

Abstract : This study concerns the calculation of two-temperature (2T) compositions of stationary and homogeneous air and water plasmas at atmospheric pressure. A complete collisional-radiative (CR) model already developed in our laboratory is compared with a pseudo-kinetic (PK) model based upon the 2T mass action law and upon the calculation of an excitation temperature T_{ex} (varying between T_e and T_h respectively electron and heavy particles temperatures, $\theta = T_e/T_h$) from simplified kinetic considerations. Significant discrepancies are observed between the two models in the temperature range corresponding to the transition between the domination of heavy particle reactions and electron collisions.

The pseudo-kinetic (PK) model

This model was developed in the case of the air. 31 chemical species are considered: 8 neutral polyatomic molecules N_2O_3 , N_2O_4 , N_2O_5 , NO_3 , NO_2 , N_2O , O_3 , N_2 ; 2 polyatomic ions NO_2^+ and N_2O^+ ; 3 neutral diatomic molecules N_2 , O_2 and NO ; 4 diatomic ions N_2^+ , O_2^+ , O_2^+ and NO^+ ; 3 neutral atoms O, N and Ar and 10 atomic ions O^+ , O^{++} , O^{+++} , O^- , N^+ , N^{++} , N^{+++} , Ar^+ , Ar^{++} , Ar^{+++} and e.

Basic equations

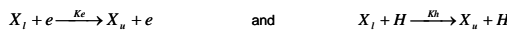
$$\text{Electrical neutrality : } \sum_{i=1}^N Z_i n_i = 0 \quad \text{Pressure conservation : } P = kT_e n_e + kT_h \sum_{i=1, i \neq e}^N n_i$$

$$\text{Stoichiometric proportions N/O and N/Ar : } \varepsilon_j \sum_{i=1}^N n_i C_{i,k} = \varepsilon_k \sum_{i=1}^N n_i C_{i,j}$$

It is possible to write these relations as a function of the population number densities of the electrons and the atoms (n_e , n_N , n_O and n_{Ar}). All other densities can be expressed from these four densities through the mass action law:

$$Q_i = Q_i^r(T_e) \cdot Q_i^{int}(T_{ex}, T_v, T_r) \cdot Q_i^{exc}(T_{ex}) = \left(\frac{2\pi m_i k T_{ex}}{h^2} \right)^{3/2} \times Q_i^{int} \times \exp\left(\frac{E_i^{ref}}{k T_{ex}} \right)$$

$T_e = T_e$ for electrons and $T_h = T_h$ for heavy particles. $T_e = T_h = T_{ex}$ (excitation temperature) and T_v (vibration temperature) are varying between T_e and T_h . They are determined from simplified chemical kinetics considerations:



K_e and K_h are the reaction rate coefficients. Their temperature dependence is supposed to follow an Arrhenius law i.e. $K_e \sim \exp(-\Delta E/kT_e)$ and $K_h \sim \exp(-\Delta E/kT_h)$ where ΔE corresponds to an average energy gap between two consecutive levels: $\Delta E \sim 1\text{eV}$ for transitions between electronic levels and $\Delta E \sim 0.1\text{eV}$ for vibrational transitions (i.e. X is a molecule). If K_h is available in the literature, a rough estimation of K_h is given by: $K_h \sim 10^4 K_e$. For vibrational transitions, heavy particles collisions are more efficient and $K_h \sim 10^2 K_e$. From the detailed balance principle, assuming Maxwellian energy distribution functions for electrons and heavy particles, the reverse rate coefficients K_e and K_h can be calculated and the ratio between the population number densities of the levels i and u is then given by:

$$\frac{n_u}{n_i} = \frac{n_e K_e(T_e) + n_H K_h(T_h)}{n_e K_e(T_e) + n_H K_h(T_h)}$$

This equation can be rewritten as:

$$\frac{g_u n_u}{g_i n_i} \equiv \exp\left(\frac{\Delta E}{kT_{ex}} \right) \cong \left\{ 10^4 n_e \exp\left[\frac{\Delta E(T_e - T_h)}{kT_e T_h} \right] + n_H \right\} \times \left\{ 10^4 n_e \exp\left[\frac{\Delta E(T_e - T_h)}{kT_e T_h} \right] \exp\left(\frac{\Delta E}{kT_e} \right) + n_H \exp\left(\frac{\Delta E}{kT_h} \right) \right\}^{-1}$$

This relation is finally used to estimate the excitation (T_{ex}) and the vibration (T_v) temperatures as a function of T_e , T_h , n_e and n_H (this last density being simply deduced from the Dalton's law).

The collisional-radiative (CR) model

Two CR codes have been developed: one for air and the other for water vapour. In these models, for each chemical species, several electronic levels are taken into account. In the case of the air: $O_2(X, a, b, A \text{ and } B)$, $O_2^+(X, a, A \text{ and } b)$, $N_2(X, A, B \text{ and } C)$, $N_2^+(X, A, B \text{ and } C)$, $NO(X, A, B, C, B' \text{ and } F)$, $NO^+(X, a, b, A \text{ and } A')$, 24 levels for the oxygen atom, 35 levels for N, 20 levels for Ar, the fundamentals states of $O^+(4S)$, $N^+(3P)$, $Ar^+(2P)$ and $O^+(2P)$ and the electrons. For the water plasma: $O_2(X, a, b, A \text{ and } B)$, $O_2^+(X, a, A \text{ and } b)$, $O_2^+(X, OH(X, A \text{ and } B))$, $OH^+(X, a, A, b \text{ and } c)$, $OH(X)$, $H_2(X, B \text{ and } C)$, $H_2^+(X)$, $H_2^+(X)$, 24 levels for O, 20 levels for H, the H^+ ion, the fundamentals states of $O^+(4S)$ and $H(1S)$ and the electrons.

Basic equations

$$\text{Electrical neutrality : } \sum_{i=1}^N Z_i n_i = 0 \quad \text{Pressure conservation : } P = kT_e n_e + kT_h \sum_{i=1, i \neq e}^N n_i$$

$$\text{Stoichiometric proportions N/O and N/Ar : } \varepsilon_j \sum_{i=1}^N n_i C_{i,k} = \varepsilon_k \sum_{i=1}^N n_i C_{i,j}$$

The system of equations to be solved is constituted of the 3 preceding relations and of a conservation equation for each electronic level. In the case of stationary and homogeneous plasma, the conservation equation of a particular electronic level is simply given by:

$$\left(\frac{\partial n_i}{\partial t} \right)_{CR} = C_i - n_i D_i = 0$$

Where n_i is the population number density of the level i. C_i and D_i depend on the population densities of the other species and on the direct and reverse rate coefficients of the chemical reactions occurring in the plasma. There is finally a system of 113 non-linear equations for the air (73 equations for water). In the non-thermal case, the critical point concerns the 2T laws (Boltzmann, Saha and Goldbergs-waage laws) used for the calculation of the reverse rate coefficients (detailed balance principle). In this work we have chosen the following formalism:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left(-\frac{E_i - E_j}{kT^*} \right)$$

$$\frac{n_u n_i}{n_i} = \frac{2g_i}{g_i} \left(\frac{2\pi m_i k T_e}{h^2} \right)^{1/2} \exp\left(\frac{-I_i}{kT^*} \right)$$

$$\frac{n_A n_B}{n_{AB}} = \frac{g_A g_B}{g_{AB}} \left(\frac{2\pi \mu_{AB} k T_h}{h^2} \right)^{1/2} \exp\left(\frac{-D_{AB}}{kT^*} \right)$$

Where E_i and E_j are the energies of the electronic levels i and j. I_i and D_{AB} are respectively the ionisation energy of the state i and the dissociation energy of the molecule AB. T^* is a temperature characteristic of the chemical process:

- \Rightarrow if an electron is involved in the reverse reaction $T^* = T_e$.
- \Rightarrow if the mechanism occurs only with heavy particles $T^* = T_h$.

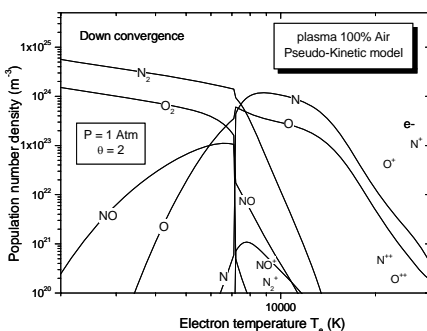


Figure 1. 2T air plasma composition 2000–30000K.

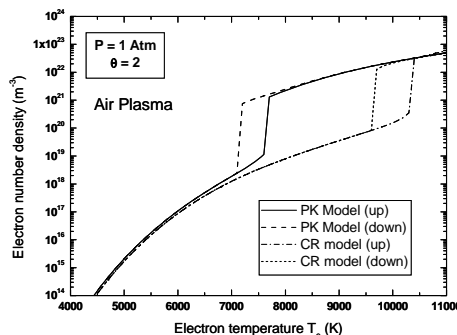


Figure 2. Comparison of electron number densities.

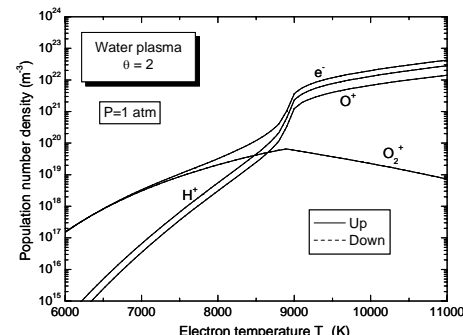


Figure 3. Main charged species in water plasma.

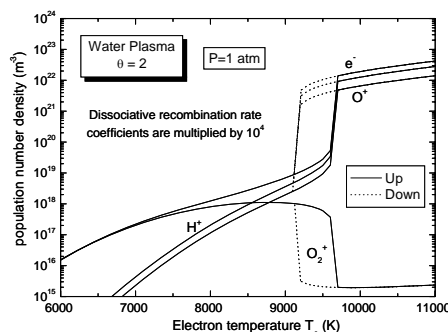


Figure 4. Main charged species in water plasma.

With the PK model, the density break is due to a rapid shift of T_{ex} between T_e to T_h . For both models, there is a zone corresponding to the transition between the domination of the heavy particles collisions (at low temperature) and the predominance of the electron impact processes (at high temperature). However, this area is not located at the same temperature for the two models (near $T_e \approx 9600 - 10500$ K for the CR code and $T_e \approx 7000 - 7700$ K with the PK method). Moreover, the results obtained with the up and down convergences are different. It means that there is not a single solution for the 2T air plasma composition in the temperature range corresponding to the transition zone. For the CR model, the appearance of two different solutions for the electron number density is due to the dissociative recombination (mainly $NO^+ + e \rightarrow N + O$) because the direct rate coefficient of this process is depending on T_e whereas the reverse one is only varying with T_h . With the PK model, the position of the transition zone is relatively dubious since its location is very sensitive to the value of ΔE and to the ratio K_e/K_h that are roughly estimated in the present study. The results of the CR model are probably more accurate provided that the forward rate coefficients of the chemical processes taken into account are known with a good precision. In the case of water, the transition between heavy particles and electron collision domination appears close to $T_e = 9000$ K but, opposite to the air, there is no differences between the up and down cases. If the rate coefficients of dissociative recombination processes ($O_2^+ + e \rightarrow O + O$, $OH^+ + e \rightarrow O + H$ and $H_2^+ + e \rightarrow H + H$) are multiplied by a factor 10^4 , there is again two different solutions.