Equilibrium Composition and Electrical Conductivity of High-Temperature Air

Jens Prager, Georgiana Baldea, Uwe Riedel, Juergen Warnatz

Interdisciplinary Center for Scientific Computing, University of Heidelberg,
Im Neuenheimer Feld 368, 69120 Heidelberg, Germany

1 Introduction

A precise transport model of high-temperature air is crucial for calculating a variety of important technological processes. Re-entry problems of space-exploration vehicles, gas discharges, circuit breakers can be mentioned as examples. The computation of the equilibrium properties gives valuable information also for calculations of all these transient processes. It provides information on larger time scales with an acceptable demand on computational time.

This work is based on previous studies that enabled the calculation of equilibrium compositions and transport properties – viscosity, heat conductivity, diffusion coefficients, and electrical conductivity – of air at pressures of 0.1 mbar to 100 bar and from room temperature to 30000 K with a small number of required input data [1, 2]. This reduction of input data is rendered possible by the use of combination rules. In the case of a 19-species model it is found that combination rules yield good results. In this work the model is extended to take account of the water and carbon dioxide content of air. Uncertainties of the thermodynamic data at very high temperatures are examined with respect to their effect on the equilibrium composition. Recently it had been shown that negative ions can have an important impact on the electrical conductivity in flames [3]. In this paper, therefore, we focus on negative ions added to improve the model of the electrical conductivity at low temperatures.

2 Model

2.1 Equilibrium composition

The calculation of the equilibrium composition presented in this paper is based on a 120-species model of gas-phase species occurring in ionized air containing the elements N, O, Ar, C, and H and electrons E^-. This calculation serves as a reference for the establishment of a reduced model used for the calculations of transport properties. The following ions are considered in the 120-species model: E^-, N_2^+, O_2^+, NO^+, N^+, O^+, N^{2+}, O^{2+}, N^{3+}, O^{3+}, Ar^+, Ar^{2+}, Ar^{3+}, N_2O^+, C^+, CH^+, CH_3O^+, CN^+, CO^+, CO_2^+, C_2^+, H^+, HCO^+, H_2^+, H_2O^+, H_3O^+, NH^+, NH_4^+, OH^+, and the anions: N^-, NO_2^-, N_2^-, O^-, O_2^-, C^-, CN^-, C_2^-, H^-, HO_2^-, H_2^-, OH^-.

The calculation of the equilibrium composition is based on the minimization of the Gibbs energy. Thermodynamic data is taken from the NASA database [4]. To extend the temperature range, for all atoms and atomic cations, thermodynamic data has been calculated by the PAC99 program [5] using spectroscopic data from NIST [6]. At very high temperatures, uncertainties in calculated thermodynamic data result from using different methods of treating the interactions of species. The PAC99 program offers two methods: ALLN in which all electronic energy levels are taken into account for the calculation

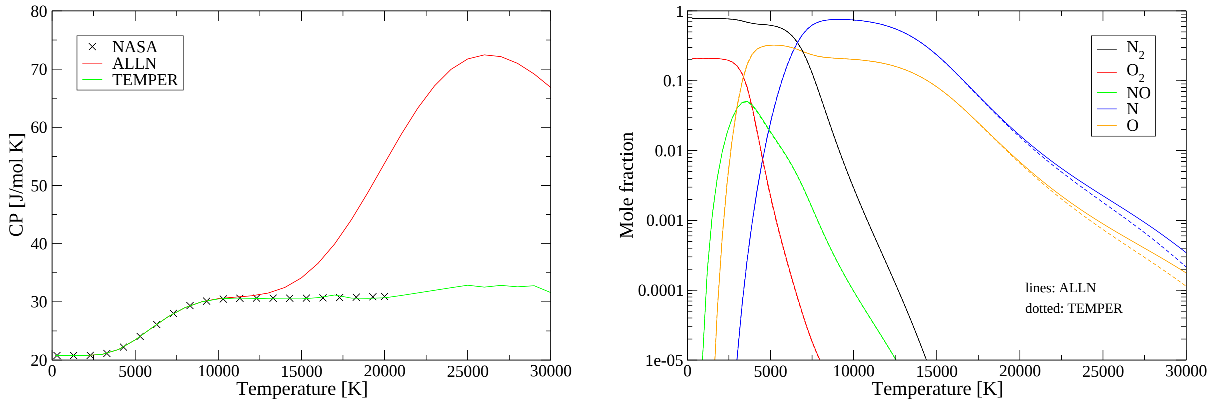

Figure 1: Left: Calculated heat capacity of N using the two methods ALLN and TEMPER. Values from the NASA database are also shown. Right: Equilibrium composition of air if thermodynamic data of N and O are varied.

of the partition function, and TEMPER in which all levels are considered up to the ionization energy reduced by kT. The composition of air is set to 77.415% N_2, 20.816% O_2, 0.892% Ar, 0.841% H_2O, and 0.036% CO_2.

2.2 Transport properties

The calculation of all the transport properties – viscosity, heat conductivity, diffusion coefficients, and electrical conductivity – is based on the Chapman-Enskog method [7]. However, in this paper we focus on the electrical conductivity only.

Details of the method and references to the input data for air without CO_2 and H_2O can be found in previous publications [1, 2]. The remaining parameters needed for the new species involving the elements C and H can be obtained from the authors. The following species are considered in the transport calculations: N_2, O_2, NO, N, O, N^+, O^+, E^-, N^{2+}, O^{2+}, N^{3+}, O^{3+}, Ar^+, Ar^{2+}, Ar^{3+}, Ar, C, C^+, CO, CO_2, H, H^+, H_2O, OH, NO^+, N_2^+, OH^-, O^-, O_2^-, NO_2^-. This is a subset of all the species considered in the computation of the equilibrium model only, but it represents the total composition to a sufficiently high percentage to give accurate results. The multi-component formulation is used to calculate the mixture properties, and second-order terms are employed for the electrons, resulting in the following formula for the electrical conductivity σ_e:

$$\sigma_e = \frac{e^2 n}{\rho RT} n_e M_e [D_{ee}]_2 \quad ,$$

using the electron density n_e, the molar mass M_e of the electron, and the second-order self diffusion coefficient $[D_{ee}]_2$.

3 Results

3.1 Equilibrium composition

First, the influence of the calculation method for the thermodynamic data on the equilibrium composition will be discussed. Fig. 1 (left plot) shows the heat capacity of the nitrogen atom obtained by using the two different cut-off methods implemented in PAC99. The ALLN method, which used all electronic levels up to the ionization energy, yields a much higher heat capacity for temperatures above 10000 K. The dataset in the NASA database has been obtained by the TEMPER method and is validated up to 20000 K. The

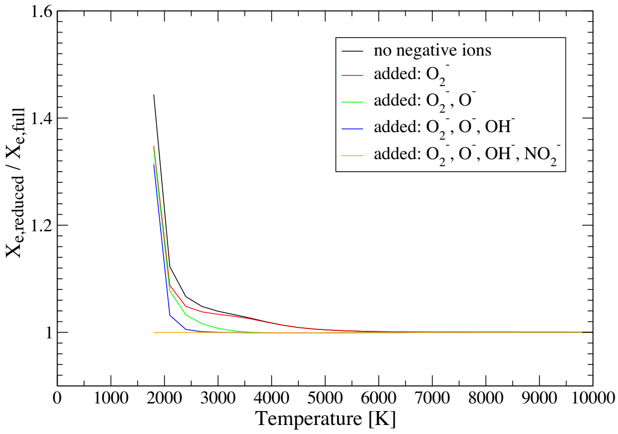

Figure 2: Ratio of the electron mole fraction in the equilibrium composition resulting from different reduced models to the electron mole fraction obtained from the full 120-species model. Different negative ions are found to be important in the low-temperature regime.

calculated heat capacities indicate the maximum amount of uncertainty at high temperatures, but the correct result is expected to be close to the TEMPER method. Similar results are obtained for the O atom.

Fig. 1 (right plot) shows the resulting equilibrium composition of air if the thermodynamic data of N and O are varied. Visual differences can be seen above 17000 K, and the maximum deviation is about 40% at 30000 K. In the temperature range in which N and O occur in significant amounts, the calculations yield the same results. It should be pointed out that even though the heat capacities show large sensitivities to the cut-off method, the error is reduced in calculating the Gibbs energy, because the errors introduced in the enthalpy and entropy partly compensate:

$$G(T) = H(T) - TS(T) = \left(H_0 + \int^T C_p(T')\, dT' \right) - T \left(S_0 + \int^T \frac{C_p(T')}{T'}\, dT' \right) \quad .$$

3.2 Electrical conductivity

An accurate electron concentration is crucial for calculating the electrical conductivity of a gas mixture. Therefore, negative ions can be important since they lower the electron concentration which reduces the electrical conductivity. A reduced model containing only the necessary anions is obtained by comparing the electron mole fraction predicted by the reduced model with the electron mole fraction which is obtained by considering all 120 species. The results are shown in Fig. 2. The model contains all cations as described before, and single anions are added. It can be seen that anions are important for temperatures below 5000 K, leading to deviations of about 40% of the electron mole fraction. O^- is found to be important between 2500-5000 K, OH^- between 2000-3000 K, and NO_2^- below 2500 K. In addition, O_2^- is included in the model.

The resulting electrical conductivity of air is presented in Fig. 3. It is also compared to the results of Capitelli et al. [8]. The calculations show that by including anions, the electrical conductivity is reduced by about 5-15% for temperatures below 2500 K. Anions can be neglected above this temperature.

4 Conclusion

Calculations of the equilibrium composition of air and its electrical conductivity are presented in the temperature range from 300 K to 30000 K. Uncertainties in thermodynamic data at high temperatures,

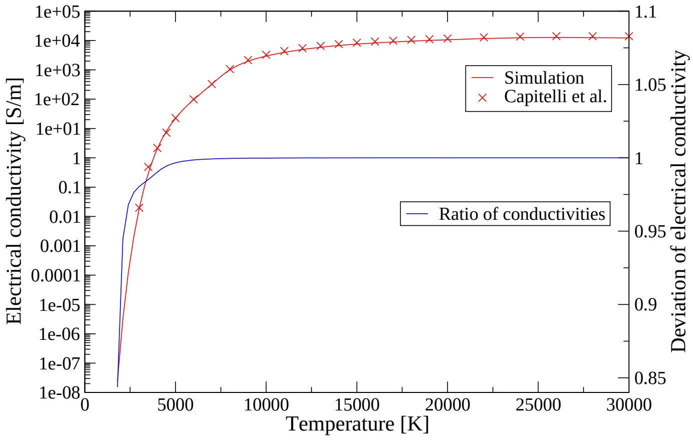

Figure 3: Calculated electrical conductivity for the model including anions and data from Capitelli et al. [8]. Ratio of the electrical conductivities calculated including anions and without anions.

originating from different methods for species interactions, are found to be of less importance for the equilibrium composition and electrical conductivity. One reason is that these uncertainties occur at temperatures at which the species occur in lower mole fractions. The second reason is that errors in heat capacities are reduced in the calculation of Gibbs energies which determine the equilibrium composition. Four anions are identified which are important charge carriers at temperatures below 5000 K: O_2^-, O^-, OH^-, and NO_2^-. Because they remove free electrons from the gas, the electrical conductivity is reduced. This effect occurs below 5000 K and is of about 15% at 1800 K.

References

[1] Selle S, Riedel U (1999). Transport properties of ionized species. In: Fauchais P et al. (eds) Heat and Mass Transfer under Plasma Conditions. The New York Academy of Sciences, pp 72-80

[2] Selle S et al. (1998). Reaction rates and transport coefficients of ionized species in high temperature air. Proc. Third Eur. Symp. Aerothermodynamics for Space Vehicles, pp 327-332

[3] Prager J et al. (2007). Modeling ion chemistry and charged species diffusion in lean methane-oxygen flames. Proc. Combustion Institute 31: 1129-1137

[4] McBride BJ et al. (2002). NASA Glen coefficients for calculating thermodynamic properties of individual species. NASA report TP-2002-211556, http://cea.grc.nasa.gov

[5] McBride BJ, Gordon S (1992). Computer Program for Calculating and Fitting Thermodynamic Functions. NASA Reference publication 1271

[6] NIST Standard Reference Database #78, Physics Laboratory, http://physics.nist.gov/PhysRefData/ASD

[7] Chapman S, Cowling TG (1994). The Mathematical Theory of Non-Uniform Gases. Cambridge University Press

[8] Capitelli M et al. (2000). Transport properties of high temperature air in local thermodynamic equilibium. Eur. Phys. J. D 11: 279-289