SELF-CONSISTENT KINETIC MODEL FOR A N_2-O_2 DC GLOW DISCHARGE

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Abstract

A detailed kinetic model for a low pressure DC glow discharge in N_2-O_2 mixtures has been carried out. The model solves the Boltzmann equation coupled to a system of steady-state rate balance equations for the vibrational levels $N_2(X\ ^1\Sigma_g^+,v)$ and $O_2(X\ ^3\Sigma_g^-,v')$, the various electronic states of N_2, and the concentrations of the species $NO(X\ ^2\Pi_r)$, $N(^4S)$ and $O(^3P)$. The maintenance electric field is self-consistently determined for each value of the fractional composition of the mixture. The results are compared with published data obtained in a N_2-O_2 discharge. The contribution of the different processes to the total production of NO, N and O are evaluated and compared.

I - INTRODUCTION

Discharges in N_2-O_2 mixtures are widely used in material treatments, such as in the test of coating materials and in surface treatments of polymers. In order to improve the performance of these processes there is a need for a better understanding of the physical and chemical processes that take place in such media. The aim of this work is to give an insight into the complex interplay kinetics presenting a self-consistent and stationary kinetic model based on the coupled solutions to the electron Boltzmann equation and the system of rate balance equations for the different heavy species. This model further determines the maintenance electric field, under steady-state operating conditions, from the ionization-loss balance.

II - THEORY

The electron Boltzmann equation takes into account rotational excitation, the inelastic and superelastic collisions of electrons with $N_2(X\ ^1\Sigma_g^+,v)$ and $O_2(X$

$^3\Sigma_g^-$,v') molecules, and the inelastic collisions for excitation of electronic states of N_2, O_2, N and O. A list of the various inelastic and superelastic processes included has been presented in [1], while the reader should refer to Ref.[2] for details about the collisional data.

The Boltzmann equation is coupled to a system of rate balance equations for the vibrational levels N_2(X, $0 \leq v \leq 45$) and O_2(X, $0 \leq v' \leq 15$), the most important electronic states of N_2(A $^3\Sigma_u^+$, B $^3\Pi_g$, B' $^3\Sigma_u^-$, C $^3\Pi_u$, a' $^1\Sigma_u^-$, a $^1\Pi_g$, w $^1\Delta_u$, a'' $^1\Sigma_g^+$), and the species NO(X $^2\Pi_r$), N(^{4}S) and O(^{3}P). These equations include, besides the electron-vibration (e-V) processes, the vibration-vibration (V-V) and the vibration-translation (V-T) energy exchange processes between equal and different collision partners (N_2-N_2, O_2-O_2, N_2-O_2, N_2-N, N_2-O, O_2-O), dissociation and reassociation mechanisms, vibrational deactivation due to collisions on the wall, and a large number of other processes taking into account the interplay of N_2(X,v), NO, N, O and N_2(A, B, B', C, a', a, w, a''). A list of the main processes involving collisions of vibrationally and electronically excited N_2 molecules with NO, N and O, as well as those among these latter species is shown in Table 1 with the corresponding reference data. The reader should refer to Ref.[1] in what concerns the data for the V-V and V-T processes, electronic and vibrational dissociation, three-body gas-phase reassociation and wall vibrational deactivation, while the main processes involving collisions of electronically excited N_2 molecules are listed, e.g., in Refs.[4,7] along with the pertinent data. The reassociation of N and O atoms on the wall have been assumed as first-order processes, with the corresponding rate frequency related to the probability γ by the expression $\nu = \gamma \langle v \rangle / 2R$, where $\langle v \rangle$ denotes the average velocity of the colliding particle and R is the tube radius. Here, we use $\gamma = 3.2 \times 10^{-6}$ [8] for the N atoms on pyrex glass and $\gamma = 2.1 \times 10^{-3}$ for the case of O atoms, obtained from a best fit to the measured concentrations of O atoms, which is a value close to the recent measurement 2.4×10^{-3} [9].

The Boltzmann equation with the present system of rate balance equations allow us to determine the electron energy distribution function (EEDF), both vibrational distributions, $\delta_v = [N_2(X,v)]/[N_2]$ and $\delta_{v'} = [O_2(X,v')]/[O_2]$, and the concentrations of all other species. In principle, these results may be obtained as a function of the independent parameters ratio of the electric field to the total gas number density, E/N, degree of ionization, n_e/N, fractional composition of N_2 in

$N_2(X, v \geq 13) + O \rightarrow NO + N$	[3]
$NO + N \rightarrow N_2(X, v \simeq 3) + O$	[4]
$N + O_2 \rightarrow NO + O$	[4]
$N_2(A^3\Sigma_u^+) + O \rightarrow NO + N^*$	[5]
$N + O + N_2 \rightarrow NO + N_2$	[4]
$O + NO + N_2 \rightarrow NO_2 + N_2$	[4]
$O + NO + O_2 \rightarrow NO_2 + O_2$	[4]
$N + N_2(A^3\Sigma_u^+) \rightarrow N^* + N_2$	[6]
$N_2(B^3\Pi_g) + O_2 \rightarrow N_2 + O + O$	[4]

Table 1: Main reactions for determination of NO, N and O, excepting those for dissociation and atomic reassociation (see text). N^* denotes an excited state $N(^2D)$ or $N(^2P)$.

the mixture, total gas density, N, gas temperature, T_g, and discharge tube radius, R. Excepting in what concerns the inclusion of the electronic states of N_2, these results have already been reported in a recent paper [1]. Here, we extend our previous work by properly taking into account the self-consistent determination of the reduced maintenance electric field using the requirement that under steady-state conditions the total rate of ionization must compensate exactly for the rate of electron loss by ambipolar diffusion to the wall. Therefore, the continuity equations for electrons and the main positive ions present in the discharge (N_2^+, N_4^+, O^+, O_2^+, NO^+) are coupled to the former system. The total rate of ionization includes both ionization by direct electron impact on N_2, O_2, O and NO, and stepwise ionization from $N_2(A)$ and $N_2(a')$, as well as the following two reactions for associative ionization [10]: $N_2(A)+N_2(a') \rightarrow N_4^+ + e$ (k=6×10^{-12} cm^3s^{-1}); $N_2(a')+N_2(a') \rightarrow N_4^+ + e$ (k=5×10^{-12} cm^3s^{-1}). The continuity equations also include various ion-molecule reactions for conversion of positive ions and the reactions of electron-ion recombination [4]. With the present extension to the model, the new set of independent variables are the pressure, the discharge current, the fractional composition of N_2 and the tube radius. The gas temperature is given in the model as an input pa-

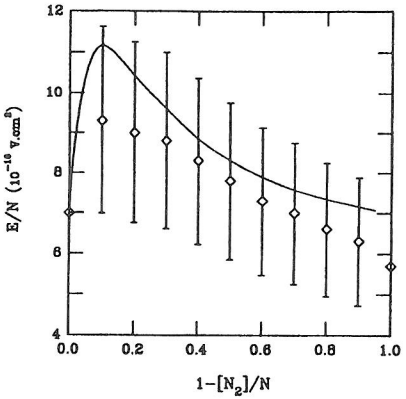

Fig. 1 - Reduced electric field vs. the fractional oxygen concentration for p=2 Torr, I=80 mA and R=0.8 cm. The data points are from Ref.[7].

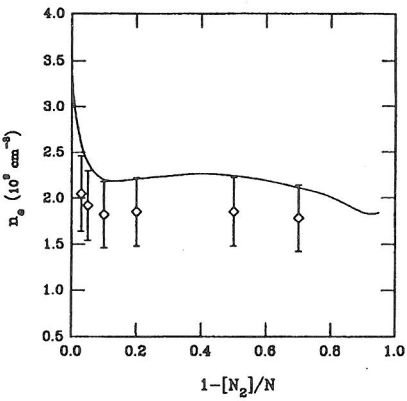

Fig. 2 - As in Fig. 1 but for the electron density.

rameter, with its values taken from experiment [7].

III - RESULTS AND DISCUSSION

Figs. 1 and 2 show the ratio of the electric field to the total gas number density and the electron density, as a function of the relative concentration of oxygen in the mixture $1-[N_2]/N \simeq [O_2]/N+[O]/N$ (the relative concentration of N atoms is always smaller than 0.5%), calculated for p=2 Torr and I=80 mA in a tube radius R=0.8 cm. The results of this model are in fair agreement with the experiment in Ref.[7], in which the electric field is measured by two electrostatic probes and the electron density is determined using a microwave cavity. The reduced electric field increases as the relative concentration of O_2 increases from pure N_2 up to $\simeq$7%, and it decreases for higher concentrations. In the range 0–7% the values of E/N increase in order to compensate the progressive neglecting of associative ionization, since the involved excited states in such mechanism $N_2(A\,^3\Sigma_u^+, a'\,^1\Sigma_u^-)$ are strongly quenched by O_2, O and NO [4]. For larger O_2 percentages the contribution from associative ionization is small and the reduction of E/N is a consequence of the enhancement of the high energy-tail of the EEDF, as the total inelastic electron cross section is considerably smaller in O_2 than in N_2 (in particular the cross section

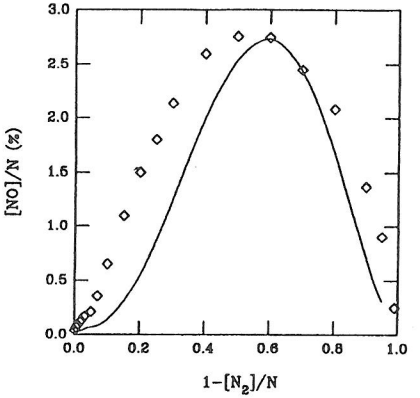

Fig. 3 - As in Fig. 1 but for the relative concentration of NO molecules.

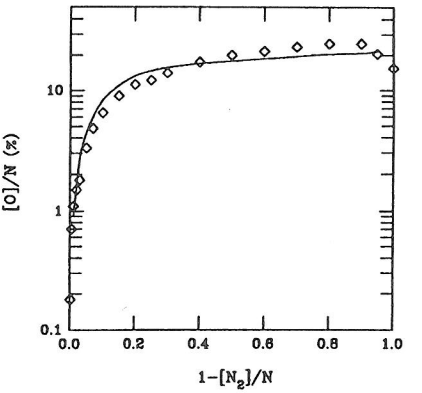

Fig. 4 - As in Fig. 1 but for the relative concentration of O atoms.

for vibration excitation). Further, the electron ionization threshold is smaller in O_2, which also explains the reduction of E/N due to the increasing contribution of electron ionization of O_2. The rapid increase of E/N in the range 0−7% produces an enhancement of the electron mobility, so that the electron density must decrease in order to keep constant the value of the discharge current (Fig. 2).

Figs. 3 and 4 show the relative concentration of NO($X\ ^2\Pi_r$) molecules and O(^{3}P) atoms, as a function of the relative concentration of oxygen in the mixture for the same conditions as in Figs. 1−2, along with the experimental data taken from Ref.[7]. Fig. 3 shows that the [NO] concentration pass through a maximum for N_2-O_2 mixtures with approximately equal composition of both gases. The present results were obtained by reducing the rate coefficients for the V-T exchanges in N_2-O collisions by a factor of 0.7 relatively to the reference data of Ref.[1]. We note that the most important mechanism for production of NO molecules is the reaction shown in Table 1 involving the collisions of O atoms with vibrationally excited N_2(X,v) molecules in levels just above v≥13, and the latter are very sensitive to the magnitude of the rate coefficients for the V-T(N_2-O) exchanges. Other mechanisms for creation of NO molecules may become important only near the limits corresponding either to pure N_2 or pure O_2, but they never exceed 20% of the total rate. The destruction of NO molecules mainly occurs via reaction NO+N

$\rightarrow N_2(X,v\simeq 3)+O$. In what concerns the O atoms, they are mainly produced by the above reaction for destruction of NO molecules, in the limit corresponding to the smallest concentrations of O_2, and by electron dissociation of O_2 for other concentrations. The quenching of $N_2(B\ ^3\Pi_g)$ molecules by O_2 plays as well a non-negligible role in the creation of O atoms. The destruction of O atoms predominantly occurs through reassociation on the wall, for which we have estimated the probability $\gamma=2.1\times10^{-3}$ from a best fit to the experiment.

Finally, we note that the probability γ for reassociation of O atoms and the above mentionated rate coefficients for the V-T(N_2-O) exchanges are the sole fitted parameters in this work. The global agreement achieved with experiment is very satisfactory and it still includes the comparison of the fractional concentration of $N(^4S)$ atoms, the vibrational temperature of $N_2(X,v)$ molecules, and the relative variations of the population in the $N_2(C\ ^3\Pi_u)$ state and of the $NO(\gamma)$ bands.

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