Surface and volume kinetics in a N_2/O_2 low pressure glow discharge

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Abstract

An experimental and theoretical study of the kinetics leading to the production of N, O atoms and NO molecules in a low pressure N_2/O_2 flowing d.c. glow discharge is presented. It is shown that these species are strongly coupled by chemical reactions and that the wall losses of N and O atoms play an important role in controlling the populations of these species.

1 Introduction

A study has been performed to investigate the kinetics of production of N and O atoms and NO molecules in DC N_2/O_2 flowing glow discharge at pressure $p = 2$ Torr for discharge currents $I = 15, 30, 80$ mA. Measurements of the plasma parameters, reduced electric field E/N, electronic density n_e, as well as of the gas temperature T_g, the vibrational temperature T_v of N_2 molecules and the concentration of N and O atoms and NO molecules have been carried out in the whole range of oxygen percentages ($\delta =$ 0 - 100 %) [1]. This set of measurements is compared to the results of a one dimensional self consistent model [2].

This model includes the calculation of electron energy distribution functions and electron rate coefficients coupled with detailed vibrational kinetics of N_2 molecules, chemical kinetics taking into account a large set of neutral, excited and charged species, interaction of N and O atoms at the discharge tube wall and the thermal balance of the discharge. The results of this model are compared with the measurements of the electronic density, the gas temperature, the reduced electric field, the vibrational N_2 temperature and the concentration of O , N atoms, NO molecules, $N_2(C)$, $N_2^+(B)$ and $NO(\gamma)$ excited states.

The interaction of N and O atoms at the pyrex tube wall is investigated in this work. The values of the wall loss probabilities γ_O and γ_N of O and N atoms, respectively, are determined in the whole range of N_2/O_2 mixture.

A kinetic model describing the interaction of the gas phase O and N atoms with the surface of the discharge tube is presented.

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This model takes into account the processes of physical adsorption and desorption of O and N atoms, the reactions of chemical adsorption at active vacant sites and the interactions between chemically adsorbed N_S and O_S atoms with both gas phase and physically adsorbed N_F and O_F atoms leading to the formation of N_2, O_2 and NO molecules.

The variations of γ_O and γ_N with N_2/O_2 gas mixture and with the wall temperature are compared with the results of this model.

2 Experimental

The experimental apparatus is shown in Fig. 1. Details are given in ref. [1].

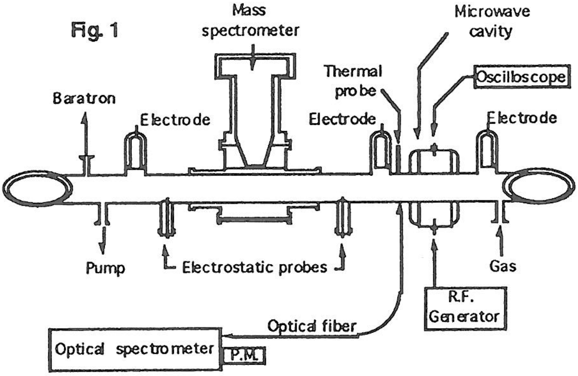

Figure 1: Experimental device

The electron density is determined using a microwave cavity, the maintaining electric field is measured by two electrostatic probes. The gas temperature is deduced from the rotational distribution of $N_2(C \rightarrow B)$ 337 nm band for $0 \leq \delta \leq 95\%$ and $O_2(b \rightarrow X)$ 760 nm band for $90 \leq \delta \leq 100\%$. The vibrational temperature T_v of $N_2(v \leq 4)$ is deduced from the $N_2(C \rightarrow B)$ emission band.

The concentration of O atoms is measured by actinometry using the oxygen $O(^3P \rightarrow {}^3S)$ 844 nm and the argon $Ar(2p_9 \rightarrow 1s_5)$ 811.5 nm lines. The concentration of NO molecules is measured by mass spectrometry. The concentration of N atoms is deduced from LIF measurements and NO titration.

3 Kinetic model for volume reactions

The eedf is self-consistently determined by solving the steady-state homogeneous Boltzmann equation taking into account electron excitation, dissociation, and ionization from $N_2, O_2(X, v = 0)$, as well as inelastic and superelastic e-V processes with $N_2(X, v > 0)$. The eedf so obtained is further used to calculate ionization and excitation rates from NO, N, O.

The vibrational kinetics of N_2 is described in detail including $e-V$, $V-V$ and $V-T$ processes, and the de-excitation of $N_2(v)$ at the wall. The model further includes a large number of physical-chemical reactions which determine the concentrations of the species O, N, NO, N_2O, O_3, N_2^+, N_4^+, O^+, O_2^+, NO^+ and O^-, as well as the populations in the excited states $N_2(A, B, a', a, C, a'')$, $O_2(a, b)$, $N(^2D,^2P)$, and $O(^1D,^1S)$. Dissociative recombination of N_2^+, O_2^+, NO^+ and N_4^+ ions, and wall de-activation of the species $N_2(v)$, $N_2(A, a')$, $O_2(a, b)$, $N(^2D,^2P)$ and $O(^1D,^1S)$ were taken into account.

The gas temperature T_g is derived from the analysis of the gas thermal balance. The main sources of gas heating are $V-V$ and $V-T$ relaxation of $N_2(X)$ molecules, deactivation of excited states (N_2, O_2, N and O) in collisions with heavy particles, exothermic chemical reactions and electronic collisions. Thermal conduction to the wall is the main gas cooling mechanism.

4 Results and discussion

The electron density increases from 5.10^9 cm^{-3} up to 2.10^{10} cm^{-3} when the discharge current is varied from 15 to 80 mA and decreases slowly when δ increases. The gas temperature decreases from 540 to 430 K for I = 15 mA, from 600 to 460 K for I = 30 mA and from 840 to 630 for I = 80 mA with increasing δ. The main mechanism for gas heating was found to be the reaction:

$$N + NO \rightarrow N_2(v = 3 - 4) + O$$

An increase in T_g for $0 < \delta \leq 0.1$ is observed due to an increase in the power deposited into the plasma caused by an increase in the electric field E. The variations of the reduced electric field E/N_g are reported in Fig. 2.

The reduced electric field exhibits a maximum for δ values in the range 0.05 - 0.1 . This is due to the fact that associative ionization, which is very important in pure N_2 or at extremely low O_2 percentages, rapidly decreases with increasing δ since the involved excited states $N_2(v \geq 12)$ and $N_2(a')$ are destroyed by O_2, O and NO. Hence, E/N_g must increase to sustain the discharge. For $\delta > 0.1$, E/N_g decreases due to increasing contribution of electronic ionization of O, O_2 and NO which have lower ionization thresholds than N_2.

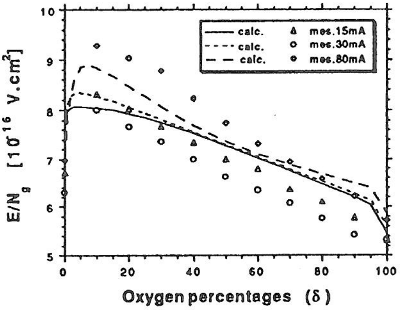

Figure 2: Reduced electric field E/N versus δ

Experimental and calculated values of T_v are represented in Fig. 3. The concentrations of N atoms are reported in Fig. 4. The increase of $[N]$ for small δ values is mainly due to the increase of direct electronic dissociation of N_2 when E/N_g increases. The decrease of $[N]$ for larger δ mainly results from destruction of N by reassociation at the wall and reactions with NO and O_2.

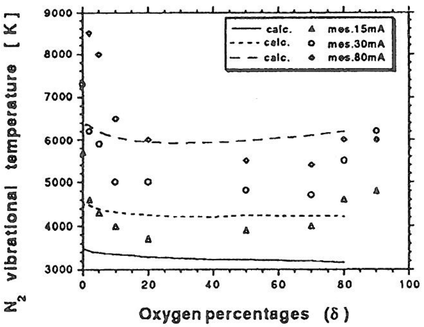

Figure 3: Vibrational temperature versus δ

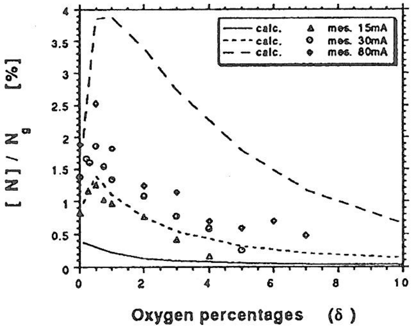

Figure 4: Nitrogen concentration versus δ

Figures 5 and 6 show the relative concentrations of O and NO, respectively, vs. the percentage O_2 concentration in the mixture, δ, for different discharge currents.

The dots are experimental data [1] while the curves represent a fit of the model predictions to experiment obtained by adjusting the probabilities γ_N and γ_O using the kinetic model of [2] and the surface reaction model given below. The fitting to the NO concentration measurements by adjusting γ_N could be achieved because our kinetic model reveals that the NO and N concentrations are strongly correlated [2] and interactions with the wall are an important loss mechanism for N atoms. It was found that the values of γ_N so derived are singly dependent on the ratio $X = [O]/[N]$ for a given current as shown in Fig.7. On the contrary, the probability γ_O as derived from the fit to the [O] measurements is independent of X over the range $5 \leq X \leq 5.10^3$ (corresponding to δ=0.1-0.9) but, as shown in Fig.8, it explicitly depends on the wall temperature in this range of δ values. For $\delta \geq 0.9$, γ_O was found to increase by a factor of 2-5 as $\delta \to 1$, in agreement with the observations of [3].

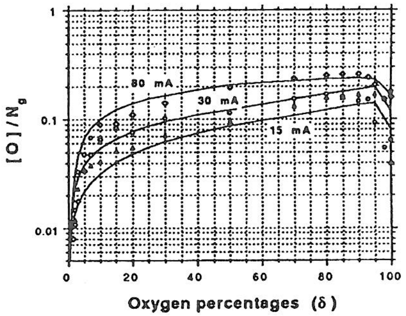

Figure 5: Oxygen concentration versus δ

5 Kinetic model for surface reactions

This model takes into account: i) physical adsorption and desorption of N and O atoms; ii) chemical adsorption of both types of atoms at vacant active sites on the surface; and

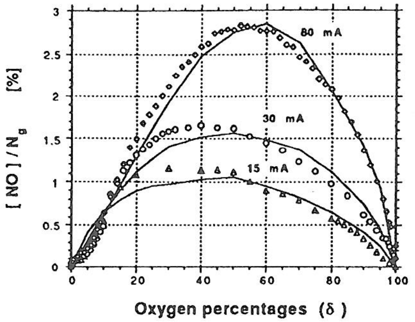

Figure 6: Nitrous oxide concentration versus δ

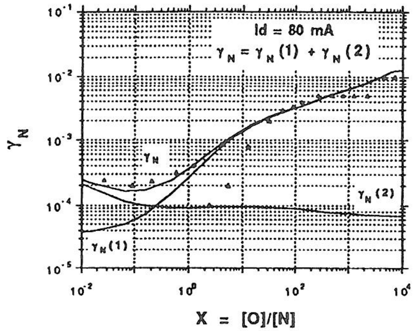

Figure 7: Probability γ_N versus δ

iii) the reactions of chemisorbed atoms, N_S and O_S, both with gas phase N and O atoms and with physisorbed atoms, N_F and O_F, leading to the formation of gas phase O_2, N_2, and NO molecules.

Reversibly adsorbed (physisorbed) atoms either are desorbed from the surface or diffuse to the nearest chemisorption site. Some of these diffusing atoms will therefore be able to react either with vacant active sites, S_v, or with chemisorbed atoms, N_S, O_S. The main reactions under our experimental conditions [2] are the following:

$$N_F + S_v \rightarrow N_S + F_v \ , \qquad (1)$$

$$N_F + N_S \rightarrow N_2 + F_v + S_v \ , \qquad (2)$$

$$O_F + S_v \rightarrow O_S + F_v \ , \qquad (3)$$

$$O_F + O_S \rightarrow O_2 + F_v + S_v \ , \qquad (4)$$

$$N_F + O_S \rightarrow NO + F_v + S_v \ , \qquad (5)$$

$$O_F + N_S \rightarrow NO + F_v + S_v \ , \qquad (6)$$

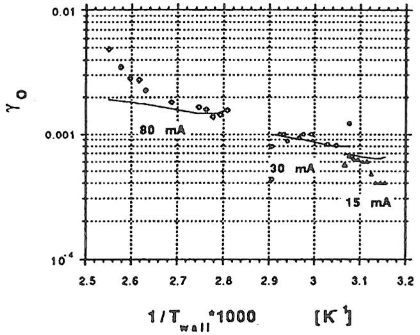

Figure 8: Probability γ_O versus 1/T$_{wall}$

Herein, F_v is the surface density of vacant physisorption sites for N and O atoms. From the master kinetic equations for processes (1)-(6) and for physisorption one readily obtains that the probabilities for wall losses of N and O atoms are in the present case given by:

$$\gamma_N \simeq \frac{P_1 + P_2\alpha_N + P_5\alpha_O}{1 + \alpha_N + \alpha_O} \qquad \gamma_O \simeq \frac{P_3 + P_4\alpha_O + P_6\alpha_N}{1 + \alpha_N + \alpha_O} \qquad (7)$$

where $\alpha_N = P_1/(P_2 + P_6X)$, $\alpha_O = P_3X/(P_5 + P_4X)$, $X = [O]/[N]$, and P_i $(i = 1 - 6)$ are the probabilities of processes (1)-(6), which are given by:

$$P_i = P_M exp(-\frac{E_i}{T_w}) \ , \tag{8}$$

E_i denoting the corresponding activation energies (in Kelvin) and T_w the wall temperature. P_M (with M=N, for i=1;2;5, and M=O, for i=3; 4; 6) are the probabilities for physisorbed atoms of reaching active sites by surface diffusion:

$$P_M \simeq \frac{K_M exp(\frac{E_M}{T_w})}{1 + K_M exp(\frac{E_M}{T_w})} \ , \tag{9}$$

where E_M are the differences in the activation energies for physical desorption and surface diffusion and K_M are constants proportional to the active sites surface density.

Using the above surface reaction model it is possible to adjust the values of E_i, E_M, and K_M so as to fit the data points shown in Figs. 7, 8. We have found however that two independent systems of active sites need to be assumed in order to achieve such a fitting. The best fitting (full curves in Figs. 7, 8) was obtained with the following data, in Kelvin (values in brackets are for the second system): E_N=3,100; E_O=4,300; $K_N \simeq K_O$=8.10^{-6} (10^{-4}); E_1=0 (900); E_2=2,800 (2,700); E_3=0 (0); E_4=2,300 (2,700); E_5=200 (3,200); E_6=6,500 (6,500).

The present model further predicts a decrease in γ_N when a small percentage of O_2 ($\delta \leq 0.05$) is admixed to a N_2 discharge, in agreement with observations.

6 Conclusion

We have presented a detailed analysis of kinetic processes in a low pressure, flowing glow discharge in which the mutual influence of electron, vibrational and chemical kinetics has been consistently taken into account. The comparison between calculated and experimental data leads to the conclusion that the NO, N and O populations are strongly coupled by the reactions

$$N_2(v > 12) + O \rightarrow NO + N$$
$$N + NO \rightarrow N_2(v \sim 3-4) + O$$
$$N + O_2 \rightarrow N + NO$$

and that wall losses play an important role in controlling the population of these species. A kinetic model for wall interaction of gas phase and adsorbed N and O atoms was developed in order to interpret the variation of γ_O and γ_N with the gas composition and the wall temperature.

References

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[2] Gordiets B. *et al., to be published in IEEE Transactions on Plasma Science, Special Issue on the Modeling of Collisional Low Temperature Plasmas*, (1995).

[3] A.R. de Souza *et al., J.Phys.D; Appl.Phys.* 26, 2164-67 (1993).