $C_p^{tr}(T)$ is simply $\frac{5}{2}R$ and $C_p(T) = C_p^{tr} + C_p^{int}$.

Given $\Delta_f H^\circ$ and $C_P(T)$ the change in enthalpy of a species undergoing a change in temperature from T_1 to T_2 can be computed as (5)

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T) dT , \quad (6)$$

where $H(T)$ includes the translational and internal contributions and the enthalpy of formation. The entropy and free energy can be computed in a comparable fashion.

There is, however, a complication for the case of very high temperature. The summation in the partition function expression for atomic species diverges because the energy spacing between adjacent energy levels goes to zero at the ionization limit. At lower temperatures, the summation exhibits a pseudo convergence when the higher energy levels are not included. If the summation is extended to the ionization limit the greater density of higher levels will result in divergence. This expression for the partition function assumes the atoms and ions are all independent, but for very high energy levels, the outermost electron has a large probability of being far from its nucleus – in fact this electron can be closer to other nuclei. It is best to demonstrate this for hydrogen atoms where the energy levels E_n are given by the expression (8-10,12-14)

$$E_n = \left(\frac{Z^2 R_y}{n^2} \right) , \quad (7)$$

where n is the principal quantum number, Z is the charge of the nucleus ($Z=1$ for hydrogen) and $R_y = 13.60569253$ eV is the Rydberg constant. The mean distance from the electron to the nucleus is given by $a_0 n^2$ where $a_0 = 0.52917721 \times 10^{-10}$ m is the Bohr radius. It is posited that the electron will no longer be bound to its nucleus if this distance is larger than the mean interparticle separation in the gas at a given temperature and pressure. However, if there are other electrons and ions present, the electron will be perturbed by the field of these charged particles and will be effectively free of its original nucleus. These phenomena, called “pressure ionization” or “continuum lowering”(15), have been observed in real gases at high

temperature and pressure (16,17). For the case of low-density plasmas, various theoretical models (12-,15,18-20) have been proposed based on the assumptions of Debye-Huckel Theory (21). It is assumed that the free electrons prefer arrangements that keep every small volume charge neutral in the plasma, so they are shielded from long-range Coulomb potential. Expressions by Griem (20), Stewart and Pyall (19) and Crowley (15) describe this situation. For the case of moderate- to high-density plasma, the situation is less clear (12-14,21,22). For the present study ($T \cong 20,000\text{K}$ and $P \cong 20\text{ bar}$) the neutral hydrogenic atom cutoff is $n_{\text{max}} \cong 8$ and the energy level truncation is approximately 1600 cm^{-1} below the ionization limit. Using the Griem (20) expression it is also approximately 1600 cm^{-1} , however the gas density is too large for the assumptions in the Debye theory to hold. This downward shift in the ionization energy is referred to as the ionization energy depression (IED). For N^+ and N^{++} $n_{\text{max}} \cong 9$ and 10 , respectively and $\text{IED} = 4700\text{ cm}^{-1}$ and 9100 cm^{-1} . These are larger than the corresponding IED values of 3224 cm^{-1} and 6337 cm^{-1} , respectively, based on the Griem formula. A more thorough analysis of the IED will be carried out for the final paper.

The scope of this work is as follows: we will construct lists of energy levels for N , N^+ , N^{++} , N^{+++} , O , O^+ , O^{++} and O^{+++} based on the NIST atomic energy level database (23) augmented by interpolation and extrapolation to include missing levels up to $n_{\text{max}}=10$ and truncated by the computed IED for various theoretical models. Using these energy levels we will compute $Q(T)$, $C_P^{\text{int}}(T)$, $H(T)$, $S(T)$ and $G(T)$ for $T \leq 100,000\text{K}$ and $P \leq 100\text{ bar}$. We will use the following analytic expression for Eq. (3)

$$C_P^{\text{int}}(T) = \frac{1}{RT^2} (\langle (E^{\text{int}})^2 \rangle - (\langle E^{\text{int}} \rangle)^2) \quad (8)$$

with

$$\langle (E^{\text{int}}(T))^2 \rangle = (Q^{\text{int}})^{-1} \sum_i g_i (E_i^{\text{int}})^2 \exp\left(-\frac{E_i^{\text{int}}}{k_B T}\right) \quad (9)$$

for the calculation of $C_p^{int}(T)$. We have compared the results with the numerical differentiation of Eq. (3)

$$C_p^{int}(T) \cong \frac{\langle E^{int}(T+\delta T) \rangle - \langle E^{int}(T-\delta T) \rangle}{2\delta T} \quad (10)$$

for $\delta T = 10K$ and found the results to agree to $R \times 10^{-3}$. We have already prepared the energy level lists for N, N⁺ and N⁺⁺ and will present results in the following section. We will fit these thermochemical data to piecewise polynomial expressions for porting into a modified version of the NASA CFD code DPLR (24). Due to the large temperature span of the data, our version of DPLR has been modified to accept a more flexible set of polynomials and multiply ionized species. Finally we will carry out CFD calculations for the test case mentioned above to determine the effect of using the new thermochemical data.

II. Results

Debye-Huckel theory, originally derived to describe electrolyte solutions, posits that the long-range Coulomb interaction between ions in a fluid is shielded by the combined effect of all the other charged particles (21). This shielding cuts off the Coulomb interaction at a certain distance from the ion – called the Debye length (D). Inside the Debye sphere ($r < D$), charged particles interact according to $V_c \sim r^{-1}$, the normal Coulomb potential and at larger distance there is no interaction. The Debye length is given by

$$D = \sqrt{\frac{\epsilon_0 k_B T / q_e^2}{N_e + \sum_i q_i N_i}} \quad (11)$$

where ϵ_0 is the vacuum permittivity, q_e is the electron charge, N_e is the electron density and q_i and N_i are the charge and density, respectively, for each kind of ion.

For a fluid of singly charged ions and electrons ($N_e = N_i$) at $P = 20$ bar and $T = 20,000\text{K}$, $D = 18 \text{ \AA}$. For the entire range of T and P considered in this work, $8 \text{ \AA} < D < 90 \text{ \AA}$.

There are two conditions given by Griem (20) for the assumptions in the Debye shielding model to be valid: that the IED is smaller than $k_B T$ and that the Debye length is greater than the mean separation between the atomic nuclei (i.e., there are numerous ions inside the Debye sphere). The first condition is satisfied throughout the entire range of T and P , but the second condition is not. In general, models for IED that are based on Debye shielding are applicable only for $P < 1$ bar and $T > 100,000\text{K}$. For example, at $P = 20$ bar and $T = 20,000\text{K}$ the ratio of interparticle spacing to Debye length is 2.8. Under plasma conditions relevant to the present study, there are no other ions in the Debye sphere and the only models that are applicable are the principal quantum number cutoff ($n_{\max}$) and the model of Unsöld (12-14, 22). We will use these models to determine the IED.

For N(I), neutral N-atoms, the ionization energy is $117,225.7 \text{ cm}^{-1}$ (14.534 eV). The NIST energy level list (23), which is based on observed emission spectra, has 132 LS and KS coupling multiplets, 20 of which have $n \geq 10$. We added 24 additional multiplets by extrapolating the various Rydberg series to $n = 8$ and 30 additional multiplets for higher angular momentum Rydberg series. Truncating this combined energy level list for $n \leq 8$ yields 166 multiplets for N(I) with the highest energy level 115624 cm^{-1} for IED = 1601 cm^{-1} . Table 1 shows the enthalpies of formation and ionization energies for atomic nitrogen and its ions. The formation enthalpies for N and N+ are taken from the JANAF compilation (5). For N⁺⁺ and N⁺⁺⁺ the NIST atomic energy database (23) is used, combined with the JANAF formation enthalpy for N⁺. The IED adjusted values are based on the $n_{\max}$ values discussed above.

Calculations of the dimensionless specific heat (C_p^{int}/R) have been carried out for N, N⁺ and N⁺⁺ using Eq. (8) for temperatures between 10,000 K and 100,000 K and the results are shown in Figures 1-3, respectively. For N and N⁺ comparisons

are made with tabulations from JANAF (5), NASA Glenn Research Center (Chemical Equilibrium with Applications or CEA) (6, 25, 26), Gurvich et al. (7) and Capitelli et al. (8-10). For N^{++} comparison is made with Capitelli et al. (8-10). For atomic nitrogen there is excellent agreement between the present work and the compilations by JANAF (5), CEA (6), Gurvich et al. (7) and Capitelli et al. (8-10) for temperatures up to 10,000 K, but at higher temperatures the data from Ref. 6-10 diverge from each other and from the results of the present study. This is due to differences in the set of excited levels included in the partition functions and the truncation of the energy levels due to the IED. For N^+ the data from all the compilations agree up to 20,000 K. If the curves for Gurvich or CEA data are not visible in the figures, it is because they are completely masked by the curves of Capitelli and the present study. The older compilations (5-7) do not account for IED, because they only provide data for $T < 20,000$ K. The tables compiled by Capitelli et al. (8) set IED at three different values (250, 500 and 1000 cm^{-1}), which are all smaller than the IED appropriate for our test case ($T = 20,000$ K and $P = 20$ bar). Capitelli et al. also augmented the NIST atomic energy level list with auto-ionizing levels that lie above the ionizing limit, even though they comment that these probably should not be included because of the truncation. They also include other electronic levels based on extrapolation to higher principal quantum numbers and also Rydberg series for the metastable states (e.g., $N\ ^2D$ and $\ ^2P$). In the present study we included similar extrapolations, but not for the metastable Rydberg states whose levels lie above the auto-ionization limit.

In the full paper we will present tables of enthalpy, entropy and free energy as well as specific heat and extend to calculations to N^{+++} and atomic oxygen and its first three cations. We will also present data for several representative pressures from 10 bar to 100 bar, using the appropriate IED values for T , P and the degree of ionization. Finally we will repeat the CFD calculations for the test case (2) using the new thermochemical functions to assess the degree of multiple ionization in these shock layers.

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Tables and Figures

Table 1. Enthalpies of formation and ionization energies with adjustment for IED.

Species	$\Delta_f H^\circ(0K)$ kJ/mol	$\Delta_f H^\circ(0K)$ kJ/mol IED adjusted	I.P. eV	I.P. eV IED adjusted
N	470.82	470.82	19.414	19.215
N ⁺	1873.17	1854.03	49.104	48.234
N ⁺⁺	4729.30	4653.93	96.459	94.550
N ⁺⁺⁺	9307.14	9122.91		

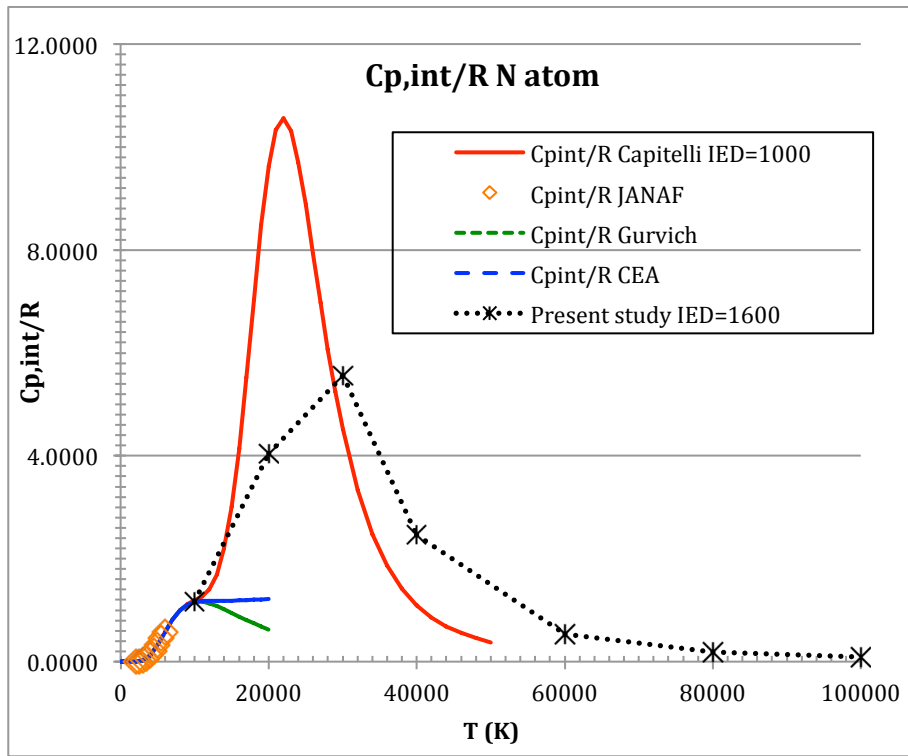


Figure 1. Dimensionless internal specific heat C_p^{int}/R for atomic nitrogen computed for temperatures up to 100,000 K. Comparison is made between the present study and the compilations of Capitelli ($T < 50,000$ K), JANAF ($T < 6000$ K), Gurvich ($T < 20,000$ K) and CEA ($T < 20,000$ K).

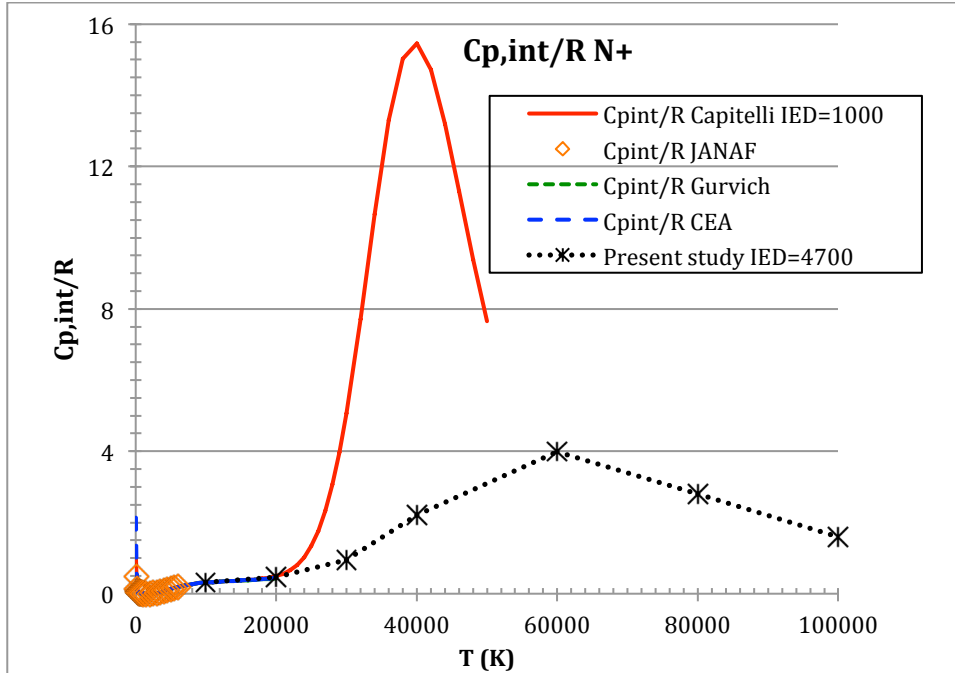


Figure 2. Dimensionless internal specific heat C_p^{int}/R for N^+ computed for temperatures up to 100,000 K. Comparison is made between the present study and the compilations of Capitelli ($T < 50,000$ K), JANAF ($T < 6000$ K), Gurvich ($T < 20,000$ K) and CEA ($T < 20,000$ K).

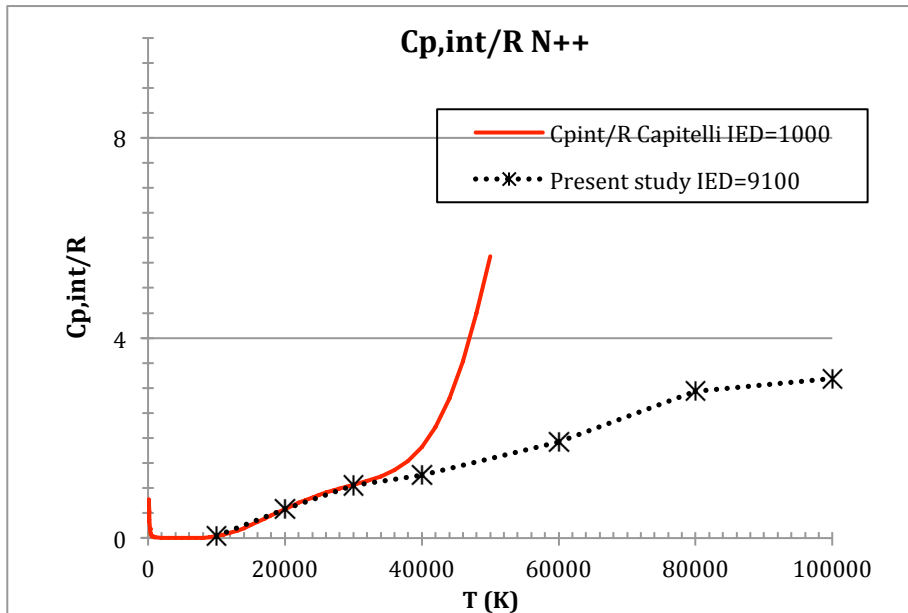


Figure 3. Dimensionless internal specific heat C_p^{int}/R for N^{++} computed for temperatures up to 100,000 K. Comparison is made between the present study and the compilation of Capitelli ($T < 50,000$ K).

