

MODELLING STUDY OF NO₂ CONVERSION IN N₂/O₂/H₂O/CO₂ MIXTURES

ESTUDIO DE MODELADO DE LA CONVERSIÓN DE NO₂ EN MEZCLAS DE N₂/O₂/H₂O/CO₂

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The main objective of this study is to understand the time evolution of the nitrogen dioxide specie in N₂/O₂/H₂O/CO₂ mixture gas induced by negative corona discharge at atmospheric pressure. The fundamental chemistry governing NO₂ evolution developed in this paper is based on a full set of processes regrouped in one hundred selected chemical reactions involving twenty molecular, excited, atomic, and charged species. The density was calculated using the continuity equation without the diffusion and convective terms. In literature it has generally been emphasized that certain radicals N, O, and O₃ influence the NO₂ conversion. In this study, we complete them by analysing others species such as negative ions and radicals. The results show that the environmental condition rate of NO₂ is well affected by the increase of reduced electric field and concentration.

El objetivo principal de este estudio es comprender la evolución del NO₂ en la mezcla gaseosa N₂/O₂/H₂O/CO₂, inducida por una descarga de corona negativa a presión atmosférica. Los fundamentos químicos presentados, que permiten controlar la evolución del NO₂, se basan en un conjunto completo de procesos reagrupados a partir de una selección de 100 reacciones químicas que involucran 20 especies. Se utilizó la ecuación de la continuidad para determinar la densidad excluyendo los términos de difusión y convección. En la literatura se enfatiza que la conversión del NO₂ está influenciada por la presencia de radicales de N, O y O₃. En este trabajo se abre el estudio, además, a la influencia de iones negativos sobre la conversión del NO₂. Los resultados alcanzados permiten relacionar el incremento de la intensidad del campo eléctrico reducido y las concentraciones de las especies con la velocidad de conversión del NO₂ en condiciones ambientales.

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I. INTRODUCTION

It is well known that gas discharge plasmas are able to initiate chemical reactions in normally inert gas mixtures [1]. These effects can also have a direct impact on the targeted applications such as electron beam processes which were particularly studied for treatment of gaseous effluents polluted by nitrogen oxides (NO_x) and/or sulfur (SO_x) [2–4], ozone production [5–7], medical applications [8–10] and surface treatment [11–13].

The chemical reactivity of the neutral gas mixture enables transformation of the toxic molecule into harmless particles (such as N₂, O or N) or to create acids (such as the nitric acid) inside the plasma. These acids can be transformed into salt (by addition of a base) [14–16].

So, the emission of nitrogen oxides remains one of the major environmental concerns when designing and optimizing combustion systems [17–19]. Gas discharge plasmas and their applications in various domains (physics, chemistry, biology, etc) are being widely studied [20–24]. They can be used for reforming the poisonous pollutants, such as NO_x, SO_x, COX, etc. These studies are based on the numerical equations for the reduction of NO_x gases in reactors. Discharges in N₂/O₂ mixtures can differ considerably from discharges in pure N₂ or O₂ in a number of characteristics (principally, in chemical and ionic composition). Theoretical modeling of kinetic processes

in N₂/O₂ discharges has been developed in several works [25–29]. In the present study, we simulate for various values of reduced electric field (100 Td, 200 Td), the time evolution of twenty chemical species (electrons e, molecules N₂, O₂, H₂O, CO₂, OH, O₃, atoms N, O, H, nitric oxides NO, NO₂, NO₃, N₂O₅, negative ions (O⁻, O₂⁻, O₃⁻, NO₂⁻) and metastables species N(²D), O(¹D), in the mixture (N₂: 76 %, O₂: 8 %, H₂O: 6 % and CO₂: 10 %). These different species react following 150 selected chemical reactions. This simulation must consider various effects induced by the passage of a corona discharge in a mixed gas. For the sake of simplification, we assume that the gas has no convective movement gradients and the pressure remains constant.

II. MATHEMATICAL MODEL

The basic formulas used in the present work consists of a system of equations that takes into account the variation of the density and the chemical kinetics of the environment. We developed a zero dimensional model for solving the transport equations for all species present in the mixture. So, in this model we ignore the spatial variation and we take only the temporal variation. Therefore, this model is designed to follow the time evolution of the species densities by a system of

ordinary differential equations of the following form:

$$\frac{dN_i}{dt} = \sum_{j=1}^{j_{max}} R_{ij}, \quad R_{ij} = G_{ij} - L_{ij}, \quad \text{where } j = 1, \dots, j_{max} \quad (1)$$

where: N_i represent the species densities, $i = 1$ up to 20 considered in the plasma and R_{ij} the source term depending on the reaction coefficients and corresponding to the contributions from different processes. G_{ij} and L_{ij} represent respectively the gain and loss of species i due to the chemical reactions $j = 1$ up to $j_{max} = 100$. The solution of such a system requires the knowledge of the initial concentrations. The total density N of the gas is given by the ideal gas law:

$$P = Nk_bT. \quad (2)$$

Where P represents the pressure, k_b Boltzmann constant and T the absolute temperature. The reactivity of the gas is taken into account in the source term R_{ij} of the density conservation (1).

$$G_{ij} = \sum_{\mu} K_{\mu}(T)(n_i n_j)_{\mu}, \quad L_{ij} = \sum_{\nu} K_{\nu}(T)(n_i n_j)_{\nu}. \quad (3)$$

$K_{\mu}(T)$ and $K_{\nu}(T)$ are the coefficients of the chemical reaction number μ or ν and $(n_i n_j)$ is the product of densities of species i and j interacting in response to the reaction μ or ν . These coefficients satisfy Arrhenius formula:

$$K_{\mu}(T) = A \exp\left(-\frac{\theta_{\mu}}{T}\right), \quad K_{\nu}(T) = B \exp\left(-\frac{\theta_{\nu}}{T}\right). \quad (4)$$

Where A and B are the constants factor and θ_{μ} and θ_{ν} are the activation energy of the reaction and T the absolute temperature of the species (Table).

III. RESULTS AND DISCUSSIONS

In Fig. 1, we have shown the time evolution of NO_2 density at numerous values of reduced electrical fields: 100, 120, 140, 160, 180 and 200 Td. We observe that for low values, the density does not vary significantly, but, when the field becomes strong the difference in density becomes important. This clearly shows the fundamental role played by the reduced electric field in the evolution of nitrogen dioxide.

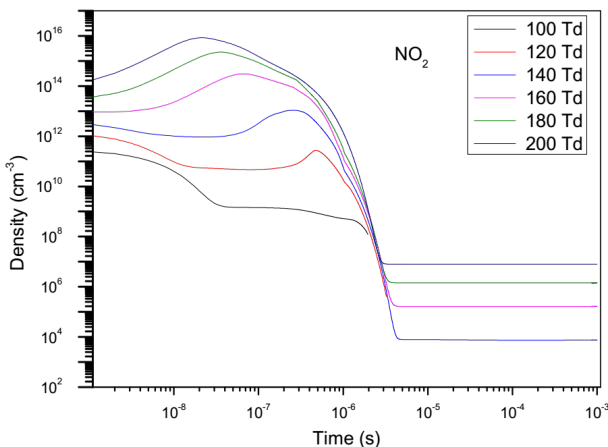


Figure 1. Time evolution of NO_2 density under various values of reduced electric fields: 100, 120, 140, 160, 180 and 200 Td.

In Figs. 2 and 3 we have shown the time evolution of rate coefficient of two reactions that participated in the NO_2 destruction. We note firstly that the effectiveness of these reactions is higher at the beginning than at the end. Secondly, plus the value of the reduced electric field is more important reaction is effective. For example, at 100 Td the rate coefficient does not vary significantly, but at 200 Td we have a significant reduction. We notice to all of these curves that the reactions become less effective after $t = 5 \times 10^{-4}$ s.

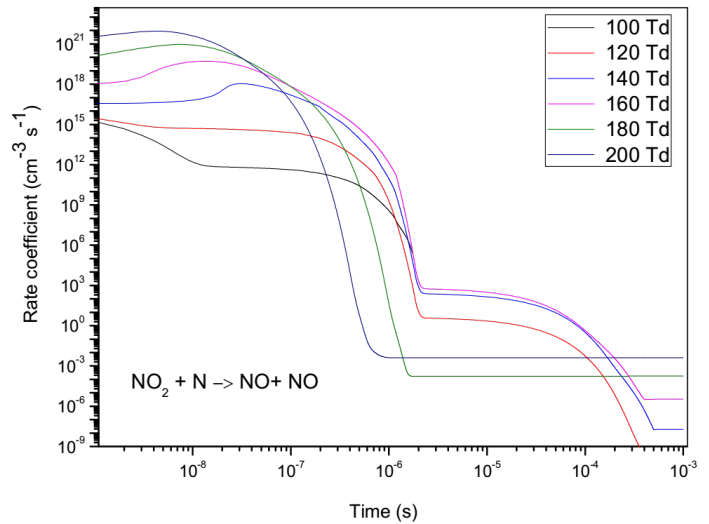


Figure 2. Time evolution of rate coefficient of reaction: $\text{NO}_2 + \text{N} \rightarrow \text{NO} + \text{NO}$ for various values of reduced electric fields: 100, 120, 140, 160, 180, and 200 Td.

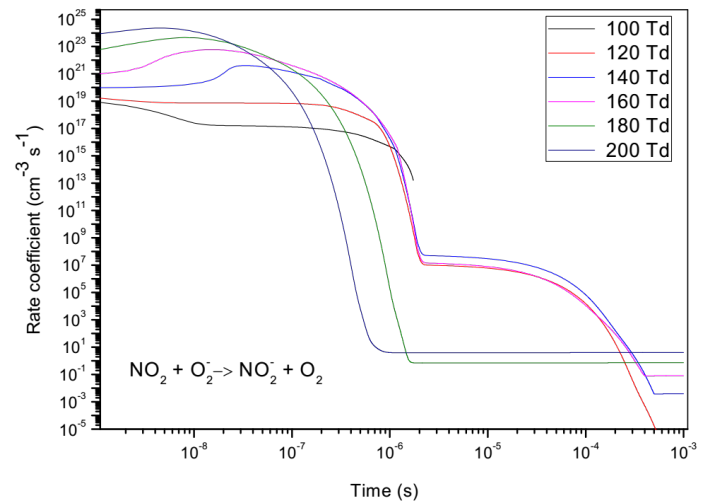


Figure 3. Time evolution of rate coefficient of reaction: $\text{NO}_2 + \text{O}_2^- \rightarrow \text{NO}_2^- + \text{O}_2$ for various values of reduced electric fields: 100, 120, 140, 160, 180, and 200 Td.

Figs. 4 and 5 show the time evolution of NO_2 creation in the same condition as above. Firstly, it is noted that the behavior is the same for all values of the reduced electric field. In the beginning, $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ is dominant, then $\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$, implying a rapid increase of density number.

Fig. 6 shows the influence of the reduced electric field on the evolution of the rate coefficient which participated on nitrogen dioxide density evolution NO_2 . We notice clearly on this figure that the influence is always important at higher values (140, 160, 180 and 200 Td).

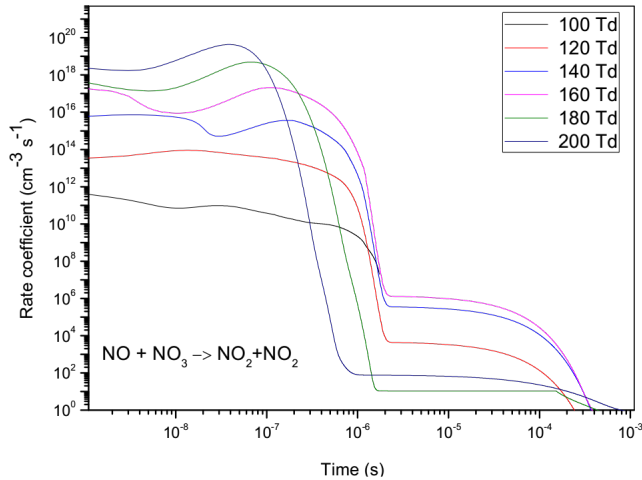


Figure 4. Time evolution of rate coefficient of reaction: $\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$ for various values of reduced electric fields: 100, 120, 140, 160, 180 and 200 Td.

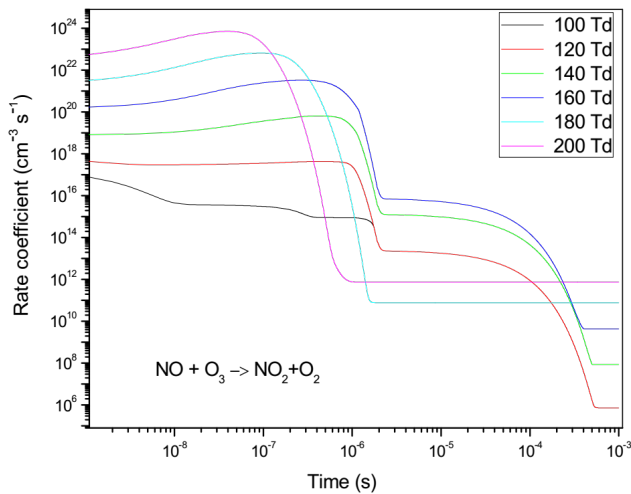


Figure 5. Time evolution of rate coefficient of reaction: $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ for various values of reduced electric fields: 100, 120, 140, 160, 180 and 200 Td.

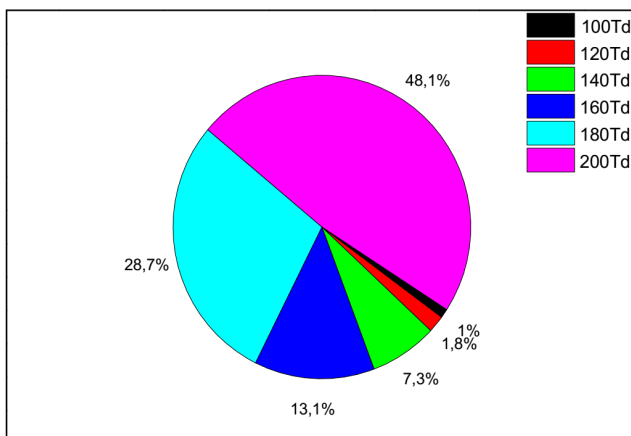


Figure 6. Percentage representation of influence of reduced electric fields: 100, 120, 140, 160, 180 and 200 Td on nitrous oxide NO_2 rate coefficient evolution.

IV. CONCLUSION

In this paper we numerically studied NO_2 conversion in $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2$ mixtures under nonuniform field from the zerodimensional model. As future research prospects, we will study this phenomenon in plasma physics in 2D. The obtained results show the significant conversion of the concentration of NO_2 which is different and depends strongly on the values of reduced electric fields. Finally, these results permit us to determine the vital role played by the reduced electric field on species evolution, and to more deeply perceive various reaction processes affecting the NO_2 magnitude within a gas mixture.

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Table 1. The main plasma reactions to generate the main species to NO creation, reduction and their reaction coefficients. (Reaction coefficients are in units of $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for two body reactions, and $\text{cm}^3 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$ for three body reactions). They are taken from the literature [30–32].

Chemical reactions	Reaction coefficients	Chemical reactions	Reaction coefficients
R1 $e + \text{O}_2 \rightarrow \text{O} + \text{O}(^1\text{D}) + e$	$k_1 = 3.2 \times 10^{-11}$	R11 $\text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$k_{11} = 0.97 \times 10^{-11}$
R2 $e + \text{N}_2 \rightarrow \text{N} + \text{N} + e$	$k_2 = 2.0 \times 10^{-11}$	R12 $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$k_{12} = 0.44 \times 10^{-11}$
R3 $e + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + e$	$k_3 = 3.35 \times 10^{-10}$	R13 $\text{N}_2\text{O}_5 + \text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_3 + \text{O}_2$	$k_{13} = 1.6 \times 10^{-19}$
R4 $e + \text{CO}_2 \rightarrow \text{CO} + \text{O} + e$	$k_4 = 8.7 \times 10^{-11}$	R14 $\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$k_{14} = 2.0 \times 10^{-11}$
R5 $\text{O}(^1\text{D}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	$k_5 = 0.14 \times 10^{-9}$	R15 $\text{NO}_2 + \text{O}_3 \rightarrow \text{O}_2 + \text{NO}_3$	$k_{15} = 1.2 \times 10^{-13}$
R6 $\text{NO} + \text{O} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2$	$k_6 = 2.5 \times 10^{-10}$	R16 $\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$k_{16} = 2.0 \times 10^{-11}$
R7 $\text{NO}_2 + \text{N} \rightarrow \text{NO} + \text{NO}$	$k_7 = 2.3 \times 10^{-12}$	R17 $\text{O}_3 + \text{N}_2 \rightarrow \text{O} + \text{O}_2 + \text{N}_2$	$k_{17} = 5.16 \times 10^{-27}$
R8 $\text{NO}_2 + \text{O}_2^- \rightarrow \text{NO}_2^- + \text{O}_2$	$k_8 = 7.0 \times 10^{-10}$	R18 $\text{NO}_2 + \text{NO}_3 + \text{N}_2 \rightarrow \text{N}_2\text{O}_5 + \text{N}_2$	$k_{18} = 1.01 \times 10^{-27}$
R9 $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$k_9 = 0.18 \times 10^{-11}$	R19 $\text{NO}_2 + \text{NO}_3 + \text{N}_2 \rightarrow \text{N}_2\text{O}_5 + \text{N}_2$	$k_{19} = 1.01 \times 10^{-27}$
R10 $\text{NO} + \text{O} \rightarrow \text{N} + 2\text{O}$	$k_{10} = 0.18 \times 10^{-11}$	R20 $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$	$k_{20} = 1.1 \times 10^{-12}$

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