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CALCULATION OF PARTICLE CONCENTRATIONS IN OXYGEN dc GLOW DISCHARGE*

KAREL MAŠEK**, LEOŠ LÁSKA**, Praha

РАСЧЁТ КОНЦЕНТРАЦИЙ ЧАСТИЦ В ТЛЕЮЩЕМ РАЗРЯДЕ В КИСЛОРОДЕ

Current dependences of the concentrations of electrons, O^- -ions, metastables $O_2^*({}^1\Delta_g)$ and atoms are numerically calculated and the dissociation degree is compared with experiments.

The concentrations of charged, excited and neutral particles are often the required quantities for plasma chemistry analyses, but they are not always available. It is due to a non-equilibrium state of the discharge plasma which makes both experimental measurements and theoretical calculations difficult. In the case of oxygen there exist only individual measurements in various types of discharges and the rare theoretical results are not quite consistent with them. It would be desirable to know not only the magnitude of these concentrations but also their dependences on the discharge parametrs, to find, for example, optimum conditions for the considered chemical reactions. The relative concentrations of oxygen atoms, metastable molecules $O_2^*({}^1\Delta_g)$, electrons, and O^- -ions as the dominant neutral and negative particles in the oxygen glow discharge are calculated and presented in this contribution.

In the steady state, in which a dc discharge is sustained by an outer electric field, the concentrations of the particles results from a balance between their total production and total losses. The particles are produced and destroyed in mutual collisions, by diffusion and recombination on the tube wall with appropriate rate coefficients. The list of the elementary processes involved in the number balance is following:

$$\begin{array}{l} e+O_2\rightarrow O_2^*({}^1\Delta_g)+e \\ e+O_2\rightarrow O+O^- \\ e+O_2\rightarrow O+O \\ e+O_2\rightarrow O_2^++2e \\ e+O_2^*({}^1\Delta_g)\rightarrow O_2+e \\ e+O_2^*({}^1\Delta_g)\rightarrow O_2^*({}^1\Sigma_g^+)+e \\ e+O_2^*({}^1\Delta_g)\rightarrow O+O^- \end{array}$$

$$\begin{array}{l} e+O_2^*({}^1\Delta_g)\rightarrow O_2^++2e \\ e+O^-\rightarrow O+2e \\ O^-+O\rightarrow O_2+e \\ O^-+O_2\rightarrow O_2+O+e \\ O^-+O_2\rightarrow O_2^-+O \\ O^-+O_2^*({}^1\Delta_g)\rightarrow O_3+e \\ O^-+O_2^+\rightarrow O_2+O\,. \end{array}$$

Some of the rate coefficients are a function of an alectric field due to a non-equilibrium form of the electron distribution function in this discharge [1].

Because of the quasineutrality supposed the diffusion flows of the charged particles are characterized by effective diffusion coefficients, D'_{ef}, [2] and the losses due to the diffusion are represented by effective first-order reactions with the rate constants given by

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** Institute of Physics, Czechosl., Acad. Sci., Na Slovance 2, CS-180 40 PRAHA 8.

$$k_i=\frac{D'_{ef}}{N}\frac{\lambda^2}{R^2},$$

(λ — the first root of the Bessel function expressing the radial density distribution, R — tube radius, N — initial concentration of molecules). If a value for the recombination coefficient of atoms, K_R, on the tube wall is accepted to be $\sim 1\times 10^{-3}$, the dissociation degree will be practically constant across the tube and the loss of atoms due to this process may be expressed as $\frac{1}{2}X_iK_R\frac{\bar{v}}{R}$ [1, 2] $\left(X_i=\frac{0}{N}, \bar{v}\right.$ — mean kinetic velocity of atoms$\left.\right)$. Comparing all the production processes with the destruction processes mentioned above, the number balance equation for every considered particle can be set up. Clearly, in this approximation a system of five non-linear algebraic equations is obtained, which must be solved numerically by a computer. The form of our algebraic equations obeys the B-invariance laws [3]. This enables us to arrange the results of the solution according to the invariant discharge parameters -I/R, NR and E/N, all of which obey Ohm's law.

The current dependences of the relative atom concetrations are plotted in Fig. 1 for several values of the concentration parameter NR. The weak dependence of the atomic concentration on the parameter NR is illustrated in Fig. 2. Comparing our calculations with experimental results, we can conclude that the calculated current and pressure dependences follow the measurmeents of Sabadil [4] and Hermoch [5]. As for absolute values an even better agreement could be obtained by changing in the

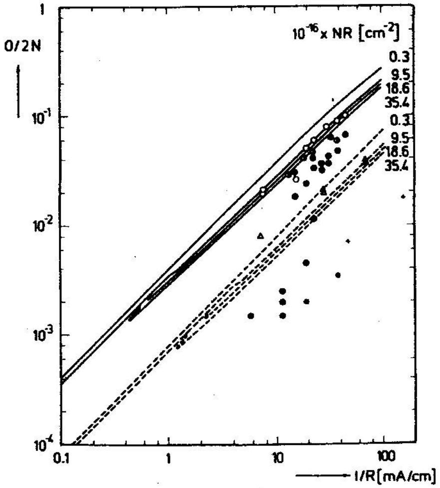

Fig. 1. Dissociation degree as a function of reduced current I/R ; full lines — the calculation with $K_R=1\times 10^{-3}$, dashed lines — $K_R=5\times 10^{-3}$. Experimental points of Sabadil [4]: ○ — $NR=4.96\times 10^{15}$ cm^{-2}; ◑ — $NR=8.27\times 10^{16}$ cm^{-2}; ● — $NR=1.65\times 10^{17}$ cm^{-2}; ∗ — $NR=3.31\times 10^{17}$ cm^{-2}. Experimental points of Hermoch [5]: △ — $NR=4.51\times 10^{16}$ cm^{-2}; ▲ — $NR=9.02\times 10^{16}$ cm^{-2}; experimental points of Penkin and Cygir [6]: + — $NR=2.29\times 10^{15}$ cm^{-2}.

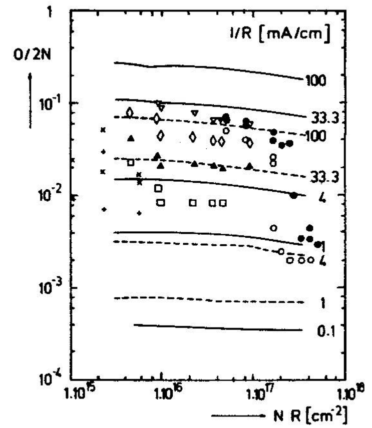

Fig. 2. Dissociation degree as a function of concentration parameter NR ; full lines — the calculation with $K_R=1\times 10^{-3}$, dashed lines — $K_R=5\times 10^{-3}$. Experimental points of Sabadil [4]: ○ — $I/R=19.23$ mA/cm; ● — $I/R=38.46$ mA/cm. Experimental points of Hermoch [5]: □ — $I/R=7.14$mA/cm; ▲ — $I/R=28.57$ mA-/cm; ◇ — $I/R=71.43$ mA/cm; ▽ — $I/R=142.85$ mA/cm. Experimental points of Pekin and Cygir [6]: + — $I/R=48$ mA/cm; × — $I/R=160$ mA/cm.

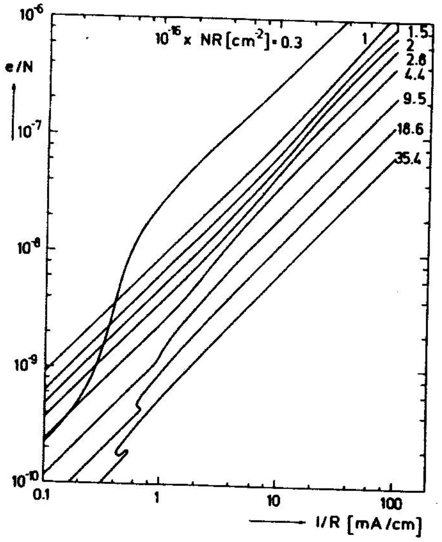

Fig. 3. Relative concentrations of electrons.

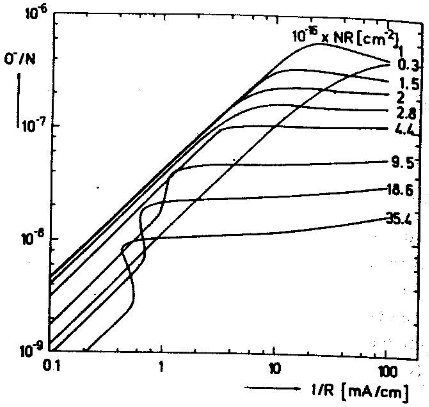

Fig. 4. Relative concentrations of O$^-$ — ions.

calculations the value of the recombination coefficient K_R approximately to $\sim 2\times 10^{-3}$. Our calculations, however, did not register the step of the atom concentration down at the transition from the *H* to *T* form of the oxygen discharge presented in both papers (see e.g. full or open points (●, o) in Fig. 2, which represent the measurement of Sabadil). A more precise fitting would be useless since we can exclude neither a vagueness of the neutral gas temperature in the experiments nor possibly different production mechanisms of the dissociation in the theory.

The current dependences of electrons and 0$^-$ — ions at constant *NR* are plotted in Fig. 3, 4. Concerning the O$^-$ — ions, a point is reached, with increasing current at a constant *NR*, when the detachment with atoms dominates over the others and balances the O$^-$ — ions production. The O$^-$ — ion population is then saturated with respect to the discharge current. The point is shifted to lower current values with the growth of neutral concentration due to the detachment process with metastables. At higher neutral gas concentrations even *S*-shaped loops occur in the current dependences demonstraiting an existance of two different ionization mechanisms on the side of the lower and the higher values of the discharge current, respectively. The electron concentration increases with the current except for a small range of the loops where only slight changes occur, while the electric field varies suddenly [7].

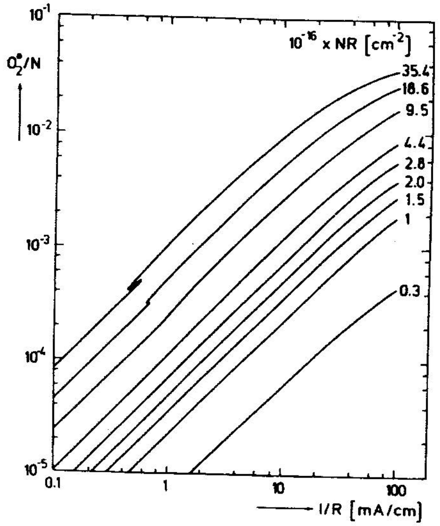

Fig. 5. Relative concetrations of metastables $O_2^*(^1\Delta_g)$.

From the viewpoint of plasma chemistry reactions on the surfaces of solids it is important to know also the densities of the excited particles with a long lifetime. The lowest metastable state $O_2^*(^1\Delta_g)$ was considered only, the steady state population of which was also calculated. In a hf discharge its concentration was experimentally found to be higher than that of the other states [8]. The dependences of the metastables on the reduced discharge current *I/R* for several values of the parameter *NR* are illustrated in Fig. 5. They were calculated under the assumption of a diffusion decay of the metastables on the discharge tube wall, which need not be always valid [6, 8].

The pressure dependences of the calculated concentrations and other information on the oxygen discharge were presented in [1].

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