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Comparison of the macroscopic properties of field-accelerated electrons in dry air and in pure oxygen

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Résumé. — La résolution numérique de l'équation de Boltzmann pour un gaz ionisé donne les propriétés macroscopiques des électrons soumis à l'action d'un champ électrique dans l'air sec et dans l'oxygène pur. En vue de la synthèse de l'ozone, le rendement de dissociation de l'oxygène est toujours d'autant plus grand que le champ est élevé. Comparée au cas de l'oxygène pur, sa dissociation dans l'air s'obtient beaucoup moins facilement que ne le laisse prévoir sa concentration.

Abstract. — The numerical solution of the Boltzmann equation for an ionized gas yields the macroscopic properties of electrons accelerated by an electric field in dry air and in pure oxygen. For the purpose of ozone generation, the stronger the field, the better the efficiency of oxygen dissociation. In air, the oxygen dissociation is found to be much less easy than that at the same amount of pure oxygen.

The macroscopic properties of the electrons in a given gas (pure gas or gas mixture) are often functions of the only variable E/N (electric field/gas density). The concentrations of metastables or ionized species may sometimes be additional variables but, for the present cases, they are assumed to be low enough to be neglected. The last two variables, to be taken into account in some cases, are the neutral temperature T and the gas density N ; the following computations are performed under standard conditions ($T = 273$ K and $N = 2.69 \times 10^{19} \text{ cm}^{-3}$). Nevertheless, for the gases and the range of E/N to be considered in this paper, T may be varied over a large range without any effect on the results; N changes only the three-body attachment coefficient, which is proportional to it, but it has no effect on the other macroscopic properties for values lower or a little higher than the standard one.

The more usual macroscopic properties are the drift velocity (v_d), the electron temperature ($T_e = \text{average energy} \times 2/3$), the ratio of the diffusion coefficient over the mobility (D/μ), the reaction rates and the energy branching ratios for the various elastic and inelastic processes taken into account. These properties are computed from the electron distribution function which is itself a solution of the classical Boltzmann equation for an ionized gas. The computer code which is used is based upon previous work [1].

Although literature deals with many gases (mainly pure gases and laser mixtures), air has only been considered in the preliminary work by Hake and

Phelps [2], which is based upon obsolete assumptions and does not provide the main macroscopic properties. The reason for this is related to the difficulty to have a satisfactory and coherent set of data available for oxygen cross-sections. Some differences between the data used in a recent paper on pure oxygen by Masšek *et al.* [3] and those used here [4, 5] are an illustration of the problem. The interest in air is not only due to the fact that it is the ambient medium; it is also a raw material for the generation of ozone in an electric discharge for the purpose of water purification. Any improvement of present industrial systems requires an insight in ozone synthesis processes, among which the most important is the dissociation of molecular oxygen by electrons. The following results allow a comparison of the possibilities for converting electric energy into oxygen dissociation in dry air and in pure oxygen. In addition, this investigation is of direct interest for the understanding of atmospheric electricity phenomena.

Elastic collisions with N_2 , O_2 , Ar and CO_2 are taken into account. The inelastic processes taken into account for N_2 and O_2 are summarized in table I. Inelastic processes with Ar and CO_2 are not given in detail since their effect is quite minor. Dry air composition is $[\text{N}_2 : \text{O}_2 : \text{Ar} : \text{CO}_2 = 7\,808 : 2\,095 : 93 : 3]$.

The differences between dry air and pure oxygen are significant for all the results displayed. Figure 1 gives the variations of the macroscopic parameters v_d , T_e and D/μ versus E/N ($1 \text{ Td} = 10^{-17} \text{ V} \cdot \text{cm}^2$). The last

Table I. — *Inelastic processes taken into account with their energy loss in eV.*

Oxygen [4]	Nitrogen [5]
0.051-3 body attachment	0.29, 0.58, 0.86; 1.13, 1.41, 1.68
0.007-rotations	1.95, 2.21, 5-vibrations
0.19, 0.38, 0.57, 0.75-vibrations	6.7-A $^3\Sigma_u^+$ excitation
0.977-a $^1\Delta_g$ excitation	8.4-a $^1\Pi_g$ excitation
1.627-b $^1\Sigma_g^+$ excitation	11.2-C $^3\Pi_u$ excitation
4.4-dissociative attachment	12.5-electronic excitations
4.5-electronic excitation(s)	14-electronic excitations
6-dissociative ? electronic excitation(s)	
8.4-B $^3\Sigma_u^-$ dissociative excitation	
10-electronic excitation	
12.2-ionization	
14.7-electronic excitation

Fig. 1. — Drift velocity and characteristic energy variations versus reduced electric field.

two are equal if the distribution function is Maxwellian; the difference between them results from the shift of the actual distribution with respect to the Maxwellian one. Figure 2 gives reaction rates as α/N_i ; (the rate coefficients in cm^3/s are the products of α/N_i in cm^2 , times the drift velocity in cm/s). Figure 3 gives the energy branching ratios for some groups of processes.

The differences of the present results for pure oxygen with those by Masěk *et al.* [3] are minor.

For air, it is clear that energy transfers to Ar, to CO_2 and by elastic collisions are all negligible. At lower fields (a few Td), the largest fraction of the energy is transferred to oxygen vibrations. At moderate fields (a few tens of Td) almost all the energy is transferred to nitrogen vibrations; this is made at the expense of oxygen singlets which are never pumped as efficiently in air as they are in the pure gas. At higher fields, the electronic excitations of oxygen (some of

Fig. 2. — Variations of some reaction rates versus reduced electric field. 1=6 eV; 2=8.4 eV; 3=a $^1\Delta_g$; 4=ionization; 5=4.5 eV; 6=b $^1\Sigma_g^+$; 7=dissociative attachment; 8=3-body attachment.

Fig. 3. — Variations of energy branching ratios versus reduced electric field. 1 = N_2 , except vibrations; 2 = O_2 , > 4 eV except ionization; 3 = N_2 , vibrations; 4 = O_2 , ionization; 5 = Ar; 6 = O_2 , singlets; 7 = O_2 , vibrations; 8 = elastic; 9 = CO_2 .

which can be dissociative) receive an energy fraction in agreement with the O_2 fraction in air. It should be noted that the N_2 excitations for this range of field are related mainly to the A $^3\Sigma_u^+$ metastable and that, consequently, a fraction of their energy can go back to electrons *via* superelastic collisions.

As a conclusion, it is possible to assess clearly that the larger fields yield the better dissociation efficiency for the purpose of ozone generation. However, with respect to the case of pure oxygen, O_2 dissociation in air is much less easy to achieve than predicted from its concentration since the proper range is then closer to the breakdown field (Figs. 2 and 3): the breakdown field is close to that for which the curves of ionization and dissociative attachment cross each other on figure 2.

References

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