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Steady-state ozone synthesis from oxygen in a pulsed discharge at low pressures

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ABSTRACT. The influence of the molecular oxygen flow velocity on the ozone synthesis is very important and it has been previously analyzed analytically for the particular case of a constant radial flow velocity. In this work, the ozone production from oxygen in a pulsed discharge considering the radial dependence of the flow velocity for a Poiseuille flow is studied. This is done by means of a system of the hydrodynamic zeroth-order rate equations. The steady state solution of this system of equations, valid at low pressures, is found by using a reported perturbative method. The expressions obtained for the atomic oxygen and ozone densities facilitate to a great degree the analysis of the ozone synthesis. In this range of pressure, such expressions can be useful as an analytical limit (non existing at present) in the fluid simulation codes for this type of problems. Results show a good agreement with those obtained through a numerical simulation previously reported. The existence of an optimal distance between electrodes as a function of the average flow velocity V_0, is shown for given temperature and pressure.

RESUMEN. La influencia de la velocidad de flujo del oxígeno molecular es muy importante en la síntesis del ozono y ésta ha sido analizada analíticamente para el caso particular de una velocidad de flujo radial constante. En este trabajo se estudia la producción de ozono a partir del oxígeno en una descarga pulsada, considerando la dependencia radial de la velocidad de flujo para un flujo de Poiseuille. Esto se decribe a través de un sistema de ecuaciones hidrodinámicas a orden cero. Se encuentra la solución estacionaria de este sistema de ecuaciones válida para presiones bajas, usando un método perturbativo reportado anteriormente. Las expresiones obtenidas para las densidades del oxígeno atómico y del ozono facilitan enormemente el análisis de la síntesis del ozono y pueden ser útiles en este intervalo de presiones, como un límite analítico (inexistente actualmente) para los códigos de simulación numérica de este tipo de problemas. Los resultados muestran una buena coincidencia con los obtenidos por medio de una simulación numérica reportados con anterioridad. Se muestra la existencia de una distancia óptima entre los electrodos en dependencia de la velocidad promedio de flujo V_0 para una temperatura y presión dadas.

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1. INTRODUCTION

The optimization of the efficiency of the ozone production is relevant for the development of its applications [1]. Due to these applications, the ozone synthesis has been the subject of extensive research over the last few years especially modelling this type of process [2, 3, 4]. More recently, the subject has continued to attract attention; of particular relevance are some works related with the analytical solutions of the system of hydrodynamic rate-equations which describes the ozone production from oxygen in a pulsed discharge [5, 6].

In a previous paper [5] a perturbative method was proposed to obtain the analytical solutions of the system of hydrodynamic rate-equations which describes the ozone production in a pulsed discharge. In such a process the influence of the molecular oxygen flow velocity introduced into the gap on the obtained ozone concentration, is very important. This dependence has been analyzed in Ref. [5] for the case of a constant average radial flow velocity. In the present paper, the steady-state solutions valid at low pressures of the system of zeroth-order simultaneous rate-equations, considering the radial dependence on the flow velocity, in the particular case of a Poiseuille flow velocity are obtained. The expressions obtained for the atomic and ozone densities greatly facilitate the analysis of the ozone synthesis and can be useful, in this range of pressure, as a non existing analytical limit for the numerical simulation of this type of problem.

The paper is organized in the following way: in Sect. 2 the basic equations are described; in section 3 the solutions, valid at low pressures, of the system of zeroth-order rate-equations assuming a Poiseuille flow velocity are obtained. Different limits are analyzed. The main results are summarized in Sect. 4.

2. BASIC EQUATIONS

In the following, the hydrodynamic model described in Ref. [2, 5] will be used. From the particle mass conservation for species σ, the Fick's law and the conservation of the total number of particles results

$$\frac{\partial}{\partial t}(nC_\sigma) + \vec{u}_0 \cdot \nabla(nC_\sigma) + nC_\sigma(\nabla \cdot \vec{u}_0) - \mathcal{D}_\sigma \Delta(nC_\sigma) = R_\sigma, \tag{1}$$

where u_0 is the flow velocity, C_σ the concentration, n the total density, R_σ the kinetic term and $\mathcal{D}_\sigma$ the diffusion coefficient. Assuming a laminar fluid ($\Delta \cdot \vec{u}_0 = 0$); a cylindrical geometry along the Oz axis of the streamer channel and a velocity $\vec{u}_0$ parallel to the Oz axis, then under conditions of small axial density-gradients as well as no azimuthal variations, Eq. (1) becomes

$$\frac{\partial n_\sigma(\rho, z, t)}{\partial t} + u_0(\rho)\frac{\partial n_\sigma(\rho, z, t)}{\partial z} = \mathcal{D}_\sigma \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial n_\sigma(\rho, z, t)}{\partial \rho}\right) + R_\sigma(\rho, z, t), \tag{2}$$

where $n_\sigma = nC_\sigma$.

The kinetic term $R_\sigma(\rho, z, t)$ is obtained using a simplified system of kinetic equations proposed in Ref. [2] and for the particular case of the atomic oxygen and ozone, the following expressions are obtained:

$$R_1(\rho, z, t) = k_5 n_2 n_3 - k_4 n_1 n_3 - k_3 n_1 n_2^2, \tag{3}$$

$$R_3(\rho, z, t) = k_3 n_1 n_2^2 - k_4 n_1 n_3 - k_5 n_2 n_3, \tag{4}$$

where k_3, k_4 and k_5 refer to the rate of each reaction.

The value of $u_0(\rho)$ in the previous equations will assume a Poiseuille flow velocity given by

$$u_0(\rho) = 2V_0 \left(1 - \frac{\rho^2}{R^2}\right), \tag{5}$$

where V_0 is the average flow velocity and R the limit radius of the reaction volume.

Now, using the dimensionless quantities introduced in Ref. [5]

$$\begin{aligned} Z &= \frac{z}{l}, & r &= \frac{\rho}{R}, & \tau &= \frac{2tV_0}{l}, & u(r) &= \frac{u_0(\rho)}{2V_0}, \\ N_1 &= \frac{n_1}{n_2}, & N_3 &= \frac{n_3}{n_2}, & D_1 &= \frac{\mathcal{D}_1 l}{2V_0R^2}, & D_3 &= \frac{\mathcal{D}_3 l}{2V_0R^2}, \\ \alpha &= \frac{l}{2V_0}K_5, & \beta &= \frac{l}{2V_0}K_4, & \gamma &= \frac{l}{2V_0}K_3, \end{aligned} \tag{6}$$

where l is the characteristic length of the streamer channel, $K_5 = k_5 n_2$, $K_4 = k_4 n_2$ and $K_3 = k_3 n_2^2$; into (2), the following equations for the dimensionless atomic oxygen and ozone concentrations are obtained [5] ($n_2 = \text{const}$)

$$\frac{\partial N_1}{\partial \tau} + u(r)\frac{\partial N_1}{\partial Z} = D_1 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial N_1}{\partial r}\right) + \alpha N_3 - \beta N_1 N_3 - \gamma N_1, \tag{7}$$

$$\frac{\partial N_3}{\partial \tau} + u(r)\frac{\partial N_3}{\partial Z} = D_3 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial N_3}{\partial r}\right) - \alpha N_3 - \beta N_1 N_3 + \gamma N_1. \tag{8}$$

From the rigid elastic sphere approximation, the diffusion coefficients (cm^2s^{-1}) in molecular oxygen can be calculated as follows [5]:

$$\mathcal{D}_1 = 7.3458 \times 10^{17}\, T^{1/2}/n_2,$$

$$\mathcal{D}_3 = 3.7764 \times 10^{17}\, T^{1/2}/n_2,$$

where T is the temperature (K).

3. STEADY-STATE SOLUTIONS

The conditions to obtain the steady-state were established in Ref. [5]. The pulsed electric discharge dissociates the molecular oxygen through electron impact, and a typical pulse width is $\Delta \approx 1.6 \times 10^{-10}$ s [3]. Considering the case in which the kinetic processes take place in times $\Delta t \gg 1.6 \times 10^{-10}$, the time dependence can be eliminated.

The steady-state solutions of Eqs. (7) and (8) have been obtained in a previous paper [5], through a proposed perturbative method for the case of a constant flow velocity $u(r) = u_m = 2/3$. It was also shown there, that the ozone recombination involved with the solution of the system of equations to the first-order is small compared with the production of ozone. In the following, the analysis will be focused on the solution of the system of equations to the zeroth-order, taking into account the radial dependence on the flow velocity, in order to obtain a better agreement with the results reported in Ref. [2].

In order to investigate the influence of the radial dependence on the flow velocity, in the ozone production, a Poiseuille velocity (5) will be assumed. In the steady-state case, the zeroth-order equations obtained from (7) and (8) have the form [5]

$$u(r)\,\frac{\partial N_1^{(0)}(r,Z)}{\partial Z} = D_1 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial N_1^{(0)}(r,Z)}{\partial r}\right) - \gamma N_1^{(0)}(r,Z), \tag{9}$$

$$u(r)\,\frac{\partial N_3^{(0)}(r,Z)}{\partial Z} = D_3 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial N_3^{(0)}(r,Z)}{\partial r}\right) + \gamma N_1^{(0)}(r,Z). \tag{10}$$

It will be also assumed that an initial atomic oxygen concentration is present on one of the electrodes and that the densities $N_1^{(0)}(r,Z)$ and $N_3^{(0)}(r,Z)$ are zero at the limit radius of the reaction volume (considering a thick reaction volume). Under these conditions, the following initial and boundary conditions are imposed upon the zeroth-order Eqs. (9) and (10) [2, 5]:

$$N_1^{(0)}(r,0) = N_0, \quad N_1^{(0)}(1,Z) = 0, \tag{11}$$

$$N_3^{(0)}(r,0) = 0, \qquad N_3^{(0)}(1,Z) = 0. \tag{12}$$

In reality, there exists a flux of atomic oxygen to the outside regions of the reaction volume, but taking into account the considered pulsed nature of the process it is feasible to assume that a portion of atomic oxygen at the edge is small, *i.e.*, it may be expected that the atomic oxygen mainly recombines with the molecular oxygen near the center of the reaction volume.

Using the method of separation of variables [7,8,9], the solution for the atomic oxygen density $N_1^{(0)}(r,Z)$ is obtained:

$$\begin{aligned} N_1^{(0)}(r,Z) = {} & N_0 e^{-[(\mu_n^{(0)})^2 D_1 + \gamma]Z - \frac{1}{2}\sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}\, r^2} \\ & \times {}_1F_1\left(\frac{1}{2} - \frac{(\mu_n^{(0)})^2}{4\sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}}, 1; \sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}\, r^2\right), \end{aligned} \tag{13}$$

where $F(a, c; x)$ is the confluent hypergeometric function. From the boundary conditions, the constants A_0, A_2 and λ are determined:

$$A_0 = (\mu_n^{(0)})^2, \qquad i\sqrt{A_2} = \sqrt{A_0 + \frac{\gamma}{D_1}}, \qquad \lambda = A_0 + \frac{\gamma}{D_1}. \tag{14}$$

Here $\mu_n^{(0)}$ is the nth root of the Bessel function $J_0(x)$ which first satisfies the condition

$$\frac{1}{2} - \frac{A_0}{4i\sqrt{A_2}} = \frac{1}{2} - \frac{(\mu_n^{(0)})^2}{4i\sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}} < 0. \tag{15}$$

(See Appendix for details on the determination of $\mu_n^{(0)}$.)

In a similar way, the inhomogeneous equation (10) can be solved. Taking into account (13) and the initial and boundary conditions (12), for the ozone density, it follows that

$$N_3^{(0)}(r, Z) = -\frac{2\gamma N_0 e^{-\frac{1}{2}\mu^{(0)} r^2}\, {}_1F_1(\frac{1}{2} - \frac{\mu^{(0)}}{2}, 1; \mu^{(0)} r^2)}{\mu^{(0)}\left[D_1 \mu^{(0)}(1 - r^2) + 2D_3(\mu^{(0)} r^2 - 2)\right]} \times \left(e^{-\frac{1}{2}(\mu^{(0)})^2 D_1 Z} - e^{-\frac{D_3 \mu^{(0)}(2 - \mu^{(0)} r^2)}{1 - r^2} Z}\right), \tag{16}$$

where $\mu^{(0)}$ is the first zero of the confluent hypergeometric function ${}_1F_1(\frac{1}{2} - \mu^{(0)}/2, 1; \mu^{(0)})$; this can be approximated to a value near the one of the first zero of the zeroth order Bessel function equal to $\mu_1^{(0)}$ (see Appendix).

In the process of solution of Eq. (10), small terms have been discarded in relation with the inequality $\mu_1^{(0)} \gg \gamma/D_1$. According to the values reported in Ref. [5], (Table 1) this limit corresponds to the case of low pressures ($P \leq 5$ Torr). In the opposite limiting case ($\mu_1^{(0)} \ll \gamma/D_1$) the solution of (10), using the method of separation of variables, does not have any physical meaning.

To analyse the degree of agreement of the results obtained here with those obtained in Ref. [2], Fig. 2 shows the radial density distributions at pressure $P = 5$ Torr at constant temperature (300 K) and for an average flow velocity of 400 $\mathrm{cm\,s^{-1}}$. Figure 3 shows the average flow dependence of the atomic oxygen and ozone density on the axis ($P = 5$ Torr, $T = 300$ K, $z = 1$ cm). Figure 4 depicts the temperature dependence of the atomic oxygen and ozone densities on the axis at $P = 5$ Torr, $V_0 = 400$ $\mathrm{cm\,s^{-1}}$ and $z = 1$ cm.

From Figs. 1 and 2 it may be noted that the maximum of ozone density (reached on the axis of the current channel), increases with pressure as has been shown in [2, 5]. In the present case we obtain for the ozone (see Figs. 1 and 2) a sharp peak at the edge of the reaction volume which is explained from the imposed boundary conditions. From the physical point of view this mathematical effect does not represent a problem as will be shown from the good agreement of the results reported here with those obtained by means of a numerical approach [2].

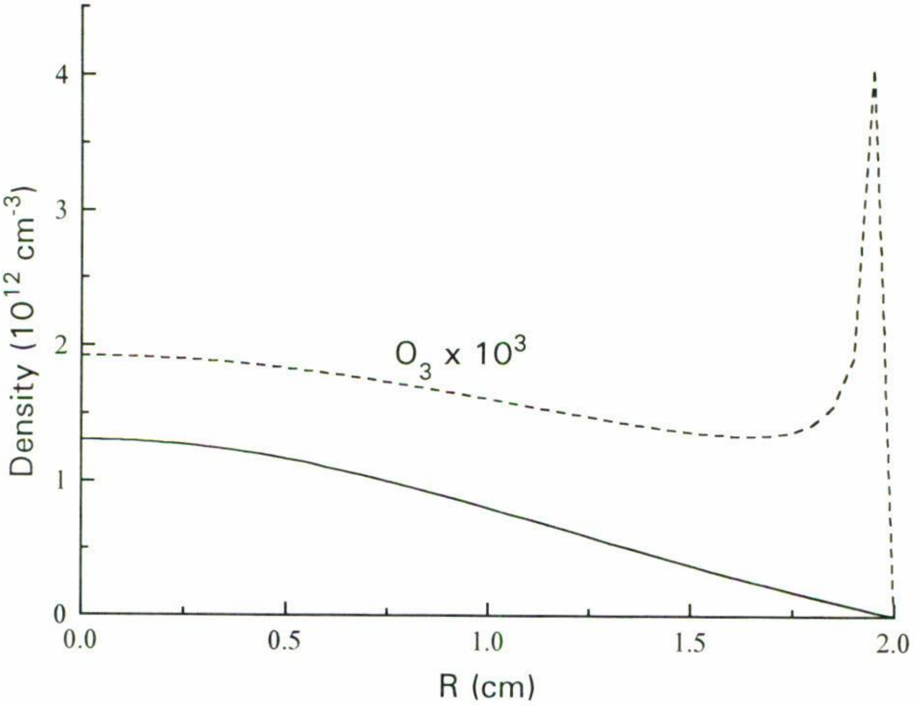

FIGURE 1. Radial distribution of atomic oxygen (solid) and ozone (dashed). $P = 1$ Torr, $T = 300$ K, $V_0 = 400$ cm s^{-1}, $z = 1$ cm.

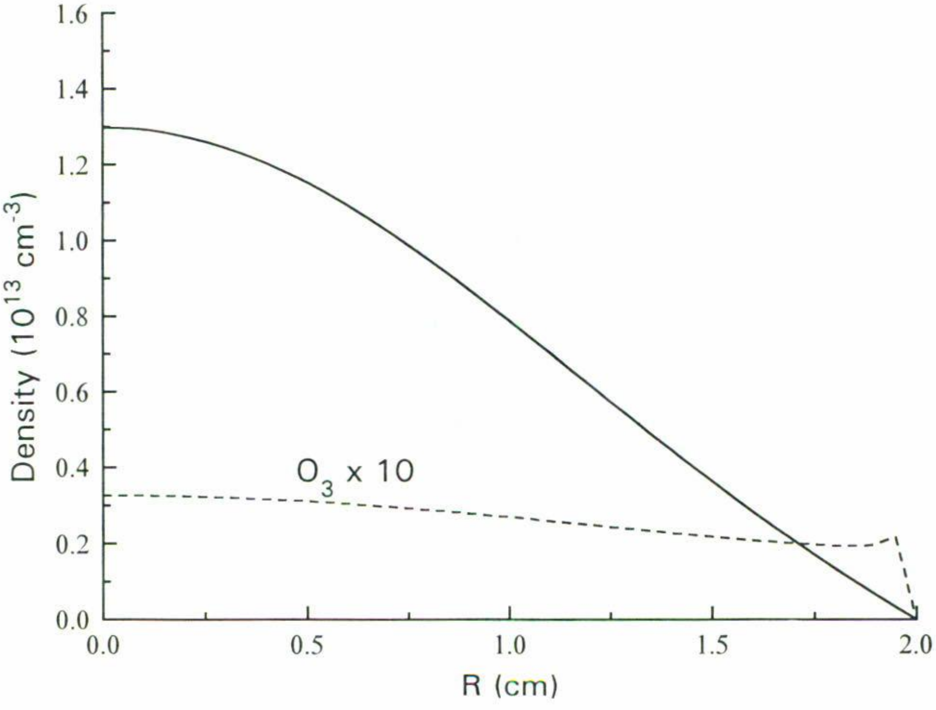

FIGURE 2. Radial distribution of atomic oxygen (solid) and ozone (dashed). $P = 5$ Torr, $T = 300$ K, $V_0 = 400$ cm s^{-1}, $z = 1$ cm.

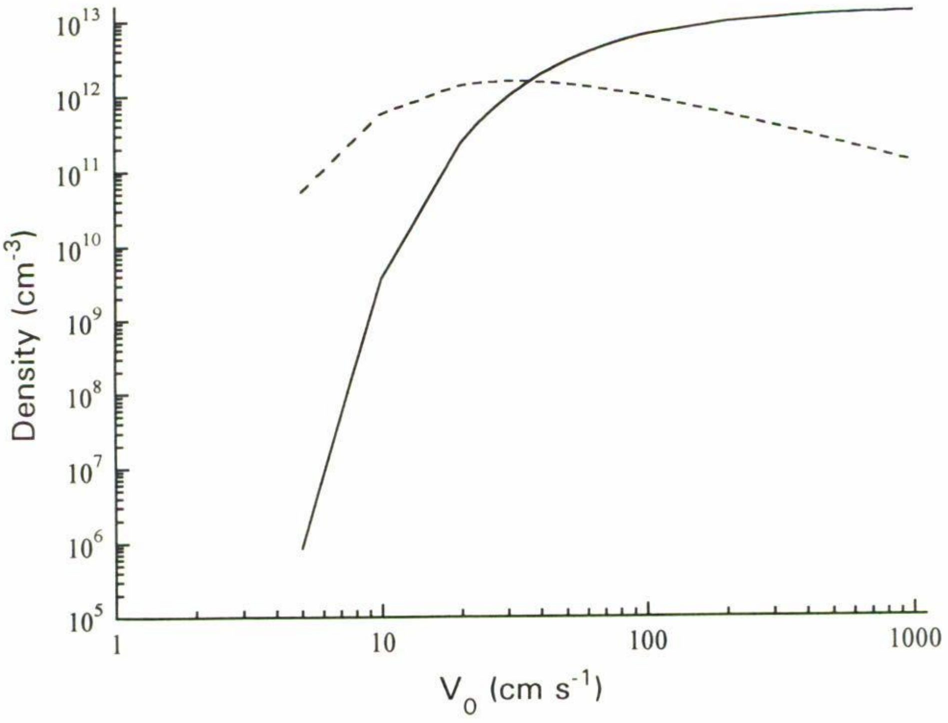

FIGURE 3. Average flow velocity dependence of the atomic oxygen (solid) and ozone (dashed) density on the axis. $P = 5$ Torr, $T = 300$ K, $z = 1$ cm, $R = 2$ cm.

In Fig. 2 the expansion of the atomic oxygen density is shown to be in agreement with the results obtained in Ref. [2]. It can be observed that quite different values for the atomic oxygen and ozone densities are obtained. These differences are related to the considered value of N_0 as has been discussed previously [5].

Figure 3 shows the maximum densities evolution with the average flow velocity. Here similar results as in Ref. [2] are obtained, *i.e.*, the atomic oxygen density increases with average flow velocity, while the ozone concentration is maximum for $V_0 \approx 32\ \mathrm{cm\,s^{-1}}$ and decreases for increasing values of V_0. This result shows, in agreement with Refs. [5, 10], that there is an optimum reaction time for ozone generation.

The temperature dependence of the atomic oxygen and ozone maximum densities are plotted in Fig. 4. Here the results confirm those obtained at $P = 5$ Torr in [2] *i.e.*, the decay of atomic oxygen (with $T = 200$ K, $n_1 = 1.318 \times 10^{13}$ and with $T = 800$ K, $n_1 = 1.180 \times 10^{13}$) and ozone densities with temperature. The last result confirm the conclusion made in Ref. [10] that the effect of the gas temperature on the efficiency of ozone formation is small which at the same time is in agreement with the fact that the most important parameter affecting the efficiency of ozone production is the atomic oxygen concentration as was determined in Ref. [5].

Finally, Fig. 5 shows the maximum ozone density distribution along z (at the axis, $\rho = 0$). From this chart it is observed that for a given temperature an optimum z for the ozone formation is obtained. The last result can be used to determine the optimal distance between electrodes in dependence of the average flow velocity V_0. This

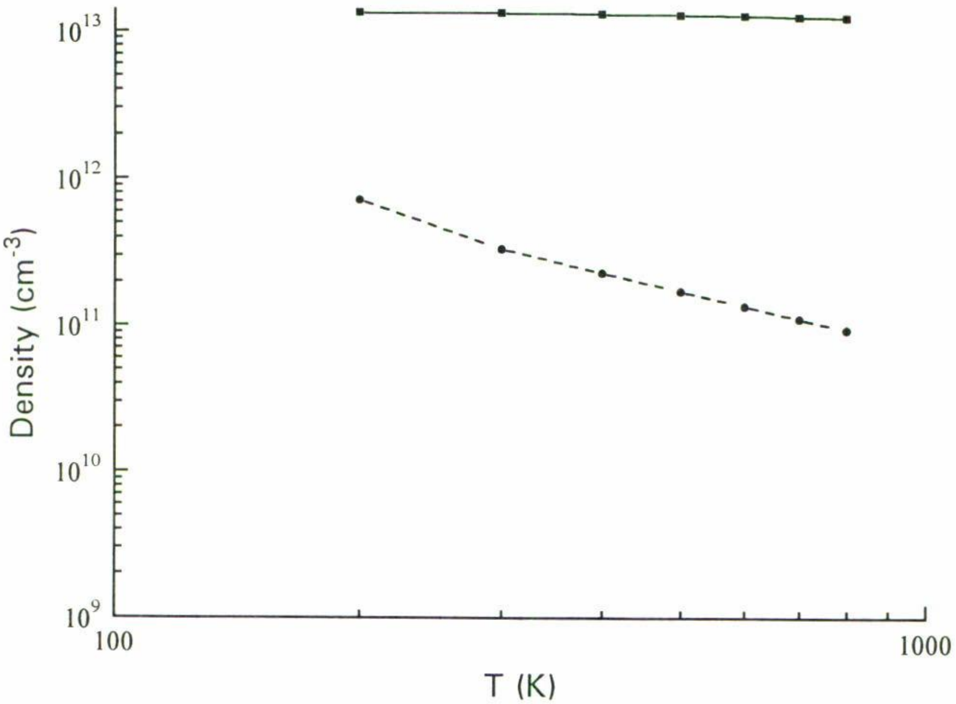

FIGURE 4. Temperature dependence of the atomic oxygen (solid) and ozone (dashed) on the axis. $P = 5$ Torr, $V_0 = 400$ cm s^{-1}, $z = 1$ cm, $R = 2$ cm.

parameter is very important, from the energetic point of view, for the construction of an ozonizer.

4. CONCLUSIONS

In this work, the steady-state ozone synthesis from oxygen at low pressures ($P \leq 5$ Torr) has been studied. The radial dependence on the flow velocity in the particular case of the Poiseuille flow velocity is taken into account. General expressions for the atomic oxygen and ozone densities, using the perturbative method proposed in Ref. [5], have been obtained.

The expressions obtained for the atomic oxygen and ozone densities facilitate greatly the analysis of the ozone synthesis and can be useful, at this range of pressure, as an analytical limit for numerical simulation of this type of problem as well.

It has been shown that the maximum of ozone density (reached on the axis of the current channel) increases with pressure as has been obtained in Refs. [2, 5]. This last conclusion can be explained by the fact that for higher pressure there will be more molecular oxygen in the gap [5].

The expansion of atomic oxygen density at pressure $P = 5$ Torr with constant temperature (300 K) and average flow velocity equal to 400 cm s^{-1} has been determined (Fig. 1 and Fig. 2). The atomic oxygen density increases with average flow velocity, while the

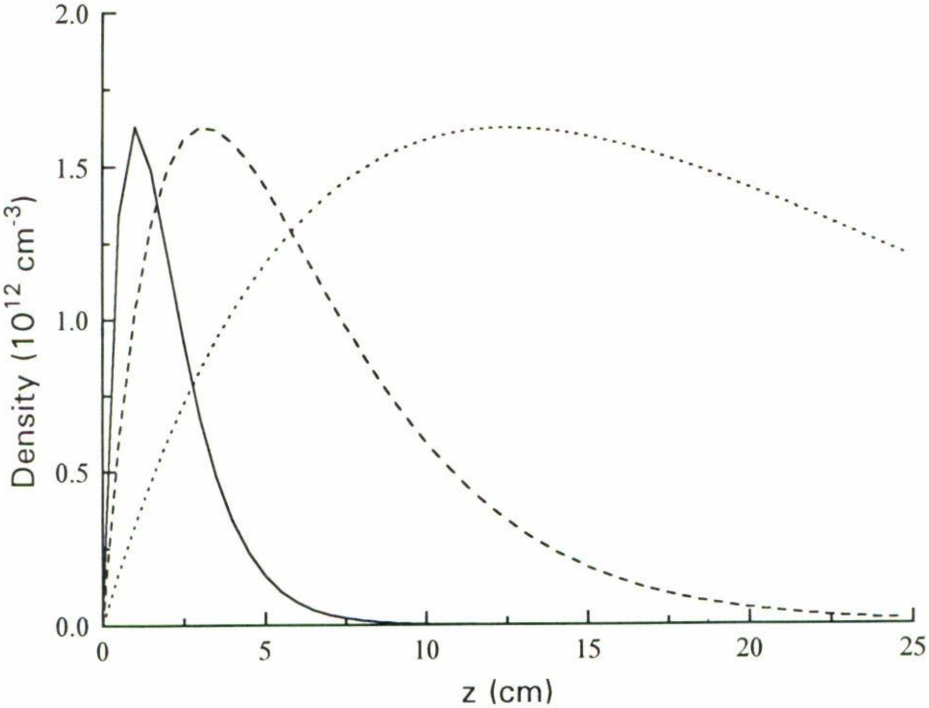

FIGURE 5. Axial distribution of zone on the axis ($\rho = 0$ cm). $P = 5$ Torr, $T = 300$ K, $V_0 = 32$ cm s^{-1} (solid), $V_0 = 100$ cm s^{-1} (dashed), $V_0 = 400$ cm s^{-1} (dotted).

ozone concentration is maximum for $V_0 \approx 32$ cm s^{-1} and decreases for increasing values of V_0 at the axis (Fig. 3). The atomic oxygen and ozone densities decrease slowly with temperature (Fig. 4). The last three results show an excellent agreement with those results obtained in Ref. [2].

Finally, the existence of an optimal distance between electrodes for a given temperature, in dependence of the average flow velocity V_0, is found (Fig. 5). This parameter is very important, from the energetic point of view, for the construction of an ozonizer.

APPENDIX

The inequality (15) can be written as

$$\mu_n^{(0)} > \sqrt{2}\sqrt{1 + \sqrt{1 + \frac{\gamma}{D_1}}}. \tag{17}$$

Using the values for $\mathcal{D}_1$ and K_3 reported in [5, Table 1] for the case of $R = 2$ cm, from (17), we find the following values for γ/D_1 and $\mu_n^{(0)}$, summarized in Table I.

The value of the first root $\mu_1^{(0)}$ of the equation $J_0(x) = 0$ is $\mu_1^{(0)} = 2.4048$, then in our

TABLE I. Values of γ/D_1 and the minimum values of $\mu_n^{(0)}$ according with the inequality (17) for pressures $P = 1$ Torr and $P = 5$ Torr respectively. $R = 2$ cm and $T = 300$ K.

P [Torr]	1	5
γ/D_1	0.00718751	0.88833
$\mu_n^{(0)} >$	2.00179	2.17907

case we can approximate the zeros of the hypergeometric function

$$ {}_1F_1\left(\frac{1}{2} - \frac{(\mu_n^{(0)})^2}{4\sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}}, 1; \sqrt{(\mu_n^{(0)})^2 + \frac{\gamma}{D_1}}\right) \tag{18} $$

using a value of $\mu_n^{(0)}$ near to the value of $\mu_1^{(0)}$. To approximate the zeros of the hypergeometric functions, the program *MATHEMATICA* version 2.1 or higher can be very useful.

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