Non-equilibrium thermodynamic and transport properties of carbon-oxygen thermal plasma mixtures including iron vapour effects

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Abstract: Thermodynamic and transport properties of different carbon-oxygen plasmas mixtures are presented for both thermal equilibrium and non-equilibrium conditions. The influence of molecular ions in the computation of non-equilibrium transport properties has been investigated. Results for non-equilibrium properties have been obtained using two different two-temperature methods: the simplified method by Devoto and the recently developed non-simplified method by Rat. Comparisons between the two methods have been reported for carbon-oxygen mixtures. For the LTE case, iron metal vapours have been included in the calculations.

Keywords: thermal plasma, transport properties, non-equilibrium

1. Introduction

Carbon-oxygen plasmas are widely encountered in metallurgical applications, for example in high-power AC three-phase furnaces with carbon electrodes where methane and oxygen are supplied within the crucible to enhance the scrap melting process. Moreover, an increasing interest has been noted in using carbon-oxygen mixtures in DC non-transferred arc torches for spraying applications: in this case, non-equilibrium conditions may exist and they could be related with the unstable behaviour of the reattachment process. Iron vapours appear in furnaces as a consequence of evaporation from melted steel scraps and they have a strong effect in reducing the total Joule power dissipated in the plasma for fixed current. The most reliable way to obtain plasma properties, for a wide variety of mixtures in the range 300-30,000 K, is the kinetic theory of ideal gases for thermodynamic properties and the approximate solution of the Boltzmann equation based on the Chapman-Enskog method for transport properties [1]. These methods have been widely studied in local thermodynamic equilibrium (LTE) and some results are reported in literature for the most commonly used pure gases and mixtures including carbon-oxygen mixtures [2-6]. However, departures from thermal equilibrium, where electron temperature differs from that of heavy species, can arise in thermal plasmas when electron concentration is not high enough to allow sufficient transfer of energy between the electrons and heavy species.

In this work, properties for plasmas out of equilibrium have been obtained using both the two-temperature theory developed by Rat [7] and a simplified theory by Devoto [8], which considers complete decoupling between heavy particles and electrons, since they assumed that the change of the perturbation function of electrons is greater than that of heavy species during interactions involving both types of particles; it is shown that for carbon-oxygen mixtures no differences between results obtained using these two theories can be appreciated for thermal and electrical conductivities; some discrepancies have been found for ordinary diffusion coefficients of the type electron-heavy particle. The influence of ionized molecules in case of thermal non-equilibrium has been highlighted: even if under LTE conditions molecular ion species have a negligible concentration and they don't affect the calculation of transport properties (a common rule is that species with molar fraction below 1e-3 could be neglected), they could play an important role in the molecular dissociation process at low heavy particle temperature and high electron temperature. The effects of Fe metal vapours on transport properties have been investigated.

2. Methods for the computation of composition, thermodynamic and transport properties

Even though results will be presented only in the temperature range 300 - 30,000 K, calculations have been carried out up to 60,000 K; for this reason, composition of carbon-oxygen plasma has been obtained considering the species C, C^+, C^{2+}, C^{3+}, C^{4+}, O_2, O_2^+, O_2^-, O, O^+, O^{2+}, O^{3+}, O^{4+}, CO, CO_2, CO^+, CO_2^+ and e^-. Molecular ions have been included in the calculations even if their LTE molar fraction at atmospheric pressure is below 10^{-3} in order to study their influence on plasma properties.

Data of the electron energy levels of atoms and ions for the evaluation of their partition functions and the ionization and dissociation energies have been taken from the NIST database; rotational and vibrational constants for the calculation of partition functions of molecules have been taken from Herzberg [9].

The appropriate method for the determination of chemical equilibrium number density in two-temperature plasmas has long been a subject of debate. In the present work, the non-equilibrium Saha equation proposed by Van de Sanden et al. [10] has been used.

A Maxwellian distribution of velocity characterized by the temperature T_h is assumed for heavy species, while electrons have the temperature T_e. The parameter of thermal non-equilibrium is defined as $\theta = T_e / T_h$.

Thermodynamic properties can be evaluated through a classical statistical mechanics approach, provided number densities and partition functions of each species are known.

The calculations of transport properties in LTE are carried out using the Chapman-Enskog method up to the third order. In case of non-equilibrium conditions, two methods have been used: the simplified method developed by Devoto and the non-simplified method by Rat. Collision integrals have been calculated using data reported in previous works [2-4,11].

3. Influence of molecular ions on non-equilibrium transport properties

The effects of molecular ions on plasma properties have been investigated calculating composition, thermodynamic properties and transport properties including and not including molecular ion species O_2^+, CO_2^+, CO^+. Computations will be presented for the CO2 mixture and for different values of the non-equilibrium parameter.

The LTE composition including molecular ion species is reported in figure 1: O_2^+ and CO^+ are responsible for the generation of electrons at low temperature (3000-5000 K); however, their concentration remains below 1e20 m^{-3} for the whole temperature range considered. Neglecting molecular ions in LTE doesn't affect the concentration of species most abundant.

In figure 2 and 3 results for θ = 3 for the cases with and without molecular ion species have been reported, respectively. In case of strong non-equilibrium, composition is strongly influenced by the inclusion of O_2^+, CO_2^+, CO^+ in the computation. Molecular ions have an effect in the production of electrons at low heavy particle temperature: in fact, up to at T_e = 8000 K, the main contribution to electron generation is given by CO_2^+, since CO_2 dissociation cannot start as a consequence of the low heavy particle temperatures.

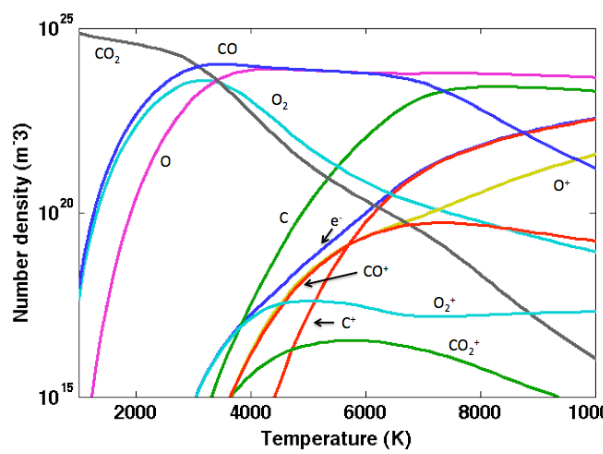

Figure 1. LTE composition for a CO_2 mixture at atmospheric pressure.

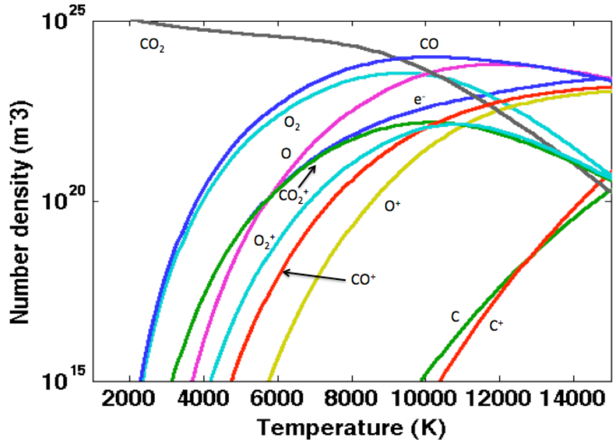

Figure 2. Non-equilibrium composition as a function of electron temperature for a CO_2 mixture at atmospheric pressure for $\theta = 3$.

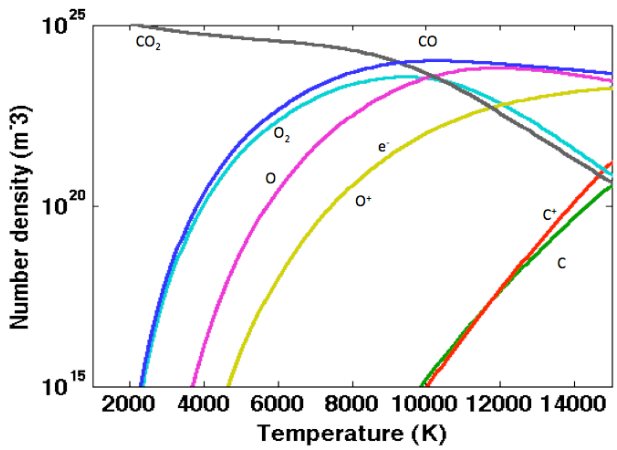

Figure 3. Non-equilibrium composition as a function of electron temperature for a CO_2 mixture at atmospheric pressure for $\theta = 3$, without considering molecular ions.

The effects of molecular ions on thermodynamic properties and transport properties are shown in figures 4-6.

In figure 4, the total specific heat is reported for different values of the non-equilibrium parameter. The inclusion of molecular ions, in this case, has a strong effect. For increasing values of θ, the dissociation peak is shifted towards higher electron temperatures and it overlaps with the ionization peaks. Neglecting the molecular ion species, the shape of the dissociation peak changes strongly. The same effect has been obtained for reaction thermal conductivity of CO_2 (not shown).

In non-equilibrium conditions, electrical conductivity (figure 5) for electron temperature below 17,000 K is greatly influenced by molecular ions, leading to higher values in the temperature ranges where molecular ion concentration is higher than that of atomic ions.

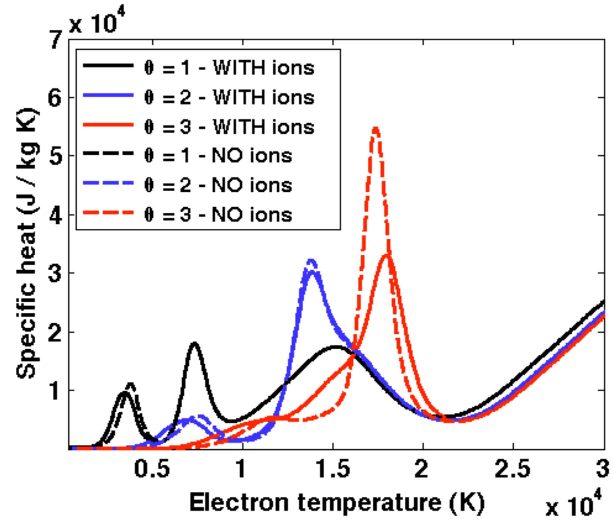

Figure 4. Total specific heat for a CO_2 mixture at atmospheric pressure for different values of the non-equilibrium parameter θ, with and without considering molecular ions.

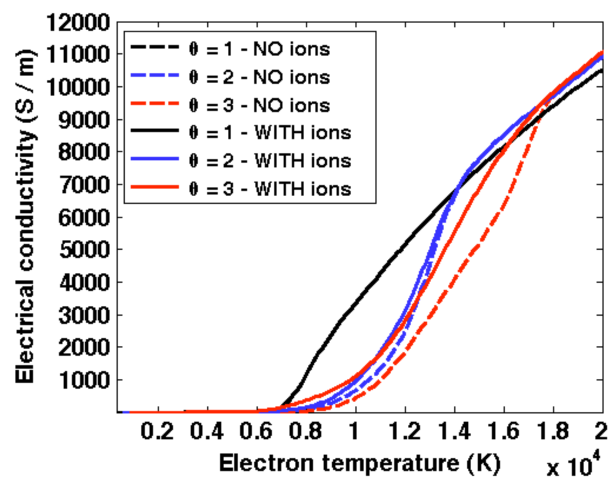

Figure 5. Electrical conductivity for a CO_2 mixture at atmospheric pressure for different values of the non-equilibrium parameter θ, with and without considering molecular ions.

4. Comparison between results of Devoto and Rat theories

Computation of transport properties in non-equilibrium has been carried out using both the simplified method of Devoto and the non-simplified method of Rat.

No remarkable differences have been obtained for thermal conductivity, electrical conductivity and thermal diffusion coefficient. Also, for ordinary diffusion coefficient of the type electron-electron, heavy-electron, and heavy-heavy, very similar results have been obtained. However, for diffusion coefficient of the type electron-heavy results of the two theories are strongly different. In figure 6, the diffusion coefficient $D_{e\text{-}c}$ has been reported for different values of the non-equilibrium parameter; no differences can be seen between the two theories for LTE conditions, whereas, for increasing values of θ, the simplified theory underestimate the diffusion coefficient.

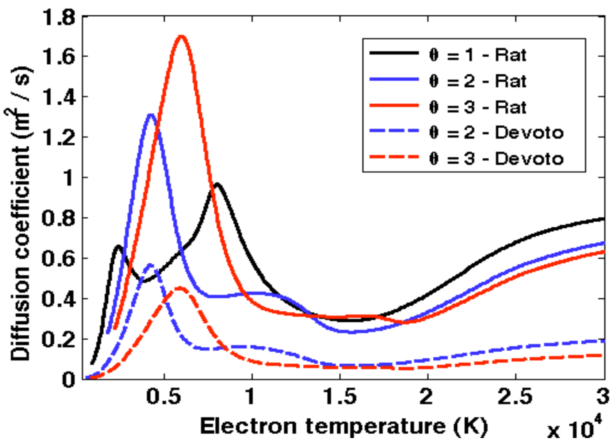

Figure 6. Diffusion coefficient $D_{e\text{-}c}$ for a CO_2 mixture at atmospheric pressure for different values of the non-equilibrium parameter θ obtained using different non-equilibrium theories.

5. Effects of metal vapours in carbon-oxygen mixtures in LTE

Metal vapours have been taken into account under LTE conditions. Four iron species have been included in the calculation: Fe, Fe^{+}, Fe^{2+} and Fe^{3+}. Iron oxides have been neglected because of their small contribution to transport properties. The main effect is the increase of electrical conductivity at below 15,000 K and a slight decrease of the electrical conductivity for higher temperatures. In figure 7, the electrical conductivity of a CO2 mixture with different concentration of iron vapours.

6. Conclusions

Plasma properties have been presented for carbon-oxygen mixtures both in equilibrium and non-equilibrium conditions. The effect of molecular ions on the calculation of composition and transport properties has been highlighted: in non-equilibrium condition, molecular ions provide electrons in the low electron temperature range. A comparison between results for non-equilibrium transport properties obtained using two different properties has been reported, showing that the simplified method by Devoto accurately reproduce results obtained with the more complicated method by Rat. Results for carbon-oxygen mixtures with Fe metal vapour inclusions have been presented. Accurate data for thermal plasma properties are requested to develop reliable modelling tools for the optimization of plasma industrial devices.

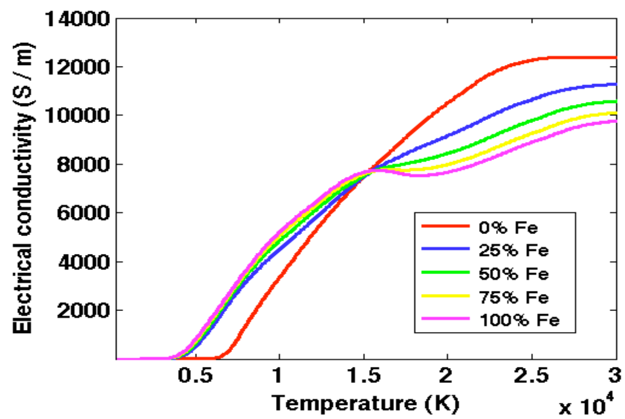

Figure 7. LTE electrical conductivity for a CO_2 mixture at atmospheric pressure for different concentrations of Fe vapours.

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