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Par :

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Sur le thème

Investigation of the Dynamic Behavior of a $N_2/O_2/NO$ Gas Mixture Subjected to a Corona Discharge"

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Dedication

With the help of Allah, who gave me strength and patience to accomplish this modest work, I dedicate it to: My eternal example, my source of happiness, my dear parents: Fatma and Belhadj for their love, generosity, efforts, and sacrifices throughout my life. Their support has been a guiding light throughout my journey. Thanks to you, I have learned the meaning of hard work and responsibility. No dedication could fully express the love, esteem, and respect I have always had for you.

This humble work is the fruit of all the sacrifices you have made for my education and training. I love you deeply and pray to Allah to grant you good health and a long, happy life.

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Summary

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Introduction

This master's research falls within the scope of numerical simulation modeling of a gas mixture composed of N_2, O_2, and NO. This study is particularly significant for advancing the understanding of atmospheric and ionospheric physics, as these gases serve as sources of reactive species (atoms, metastable molecules, ions, etc.). Additionally, the work has practical relevance in plasma chemistry, particularly in industrial processes that play a vital role in treating toxic gas emissions, oxidation processes, and environmental remediation[1-2]

The physico-chemical interest in the non-equilibrium kinetics of plasmas is heightened by the decomposition of species and the need to understand the processes occurring in the atmosphere. This understanding provides valuable analytical insight into the determination of various rate coefficients and transport properties, as a function of the electric field (E), the vibrational temperature of the gas mixture, and the evolution and concentration of different species present in the plasma (electrons, ions, radicals, oxides, etc.). These parameters depend on discharge conditions such as pressure, temperature, electrode spacing, and the applied electric field, as well as the chemical composition of the gas mixtures (i.e., the initial density of species in the mixture). Theoretical modeling of kinetic processes in $N_2 + O_2$+ NO mixtures has been developed in several studies [3-4].

For the creation or decomposition of nitrogen oxides, the use of plasma reactors generated by corona discharges is considered one of the most suitable techniques for treating polluted gases[5-6]

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[1] Abian. M., Alzueta.M. U., Glarborg. P, "Formation of NO from N_2/O_2 mixtures in a flow reactor: toward an accurate prediction of thermal NO". International Journal of Chemical Kinetics, 47(8), 518 532, (2015).

[2] Haefliger.p , Hösl. A an, Franck. C. M. "Experimentally derived rate coefficients for electron ionization, attachment and detachment as well as ion conversion in pure O_2 and N_2–O_2 mixtures", J. Phys. D: Appl. Phys. 51, 355201, (2018).

[3] P Haefliger , A Hösl and C M Franck, Experimentally derived rate coefficients for electron ionization, attachment and detachment as well as ion conversion in pure O_2 and N_2–O_2 mixtures, J. Phys. D: Appl. Phys. 51, 355201, (2018).

[4].Mizuno. A, Shimizu. K, Chakrabarti. A, Desclescu. I, Furuta. S «NOx removal process using pulsed discharge plasma", IEEE Trans. Ind. Applicat., Vol. 31, 957-961,2001.

[5] Ferouani, A.K., Lemerini, M., Merad, L., and Houalef, M., "Numerical modelling point-to-plane of negative corona discharge in N_2 under non-uniform electric field", Plasma Sci. and Technol., vol. 17, no. 6, pp. 469 – 474, (2015).

[6] Yoshida, K., Rajanikanth, B.S., and Okubo, M., "NO_X reduction and desorption studies under electric discharge plasma using a simulated gas mixture: A case study on the effect of corona electrodes", Plasma Technol. Sci. , vol. 11, no. 7, pp. 327–333, (2009).

When the corona discharge passes through our mixture, no fewer than 10 species can be identified, reacting through a large number of chemical processes. However, some species and certain processes have limited impact on the overall kinetics. Therefore, it is possible to select the dominant reactions in order to achieve a reasonably accurate reproduction of the complete model. In our simplified model, we have considered 23 chemical reactions.

The content of the various chapters of this manuscript is presented as follows:

Following the general introduction, in which the objective of this master's thesis is established to study the particle dynamics of a gaseous mixture composed of N_2, O_2, and NO under energy transfer induced by an electrical discharge the manuscript is structured into three main chapters:

- **Chapter One** provides a broad bibliographic overview of plasma physics, with a focus on the point-to-plane corona electric discharge. It also introduces some key physical and chemical properties of the species involved: nitrogen (N_2), oxygen (O_2), and nitric oxide (NO).
- **Chapter Two** presents the development of the mathematical model. It includes the classical fluid dynamics equations, which are based on the Boltzmann equation and its moment equations, coupled with chemical kinetics equations. The resolution method is based on the Flux-Corrected Transport (FCT) technique.
- **Chapter Three** outlines the simulation conditions and presents the results obtained from the model describing the dynamics of the reactive neutral gas in the post-discharge phase. It also includes a detailed analysis of the results, incorporating chemical kinetics.

The manuscript concludes with a general conclusion that validates the proposed model through the consistency of the results. It highlights the significant influence of various physical phenomena; such as reaction processes and transport mechanisms on chemical kinetics.

Chapter I

Bibliographic review

I.1. The main concepts of plasma:

I.1.1.Definition of plasma:

Plasma is often described as the fourth state of matter, distinct from solids, liquids, and gases. It consists of a collection of free-moving charged particles ions and electrons that exhibit collective behaviour due to long-range electromagnetic forces.[7] This ionized state arises when energy, such as heat or electromagnetic radiation, is sufficient to strip electrons from atoms, resulting in a mixture of charged and neutral particles. Unlike neutral gases, plasmas are electrically conductive and responsive to electric and magnetic fields, which leads to complex and dynamic behaviours.[8]

I.1.2.Types of Collisions in Plasma:

Within plasma, particles undergo various collisions that significantly influence its behaviour and characteristics:

I.1.2.1.Elastic Collisions: These occur when colliding particles conserve their total kinetic energy and internal state. Essentially, the particles rebound without any change in their internal energy levels.

I.1.2.2.Inelastic Collisions: In these interactions, the internal energy states of the particles change, leading to a transformation of kinetic energy into internal energy or vice versa. [9]

Inelastic collisions encompass several processes:

- **Excitation**: An electron collides with an atom or molecule, elevating it to a higher energy state without ionizing it.
- **Ionization**: A collision imparts sufficient energy to eject an electron from an atom or molecule, resulting in the formation of an ion.
- **Recombination**: An electron recombines with an ion, releasing energy, often in the form of photons.
- **Detachment:** This occurs when an ion loses its additional electron.[10]

[7] Chapter Three: Physics of Plasma, 6_2019_01_02!10_09_45_PM.pdf, page 1-3

[8] Introduction to Plasma Physics , Published by CERN in the Proceedings of the CAS-CERN Accelerator School: Plasma Wake Acceleration, Geneva, Switzerland, 23–29 November 2014, edited by B. Holzer, CERN-2016-001 (CERN, Geneva, 2016), page 52-53

[9] plasma chemistry, Elementary plasma-chamical reaction, presented by Si Thu Han, date 19-04-2020, page 2

I.1.3.Fundamental Plasma Parameters:

Several key parameters define plasma’s properties:

- **Electron Density (n_e)**: The number of free electrons per unit volume. This parameter influences the plasma's electrical conductivity and over all behaviour.

- **Electron Temperature (T_e):** A measure of the average kinetic energy of electrons. The temperature, which defines the Maxwell-Boltzmann distribution of particles in plasma is represented in electron volts (eV).

We can directly transition from **T** to T_e using the relation:

$$\frac{K_\beta T}{e} = T_e \tag{I.1}$$

Where $K_\beta$the Boltzmann constant, *T* is the temperature in°K, and *e* is the charge.

The temperature represents only two-thirds of the average energy of plasma particles.

- **Debye Length ($\boldsymbol{\lambda}_D$) :** The Debye length defines the distance beyond which the Coulomb electric field of a charged particle is neutralized by a surrounding group of oppositely charged particles in the surrounding volume. It is given by the following equation:

$$\boldsymbol{\lambda}_D = \sqrt{\frac{\varepsilon_0 K_\beta T_e}{n_e e^2}} \tag{I.2}$$

Where ε_0 is the permittivity of free space, K_β is the Boltzmann constant, n_e is the electron density, and T_e is the electron temperature (K).

$\varepsilon_0 = 8.84 \times 10^{-12}\ F.m^{-1}$, K_β = 1.3806×$10^{-23} J.K^{-1}.mol^{-1}$

- **Mean Free Path** This represents the average distance a particle moves before undergoing a collision. It plays a crucial role in plasma behaviour, affecting transport processes such as conductivity and diffusion.

[10] BOUHADBA, A. E. H**.** « Étude de la production de l’ozone et du traitement des molécules NOx dans le mélange N_2/O_2 par décharge électrique pulsée ». Mémoire de Master, 2015, p.2.

- **Degree of Ionization (α)**: The ratio of ionized particles to the total number of particles, indicating how much of the gas is ionized.

The ionization rate is then given by:

$$\propto = \frac{n_e}{n_e + n_n} \quad (I.3)$$

Where n_e is the electron density and n_n is the neutral particle density.

If $\alpha < 10^{-4}$, the gas is considered weakly ionized, where the main interactions occur between electrons and neutral particles.

Conversely, if $\alpha > 10^{-4}$, the gas is strongly ionized, with dominant interactions involving electron-electron or electron-ion collisions.

Understanding these parameters is crucial for analyzing plasma behaviour and optimizing its applications across various fields.

I.1.4. Classification of Plasmas

Plasmas are classified into thermal plasmas and non-thermal plasmas based on the temperature distribution among their particles. The key difference lies in how energy is distributed between electrons, ions, and neutral particles.

I.1.4.1. Thermal Plasmas

In thermal plasmas, all particle species (electrons, ions, and neutrals) are in or near local thermodynamic equilibrium (LTE), meaning they share a similar temperature. This occurs because collisions between particles are frequent, allowing energy to be quickly transferred from hot electrons to heavier ions and neutrals.

Characteristics:

- Uniform temperature distribution: Electrons, ions, and neutrals have almost the same temperature.
- High temperatures, often exceeding 10,000 K, making them extremely energetic.
- High pressures.

I.1.4.2. Non-Thermal Plasmas

In non-thermal plasmas, there is a significant temperature difference between electrons and heavier particles. Electrons reach high temperatures (~10,000 K or 1 eV), while the ions and neutral particles remain near room temperature. This happens because electrons gain energy from the electric field but lose only a small fraction of it during collisions with heavier particles.

- **Characteristics:**
  - Electrons are much hotter than ions and neutrals (i.e., $T_e \gg T_i \approx T_0$)
  - Low pressures.[11-12]

I.2. Corona discharge:

The term "corona discharge" originates from the crown-shaped luminous halo that forms around a sharply curved electrode when the discharge begins.

Corona discharge is a non-homogenous electrical discharge that occurs at atmospheric pressure within an electrode system characterized by strong asymmetry. It is typically generated between an active electrode and a passive (grounded) electrode. The active electrode is usually a pointed tip or a thin wire to which a high voltage is applied, while the passive electrode takes the form of a plate or a grid.

The electric field intensity is highest near the active electrode (anode) and decreases rapidly as one moves toward the planar cathode. In the vicinity of the anode tip, the strong localized electric field enables the generation of electrons with sufficiently high kinetic energy to ionize the surrounding gas. This region becomes the site of electron avalanches, leading to the rapid build-up of space charge, which in turn initiates and sustains the discharge propagation.

The asymmetry between the electrodes results in a non-uniform electric field across the inter-electrode gap. This field in homogeneity plays a crucial role in ionizing the neutral gas species present.[13-14]

[11] Fridman, A. " Plasma Chemistry". Cambridge: Cambridge University Press, 2008, p. 4.
[12] Harbovsky, M." Thermal Plasmas: Properties, Generation, Diagnostics and Applications". Praha : Institute of Plasma Physics AS CR, 2004, p. 4.
[13] BOUAZZA.M.R. "Contribution à l'étude de la génération du vent ionique par une décharge électrique couronne ». Thèse de doctorat, 2019, p. 19.
[14] BOUHADBA. A. E. H**.** « Étude de la production de l'ozone et du traitement des molécules NOx dans le mélange N_2/O_2 par décharge électrique pulsée ». Mémoire de Master, 2015, p. 7

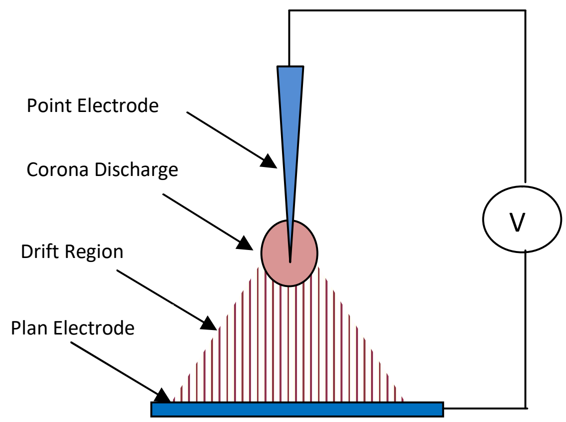


Figure.I.1: Schematic Diagram of a Corona Discharge

Common electrode configurations include point-to-plane, multi-point-to-plane, wire-to-cylinder, blade-to-cylinder, and cylinder-to-cylinder setups, as illustrated in Figure (I.2).

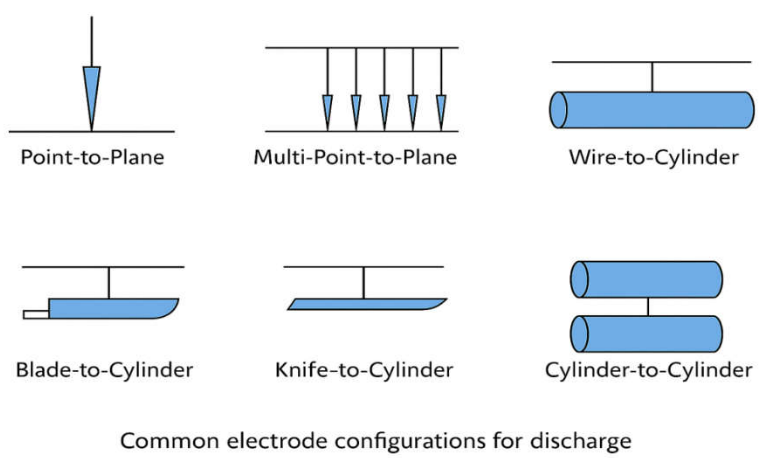


Figure.I.2: Common electrode configuration for corona discharge

Naturally, in the region near the electrode tip, ionization processes dominate over electron attachment. However, as the distance from the point increases, the electric field strength gradually decreases. One of the main advantages of corona discharges is their compatibility with various types of power supplies, along with their ease of generation under stable and reproducible conditions.

The main challenge associated with this type of discharge is the risk of transition to an electric arc.[15] This transition is marked by a significant rise in the current through the discharge, leading to a sharp increase in gas temperature. As a result, the plasma tends to approach thermodynamic equilibrium, and most of the energy delivered to the gas is lost as Joule heating. In most applications involving corona discharges, arc formation is deliberately avoided to prevent damage to the electrodes and to maximize the generation of reactive species relative to the energy input.[16]

I.2.1. Factors Affecting Corona Discharge

Several elements influence both the onset voltage and behaviour of corona discharges. These factors can be broadly grouped into three main categories:

I.2.1.1. Geometric Factors

- ***Radius of Curvature***

As the radius of curvature of the electrode increases, the intensity of the electric field between electrodes decreases. This results in a higher onset voltage for corona formation and a reduction in the discharge current.

- ***Electrode Gap Distance***

We illustrate how the spacing between electrodes affects corona discharge parameters.

According to the figure I.3, a smaller gap leads to a more rapid increase in current with applied voltage. In addition, the corona discharge initiates at lower voltages when the electrodes are closely spaced.

[15] Hassouni. K, Massines. F, et Pouvesle J. M, « Plasmas hors-équilibre à des pressions atmosphériques ». PUSE-MRCT-CNRS, 2004.

[16] BOUAZZA.M. R. « Contribution à l'étude de la génération du vent ionique par une décharge électrique couronne ». Thèse de doctorat, 2019, p. 20.

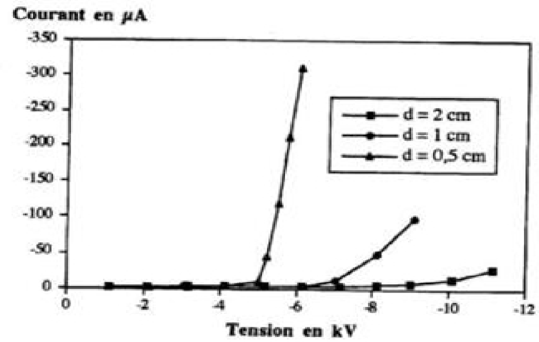


Figure.I.3: Current-voltage characteristics as a function of inter-electrode distance [17]

I.2.1.2. Physical Factors

These include the type of gas, its pressure, humidity level, and temperature, all of which influence corona discharge behaviour.

- ***Type of Gas***

Experimental studies reveal that corona onset voltage varies depending on the gas. Electronegative gases like SF_6 tend to favour electron attachment processes, thereby influencing corona formation.

- ***Gas Pressure***

An increase in gas pressure generally raises the corona inception voltage. This is because higher pressure shortens the mean free path of electrons, limiting their ability to gain sufficient energy between collisions.

- ***Temperature Influence***

At standard pressure, increasing the temperature reduces the dielectric strength of air. This facilitates corona discharge by increasing the mean free path of electrons, allowing them to accelerate more effectively.

- ***Humidity Influence***

Humidity significantly impacts the dielectric strength of air, particularly in non-uniform electric fields. As humidity rises, the corona onset voltage increases. This is because water vapor tends to

[17] M. P. Panaget, Etude en laboratoire des effets physico-chimiques induits par les pertes electriques des lignes de transport a haute tension. Paris 6, 1997.

condense around free electrons, increasing their mass and reducing their mobility and ionization capability. [18]

I.2.1.3. Electrical Factors

The characteristics of corona discharge also vary based on the type of voltage applied whether DC or AC. While similar charge emission modes occur in both cases, there is a key difference: under AC voltage, emissions peak near the sinusoidal voltage crest, whereas with DC voltage, charge emission remains steady over time. [19]

I.2.2. Point-plane corona discharge:

A corona discharge occurs when a high electric field ionizes the air around a conductor, usually in non-uniform fields like those around a sharp point. In a point-plane setup, a sharp point (electrode) makes faces a flat grounded plane.

In the point-plane setup, the electric field becomes highly concentrated near the tip of the point electrode. This intense field is sufficient to initiate ionization in the surrounding air. The ionization zone appears as a bluish glow around the tip. Beyond this ionized region, the electric field weakens, allowing the ionized particles to drift away. The passive electrode, typically the plane, functions as a collector of these charged particles.

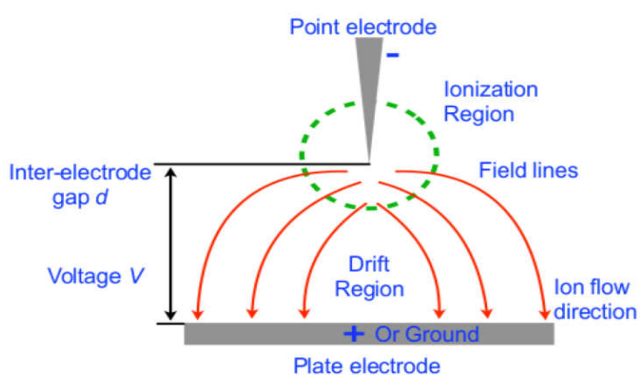


Figure.I.4: Corona discharge in a point-to-plane configuration[20]

[18] Tifaoui, D., & Ladjel, A. « Étude de la décharge couronne en géométrie pointe-plan sous tension continue » (Mémoire de master, Université Mouloud Mammeri de Tizi-Ouzou), 2016.
[19] Sakloul, I., & Kechiti, Z. « Étude de la décharge couronne dans un système d'électrodes en configuration fil-cylindre » . Mémoire de Master, 2022, pp. 15–16.
[20] Okinawa, Institute of Science and Technology (OIST). "Electrocharging Face Masks with Corona Discharge Treatment", 2020.

I.2.2. 1.Theory of Corona Discharge

Hartmann developed a mathematical expression for the electric field E along the axis of symmetry x in relation to the voltage applied to the tip. The equation is given as:

$$E(x) = \frac{V}{(x+\frac{r}{2})ln\left[\frac{2d+r}{r}\right]} \quad \text{(I.4)}$$

- V is the applied voltage,
- d is the distance between electrodes,
- r is the radius of curvature of the point,
- x is the distance from the tip, taken as the origin.

In the wire-to-plane configuration, a different expression is used:

$$E(x) = E_i \frac{r}{x} \quad \text{(I.5)}$$

E_i represent the electric field at the surface of the wire.
Depending on the polarity of the applied voltage, different types of corona discharges can occur namely, positive corona, negative corona, or pulsed corona discharge. These variations will be explored in the following section.

I.2.2. 2.Types of Point-plane corona discharge

There are two main types based on the polarity of the point:

- **Positive Corona:**

A positive corona discharge occurs when the point electrode is at a positive potential and the plane electrode is grounded. In this configuration, within the region of intense electric field surrounding the point, electrons are generated through photo ionization and are accelerated toward the anode (the point). These results in a highly ionized area forming near the tip illustrated as the dotted region in Figure (I.5). The positive ions created in this zone are repelled from the anode due to Coulomb forces and drift outward up to a certain distance (less than a millimeter), beyond which the electric field strength becomes insufficient (<30 kV/cm in atmospheric air) to sustain further ionization. These ions then migrate toward the cathode (the plane). This region, containing only positive ions, is referred to as the "drift region".

In a positive corona discharge, the plasma corona region coincides with the ionization zone unlike in a negative corona discharge.

In the latter, the discharge tends to be uniform and stable, making it ideal for applications that require gentle, well-controlled plasma environments such as surface treatment or low-damage sterilization.[21]

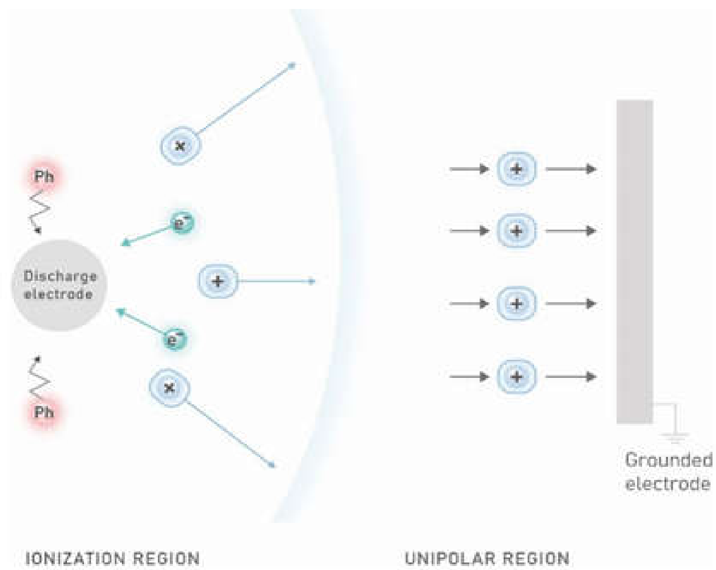


Figure.I.5: Physical description of positive corona discharge

- **Negative Corona:**

When the tip is held at a negative potential, photo-ionization consistently generates electrons, leading to the formation of an ionization region around the tip. As a result, the positively charged ions created in this area are rapidly drawn back toward the cathode, Figure (II.6). Only the negatively charged ions formed through attachment in regions where the electric field is weaker can migrate toward the plane. Additionally, when the high voltage surpasses a certain threshold, an arc discharge can occur.

The current in this discharge is characterized by Trichel pulses, whose frequency depends on the applied voltage. These pulses are periodic and are linked to the weakening of the electric field near the cathode. The presence of negative ions inhibits the formation of new electron avalanches. Once these ions have moved toward the anode, fresh avalanches can develop.

[21] BOUHADBA. E. H. « Étude de la production de l'ozone et du traitement des molécules NOx dans le mélange N_2/O_2 par décharge électrique pulsée ». Mémoire de Master, 2015, page 10-11.

Therefore, the time between two Trichel pulses corresponds to the duration it takes for the negative ions to reach the anode. [22]

This mode tends to produce a denser population of electrons and reactive radicals, resulting more energetic and chemically active plasma.

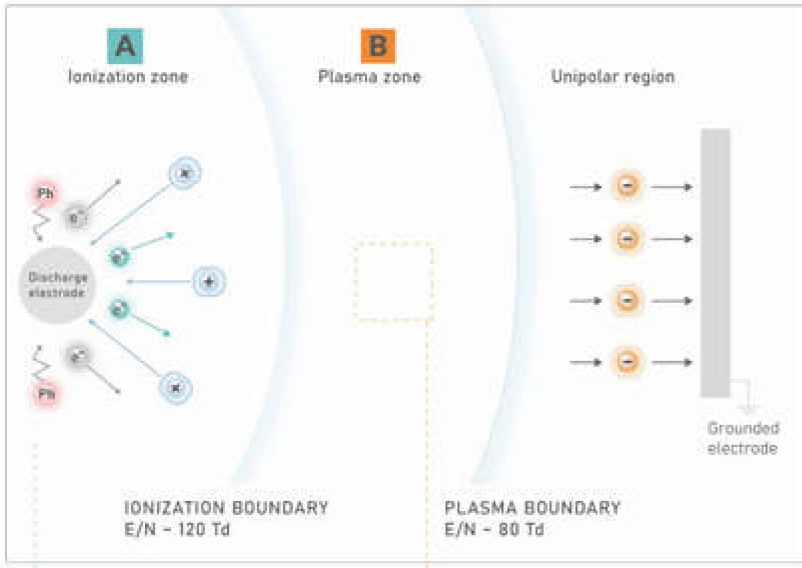


Figure.I.6: Physical description of negative corona discharge

- **Pulsed Corona Discharge**

Depending on the intended application, high voltage is typically applied to the active electrode and can be delivered in pulsed, alternating, or continuous modes, with either positive or negative polarity. Using a pulsed power supply enables the generation of high current peaks over extremely short durations (typically 500 A for 100 ns), allowing the production of high-energy electrons without transitioning to an arc discharge. These electrons are particularly suitable for treating specific pollutants. Operating voltages generally range from a few kilovolts up to around 30 kilovolts, while power levels usually remain below a few kilowatts. Pulsed high voltage is commonly used to achieve efficient ozone generation over a broad area. [23]

[22] BOUHADBA, A. E. H**.** « Étude de la production de l'ozone et du traitement des molécules NOx dans le mélange N_2/O_2 par décharge électrique pulsée ». Mémoire de Master, 2015, page 11-12.

[23] BOUHADBA.A. E. H**,** « Étude de la production de l'ozone et du traitement des molécules NOx dans le mélange N_2/O_2 par décharge électrique pulsée ». Mémoire de Master, 2015,page 12.

I.3. Prosperities of gas $N_2/O_2/NO$

I.3.1. Gas N_2:

In plasma environments, nitrogen molecules N_2 can undergo dissociation into various reactive nitrogen species or be activated into excited states.

The atomic and ionic nitrogen species formed through dissociation and ionization of N_2 in the plasma. They play a critical role in thin film deposition and surface chemical reactions.
These species include atomic nitrogen (N), excited nitrogen molecules (${N_2}^*$), and nitrogen ions (${N_2}^+,\ N^+$).[24]
The nitrogen molecule (N_2) is characterized by a very strong triple bond, making it one of the most stable diatomic molecules. The dissociation energy required to break this bond and separate N_2 into two nitrogen atoms is approximately 9.75 eV [25]. Additionally, the first ionization energy of N_2 the energy needed to remove an electron and form the N_2^+ ion is about 15.58 eV and that of atomic nitrogen is 14.53 eV to get N^+ [26].

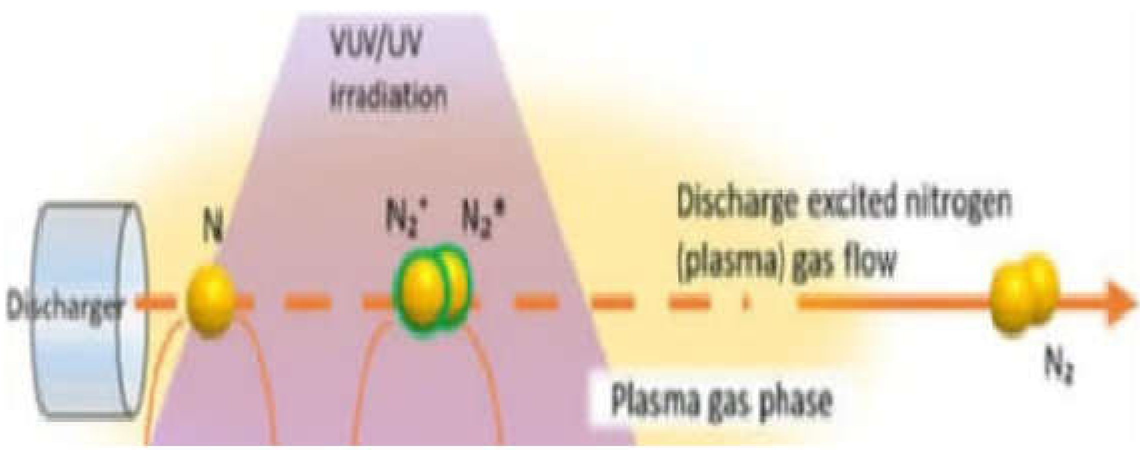


Figure.I.7: The Interaction Process of Discharge-Generated Nitrogen Species in the Plasma Gas Phase

24 Hendrie.J."The journal of chemical properties, Dissociation Energy of N_2". Edited in September, 1954
25 Douglas, A. E. "The near ultraviolet bands of N_2^+ and the dissociation energies of the N_2^+ and N_2 molecules". Canadian Journal of Physics. Edited in 1952.
26 Hutchinson, J. E. (n.d.). Observation 3: "Ionization energies of diatomic molecules. In Concept Development Studies in Chemistry". LibreTexts. Retrieved February 26, 2025

I.3.2. Gas O_2:

Oxygen plasma is a partially ionized gas comprising electrons, ions, and neutral particles. It is created by subjecting a low-pressure gas, typically oxygen, to an electric field or electromagnetic radiation. When oxygen gas undergoes ionization, it transforms into oxygen plasma, characterized by its high reactivity and energy levels. This process causes the gas molecules to dissociate and ionize, forming a complex mixture of reactive species, including ions, free radicals, and excited molecules.[27]

These types of highly reactive species, including O^+, O^-, O_2^-, O, O_3 (ionized ozone), excited O_2, and electrons. [28]

This method is commonly used for surface cleaning and can also be combined with other gases to etch materials like polymers and rubber components.

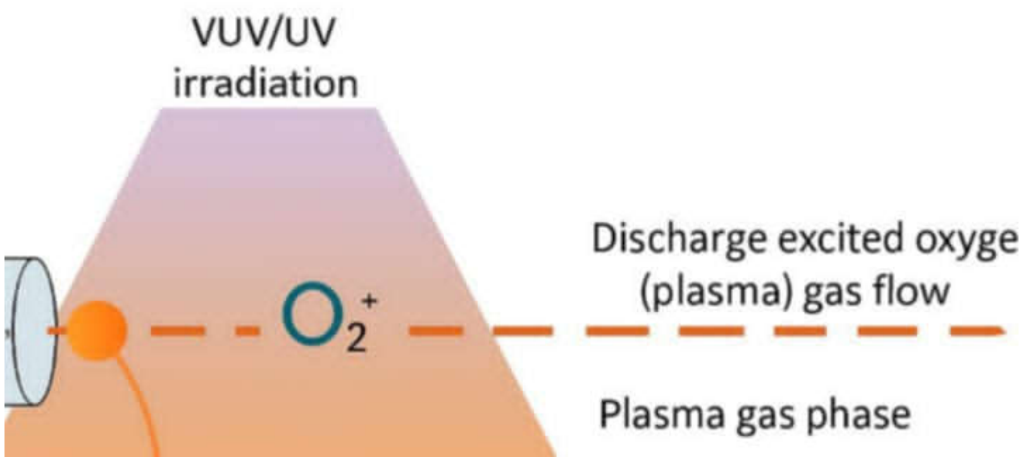


Figure.I.8: The Interaction Process of Discharge-Generated Oxygen Species in the Plasma Gas Phase

[27] Understanding Oxygen Plasma and Its Role in Industrial Processes. (2024, March 27).

[28] Plasol. (n.d.). Plasma Surface Treatment. Consulté le 28 Février 2025.

I.3.3. Gas NO_x

Atmospheric pressure plasma is regarded as an efficient technique for generating nitrogen oxides (NOx). These compounds typically form during combustion, not only from nitrogen-containing substances in the fuel but also primarily through the reaction between atmospheric nitrogen and oxygen at high temperatures within the flame.

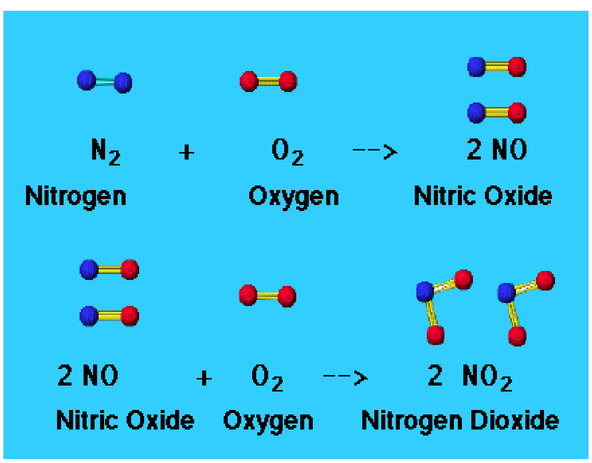
Nitric oxide (NO) is produced when nitrogen gas reacts with oxygen, a process typically initiated by high temperatures or electrical sparks. The reaction can be represented as:

$$N_2 + O_2 \rightarrow 2NO$$

Once formed, nitric oxide readily combines with additional oxygen molecules to generate nitrogen dioxide (NO_2):

$$2NO + O_2 \longrightarrow 2\ NO_2$$

These two nitrogen-based gases NO and NO_2 are collectively referred to as nitrogen oxides, commonly abbreviated as NO_x. [29]



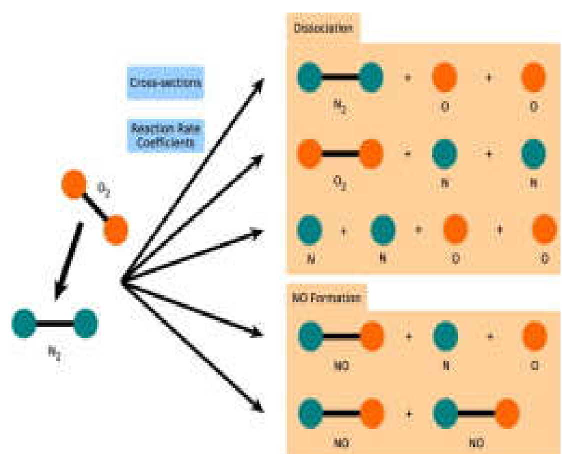


Figure .I.9 [29]- Formation of Nitric Oxide **Figure .I.10**[30]**:**Formation of Nitrogen Dioxide

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[29] LibreTexts Chemistry**.** *(*n.d.). Sources of Nitrogen Oxides. Retrieved February 28, 2025

[30] Zhang, Y, & Wang, Y.” Enhanced electrostatic properties of polypropylene nonwoven fabrics via corona discharge treatment for efficient air filtration”.Edited in 2018.

Chapter II

Mathematical model

of plasma

II.1. Introduction

Discharge plasma modeling is recognized as a crucial tool for the analysis and optimization of plasma reactors. Through numerical simulation, we are able to precisely design these reactors by determining ideal operating conditions, including gas composition, pressure, flow rate, electrode configuration, and temperature. This allows us to assess the impact of each parameter on the reactor's performance and overall efficiency.

In this section, we study the dynamics of particles in a gaseous mixture of $N_2/O_2/NO$ under the influence of energy transfer induced by an electrical discharge [31]. This modeling approach begins with the description of average physical quantities and the formulation of the Boltzmann equation. We then detail the interactions between ionized particles and the gas mixture, which are computed using transport equations for density, momentum, and energy.

Modeling the chemical kinetics in electrical discharges allows for the prediction of species formed during the reaction phase and provides insight into their temporal evolution.

II.2. Distribution Function

II.2.1. The Boltzmann Equation

The Boltzmann equation [32] is a fundamental tool for studying the evolution of the distribution function of particles in a gas. It describes how the distribution function changes in time and space due to particle movement and collisions.

Let $f(\vec{r}, \vec{v}, t)$ be the distribution function of the electrons, which represents the number of particles per unit volume in the phase space (position and velocity). The Boltzmann equation is written as:

$$\frac{df(r,v,t)}{dt} = \left(\frac{\delta f(r,v,t)}{\delta t}\right)_{collisions} \quad \text{(II.1)}$$

[31] Kossyi.I.A, Kostinsky. A. Y,.Matveyev. A. A, and Silakov. V. P, "Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures", Plasma Sources Science and Technology, **1**(3), 207-220 (1992).
[32] Boeuf. J. P, "Numerical model of RF glow discharges", Phy. Rev. A, **36**, 2782-2792 (1987).

$$\frac{df(r,v,t)}{dt} = \frac{\delta f}{\delta t} + \frac{\delta f \delta r}{\delta r \delta t} + \frac{\delta f \delta v}{\delta v \delta t} \quad \text{(II.2)}$$

$$\frac{df(r,v,t)}{dt} = \frac{\delta f}{\delta t} + \vec{v}\,\overrightarrow{\nabla_r}\, f + \frac{\vec{F}}{m}\overrightarrow{\nabla_v}\, f = (\frac{\delta f(r,v,t)}{\delta t})_{collisions} \quad \text{(II.3)}$$

- $\overrightarrow{\nabla_r}$:The gradient in position space *(x, y, z)*
- $\overrightarrow{\nabla_v}$: The gradient in velocity space *(v_x, v_y, v_z)*
- The first term $\frac{\partial f}{\partial t}$ represents the temporal evolution of the distribution function.
- The second term $\vec{v}\,\overrightarrow{\nabla_r}\, f$ represents the influence of diffusion phenomena
- The third term $\frac{\vec{F}}{m}\overrightarrow{\nabla_v}\, f$ corresponds to the force acting on the particles, such as the electric field.
- The right-hand side $(\frac{\partial f}{\partial t})_{coll}$ represents the variation due to collisions between particles.

From this distribution function, it is possible to derive all macroscopic quantities, such as density, average velocity, and mean energy, among others. However, directly solving the Boltzmann equation numerically is currently unfeasible for problems where collision interactions dominate. For instance, the typical frequency of electron-neutral collisions is on the order of $10^{12} s^{-1}$, while neutral-neutral collisions occur at a rate of approximately $10^{10} s^{-1}$.

As a result, modeling efforts naturally turn toward a macroscopic description of particle transport. This involves formulating a Boltzmann equation for each species and extracting its various moments to derive a set of coupled hydrodynamic equations. In gas discharges involving mixtures primarily composed of nitrogen and oxygen such as air the chemical kinetics become particularly rich and intricate. Some advanced models account for as many as 140 chemical species and over 450 reaction pathways.[33]

[33]Bouazza, M. R. « Contribution à l'étude de la génération du vent ionique par une décharge électrique couronne » (Thèse de doctorat, Université Ibn Khaldoun – Tiaret). 2019, page 35

2.2. The relation between the Boltzmann equation and the Poisson Equation:

In transient discharges, the space charges created by ions and electrons are significant enough to distort the electric field. These changes in the electric field influence the evolution of the distribution function, particularly through the term that accounts for the effect of external forces. To accurately model the discharge behaviour, it is therefore essential to solve the Boltzmann equation in conjunction with Poisson's equation, which describes how the electric field varies in response to the space charge distribution.

The Poisson equation is written:

$$\vec{\nabla}\vec{E} = \frac{\sum_i e_i N_i}{\varepsilon} \tag{II.4}$$

The Boltzmann equation, when coupled with Poisson's equation, constitutes a self-consistent electrical model of the discharge. The only required input data are the cross-sections for each type of collision. Solving the Boltzmann equation would provide a complete description of the transport phenomena involved.

To make the Boltzmann equation more tractable, it is common to use averaged quantities that describe the system's state. These macroscopic parameters are defined at each point in space and are linked through what are known as the "moments of the Boltzmann equation." In this context, we focus on the first two moments, which lead to the continuity equation and the momentum transfer equation. [34]

The moments are derived by integrating the Boltzmann equation over velocity space after multiplying it by a test function χ (v⃗)), is:

$$\int\left(\frac{\delta f}{\delta t} + \vec{v}\,\overrightarrow{\nabla_r} f + \frac{\vec{F}}{m}\overrightarrow{\nabla_v} f\right)\chi(v)d^3v = \int\left(\frac{\delta f(r,v,t)}{\delta t}\right)_{coll}\chi(v)d^3v \tag{II.5}$$

Assuming the quantities involved are independent of space and time, equation simplifies to:

$$\frac{\delta}{\delta t}\left(n\langle\chi(v)\rangle\right) + \frac{\delta}{\delta r}\left(n\langle\chi(v)v\rangle\right) - \gamma n\left\langle\frac{\delta}{\delta v}\chi(v)\right\rangle = \int\left(\frac{\delta}{\delta t} f\right)_{coll}\chi(v)d^3v \tag{II.6}$$

[34] Bouhadba, A. E. H. « Étude de la production de l'ozone et du traitement des molécules NOx dans le mélange N2/O2 par décharge électrique pulsée » (Mémoire de magistère, Université des Sciences et de la Technologie d'Oran Mohamed-Boudiaf). 2015, page 40-41

II.2.2. The Fundamental Conservation Equations

II.2.2.1. Continuity Equation

This equation, which represents a zero-order model, is derived by replacing $\chi(\vec{v})$with 1 in equation (II.6), the resulting form is:

$$\frac{\partial N}{\partial t}+\frac{\partial N<v>}{\partial r}=(\frac{\partial N}{\partial t})_{coll} \quad \text{(II.7)}$$

Here, $N(\vec{r}\,,t\,)=\int f(\vec{r}\,,\vec{v}\,,t)\;d\,\vec{v}$:is the particle density.

and $N(\vec{v}\,,)=\int \vec{v}f(\vec{r}\,,\vec{v}\,,t)\;d^3\,\vec{v}$: is the particle flux.

with $\langle\vec{v}\rangle$: representing the average velocity of the particles.[35]

$$(\frac{\partial N}{\partial t})_{coll}=S_e \quad \text{(II.8)}$$

The term $(\frac{\partial N}{\partial t})_{coll}$ accounts for sources and losses of particles due to collision-related creation or destruction processes.

For example, in the case of electrons, the equation is written as:

$$S_e=n_e\big(v_i(\vec{r},t)-v_\alpha(\vec{r},t)\big)-\beta_{e,p}(\vec{r},t)n_e n_p \quad \text{(II.9)}$$

Where:

- v_i is the ionization frequency.
- v_a is the attachment frequency.
- $\beta_{e,p}$ is the electron-ion recombination coefficient (representing losses).

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[35] ANSYS, Inc. ANSYS FLUENT 12.0 Theory Guide. released on January 23, 2009

II.2.2.2. The Momentum Transfer Equation:

When the test function $\chi(\vec{v})$ is taken as $m\vec{v}$, representing momentum, the momentum transfer equation is obtained by integrating the Boltzmann equation over velocity space: [36]

$$\frac{\delta}{\delta t}(nm\vec{v}) + nm\left(\vec{v}.\frac{\delta}{\delta\vec{r}}\right)(\vec{v}) - \vec{v}(\frac{\delta}{\delta\vec{r}}(nm\vec{v}) + \overrightarrow{\nabla_r} \otimes \overleftrightarrow{p} - n\vec{F} = \int\left(\frac{\delta}{\delta t}f\right)_{coll} d^3v \qquad \text{(II.10)}$$

- $\vec{F}$: Represents the external forces acting on the system, such as those due to electric or magnetic fields (if present).
- $\overleftrightarrow{p}$: is the kinetic pressure tensor, which describes the flux of momentum in a reference frame moving with the average velocity of the particles.
- The term on the right-hand side represents the change in momentum due to collisions between particles.

II.2.2.3. The Energy equation

By substituting $\chi(\vec{v}) = \frac{1}{2}\, mv^2$ into equation, we obtain the scalar energy equation**,** which corresponds to the third moment of the Boltzmann equation:

$$\frac{\delta}{\delta t}\left(n\frac{1}{2}mv^2\right) + \frac{\delta}{\delta r}\left(n\,\langle\frac{1}{2}mv^2\rangle\right) - \gamma n\,\langle\frac{\delta}{\delta v}\,\frac{1}{2}mv^2\rangle = \int\left(\frac{\delta}{\delta t}f\right)_{coll}\frac{1}{2}mv^2\,d^3v \qquad \text{(II.11)}$$

$$\Rightarrow \quad \frac{\delta}{\delta t}(nv^2) + \frac{\delta}{\delta r}(n\langle v^2 v\rangle) - 2\frac{\vec{F}}{m}\,\vec{v}n \;= \int\left(\frac{\delta}{\delta t}f\right)_{coll} v^2\,d^3v \qquad \text{(II.12)}$$

With: $\gamma = \frac{F}{m}$

These three moments of the Boltzmann equation form an open system, which on its own is insufficient to fully describe the behaviour of charged particles in an electric discharge.[37]

[36] Inan, U. S., & Gołkowski, M."Principles of Plasma Physics for Engineers and Scientists". Published online by Cambridge University Press: 05 June 2012

[37] Bouazza, M. R**,** «Contribution à l'étude de la génération du vent ionique par une décharge électrique couronne » (Thèse de doctorat, Université Ibn Khaldoun – Tiaret). 2019, page 40 - 41

II.3. Flux-Corrected Transport (FCT) Method:

The Flux-Corrected Transport (FCT) method improves the accuracy of transport simulations by controlling numerical artefacts like spurious oscillations, which often occur in dispersive numerical schemes. The approach involves applying a corrective diffusion that acts only in regions where such oscillations appear. This diffusion is nonlinear because it depends on local values of mass or charge density. Crucially, the method is conservative: any fluid removed from one point is exactly redistributed to other points. This local redistribution preserves the total quantity in the system, ensuring that no artificial gain or loss occurs during the correction process. It consists of two main steps:

II.3.1. The transport step,

In this step (step I), a low-order, highly diffusive scheme is employed to ensure numerical stability and preserve the positivity of the solution. Each trapezoidal surface element formed by connecting adjacent density values with straight-line segments is considered individually. The small arrows at grid points j and $j+1$ represent the characteristic movements that the fluid may undergo at those locations. [38]

The trajectory of a fluid element is followed over a time step. By the end of this interval, the element has undergone both convection and deformation, as depicted in Figure (II.1). As a result, we obtain:

[38] Boris and David L Book, “Flux_Corrected_Transport”, received in November 30, 1973, page 40

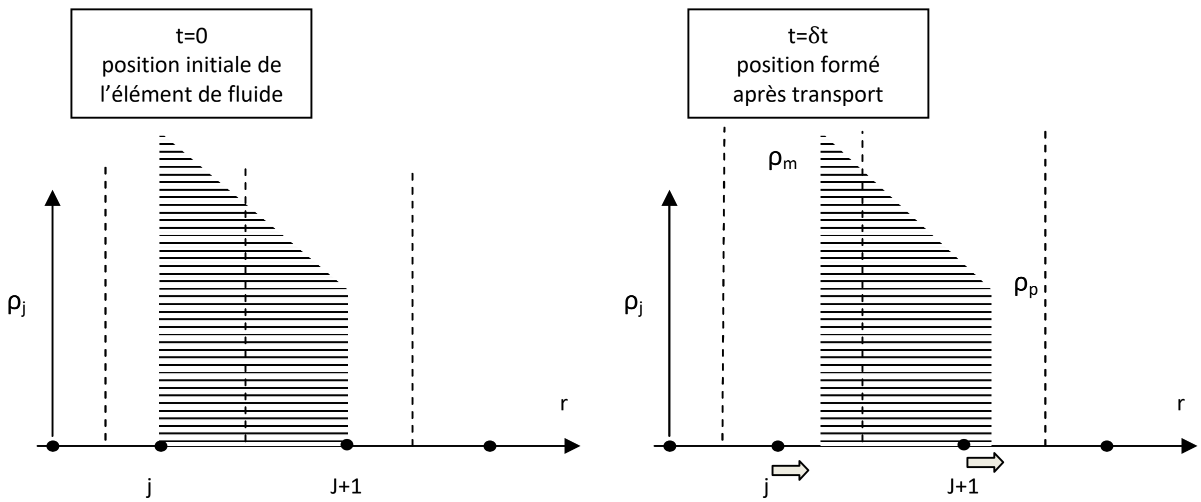

Figure II.1. : The first step of FCT: The transport

II.3.2. The antidiffusion step

The antidiffusion expression is designed to remove the net artificial diffusion introduced in the previous step. As illustrated in Figure (II.2), this antidiffusive term is not necessarily positive. In Step II, a high-order correction is applied with the primary objective of eliminating the numerical errors generated during Step I. However, this correction can inadvertently introduce additional errors at grid points *j* and *j+1*. Therefore, the antidiffusive flux must be carefully limited to recover sharp gradients while avoiding the onset of new instabilities.[39]

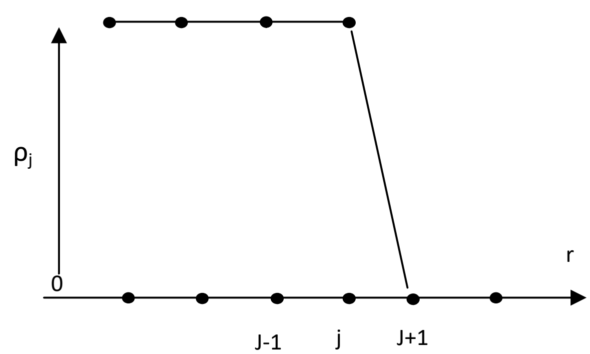

Figure II.2. : The second step of FCT: The antidiffusion

39 Kuzmin.D, Lohner. R,"Flux corrected transport: Principals, Algorithms and Applications" edition Spinger 2004

The SHASTA algorithm (Sharp and Smooth Transport Algorithm) is a specific implementation of the FCT method. It applies these two steps systematically and includes nonlinear flux limiters during the antidiffusion phase to maintain accuracy without compromising stability. In this way, SHASTA brings the general principles of FCT into practical application, especially for one- and two-dimensional problems in computational fluid dynamics and plasma simulations.[40]

II.4. Chemical Kinetic Modeling of Corona Discharge

Electrical discharges occurring in air are characterized by highly complex and rich chemical kinetics. In a comprehensive model developed by Kossyi et al, up to 140 different species and over 450 chemical reactions are described. However, due to the computational burden, implementing such a detailed model in numerical simulations is not feasible. Therefore, identifying a reduced set of dominant reactions becomes essential.

Among the key processes to be included first are electron impact ionization and electron attachment. Ionization is crucial, as it initiates the electron avalanche that leads to the onset of the discharge. Meanwhile, electron attachment reflects the electronegative nature of molecular oxygen in air and facilitates the formation of negative ions. Electron-ion recombination reactions, involving both positive and negative ions, are also typically considered, as they contribute to reducing the overall ion population.

The conversion of atmospheric pollutants in a non-thermal plasma involves a complex interplay of physical and chemical processes. Modeling the chemical kinetics within the discharge helps predict the formation of various species during the reaction phase. The objective is to describe the evolution of neutral, excited, and ionized species over time.

This modeling approach relies on solving both the continuity equation for each species and the energy equation. These correspond to the first and third moments of the Boltzmann equation, respectively.

[40] Boris and David L Book, Flux_Corrected_Transport, received in November 30, 1973, page 40

The continuity equation for a given species k can be expressed as follows:

$$\frac{d[\Upsilon_{\text{P}}]}{dt} = S_{\text{P}} \tag{II.13}$$

Where $[\Upsilon_{\text{P}}]$ represents the density of species k,

$S_{ќ}$:is the source term in the continuity equation, accounting for all the processes that contribute to the creation and loss of species ќ.

These processes include stepwise ionization, Penning ionization, excitation, formation of dimer ions, recombination, charge exchange, neutral kinetics, spontaneous emission, and wall losses due to the diffusion of metastable species.[41]

II.4.1. Chemical Kinetics Model in N_2/O_2 /NO mixtures:

The model considers a wide range of species, including: e^- O, N, NO, O_3, NO_2, NO_3, and N_2O

For each of these species, the change in concentration at any given time is determined by the sum of gains (species produced) and losses (species consumed) resulting from the following chemical reaction: αR + βS $\overset{k}{\rightarrow}$ γP+λT

$$ќ\,[R]^{\alpha}.\,[S]^{\beta} = -\frac{1}{\alpha}\frac{d[R]}{dt} = -\frac{1}{\beta}\frac{d[S]}{dt} = +\frac{1}{\gamma}\frac{d[P]}{dt} = +\frac{1}{\lambda}\frac{d[T]}{dt} \tag{II.14}$$

Where $[R]$ is the concentration of species R, and k is the rate coefficient for the reaction.

These reactions are typically characterized by the rate coefficient ќ, which is defined by the Arrhenius equation:

$$ќ\,(t) = \delta \exp\left(-\frac{Ea}{R\,T}\right) \tag{II.15}$$

- E_{α} : is the Arrhenius activation energy, representing the minimum energy required for molecules to react.
- R : is the ideal gas constant.
- δ is the pre-exponential factor, which accounts for the frequency and orientation of molecular collisions.[42]

[41] Bouhadba, A. E. H. (Mémoire de magistère, Université des Sciences et de la Technologie d'Oran Mohamed-Boudiaf). 2015, page 46

II.4.2. Structure of the relation between physical model and kinetic Model:

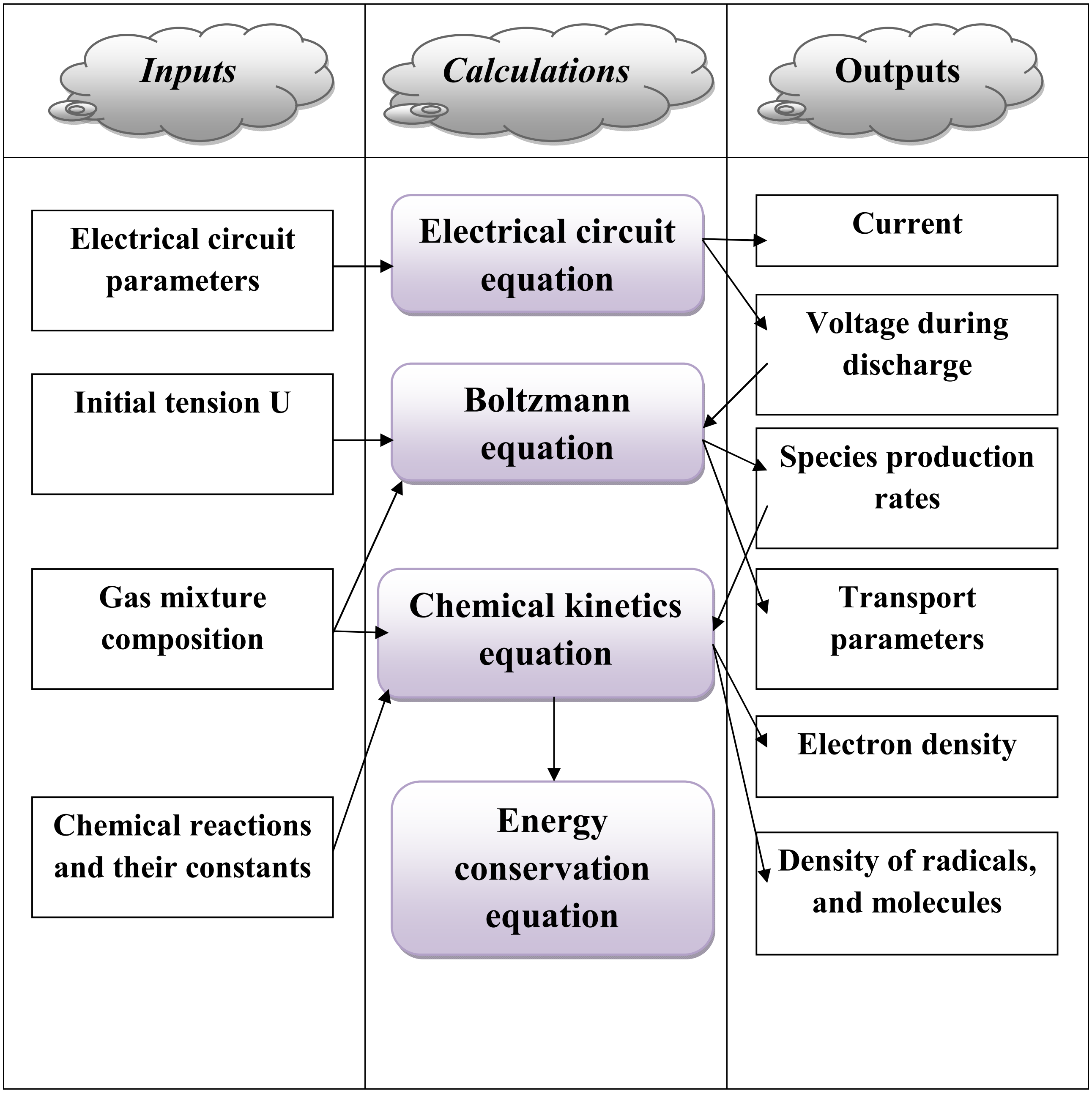

Figure II.3. : Algorithm between physical model and kinetic Model

[42] Michau A, Rond. C, Dufour. B, « Modélisation Plasma-liquide », Nancy, France – Juillet 2021, p21

Chapter III

Results § Discussions

III.1. Problem Statement

The objective of the chemical kinetics model is to provide insight into the evolution of various species within the gas mixture, with particular focus on nitrogen oxides, under specific electrical discharge conditions.

It is important to note that chemical kinetics is generally analyzed under the assumption that the gas temperature remains constant during both phases of the process: first, corresponding to the passage of the discharge and the formation of primary radicals, and second, involving the generation of secondary radicals responsible for the reduction of oxides.

To this end, we used a chemical kinetics simulation code to study the evolution of several species present in a typical gas mixture [43] composed of 75% N_2, 25% O_2, and 350 ppm of NO, for two different applied voltage levels.

In the following, we present selected results from the chemical kinetics model, focusing on the temporal evolution of certain primary and secondary radicals. These results provide insights, particularly into the reduction mechanisms of NO_2 [44].

III.2. Simulation Conditions

It is worth recalling that the simulation is based on a corona discharge configuration of the point-to-plane type, into which a gas mixture of $N_2/O_2/NO$ is introduce

[43] Medjahdi I.S, Ferouani. A. K, Lemerini. M, and Sahlaoui.M , 'Numerical Modeling of Impact Effect of Chemical Reactions on Nitrogen Oxide Conversion in N_2/O_2 Mixtures Under Various X%O_2 Concentrations", IEEE Transactions on Plasma Science, 49, 1181-1189 (2021).

[44] Eichwald. O,. Guntoro. N. A, Yousfi. M, and Benhenni.M, "Chemical kinetics with electrical and gas dynamics modelization for NO_xremoval in an air corona discharge", J. Phys. D: Appl. Phys., 35, 439–450 (2002).

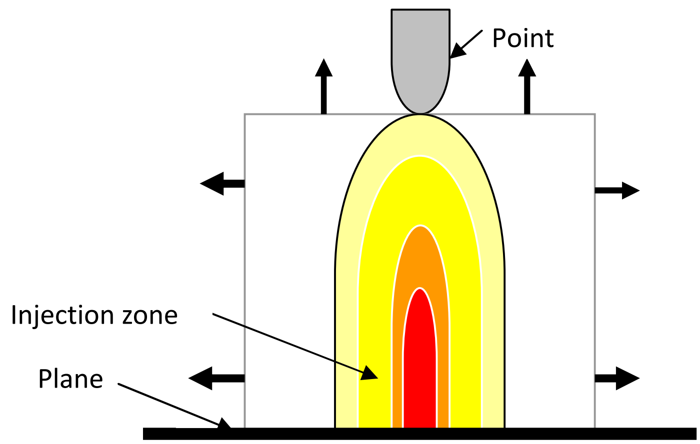

Figure III.1: The configuration of the point-plane type corona discharge

III.2.1 Discharge Characteristics

The boundary conditions used in this simulation are as follows:

- ✓ Atmospheric pressure ⟹ $P = 10^5$ Pa
- ✓ Ambient temperature ⟹ $T = 300$K.
- ✓ Applied voltage ⟹ $U = 4$KV and 9KV
- ✓ Inter-electrode distance ⟹ $d = 20$ mm.
- ✓ Discharge duration ⟹ 10^{-8} ns $\leq$ t $\leq 10^{-4}$n s.

III.2.2. Gas Characteristics

The aim of this study is to simulate the temporal evolution of several chemical species that react through a specific set of chemical reactions, selected for their relevance to our work. The species considered include:

- ✓ **Electrons:** e^-
- ✓ **Molecules:** N_2, O_2, O_3
- ✓ **Atoms:** N, O
- ✓ **Target oxides:** NO, N_2O, NO_2, NO_3

III.3. Results & Discussion

Our gas mixture consists of 75% nitrogen (N_2) and 25% oxygen (O_2), contaminated with nitric oxide (NO). We present and discuss the results related to the temporal evolution of species formed following a corona discharge, for two applied voltage values: 4 kV and 9 kV.

In the following analysis, we use the Boltzmann equation to study the spatio-temporal evolution along the discharge axis. We focus first on the density of primary radicals [45](O, N), then on the secondary radicals [46] (O_3, N_2O, NO_2, and NO_3), and finally on the evolution of the pollutant (NO) within the mixture composed of 75% N_2, 25% O_2, and 350 ppm of (NO).

The results are shown in Figures (III.2) through (III.8). Across this set of curves, we observe a spatial deviation in the inter-electrode region for both applied voltages, 4 kV and 9 kV. However, it is evident that these deviations begin to appear at different points for each species, depending on the specific chemical processes contributing to their evolution.

Figures (III-2) and (III-3) show the evolution of the density of primary radicals (O and N), which marks the onset of chemical reactivity. These figures reveal how the densities vary over time under the influence of the two applied voltage values, with noticeable deviations appearing as a result.

[45].Ferouani. A.K , Lemerini.M , Merad.L, and Houalef.M, "NumericalModelling Point-to-Plane of Negative Corona Discharge in N_2 Under Non-Uniform Electric Field". Plasma Science and Technology,17(6),469 (2015).

[46] Lemerini.M, Ferouani.A.K , Medjahdi.I.S "Numerical simulation of ozone dynamics in negative-corona discharge DC" International Review on Modelling and Simulation, 2, 291-295. 2009.

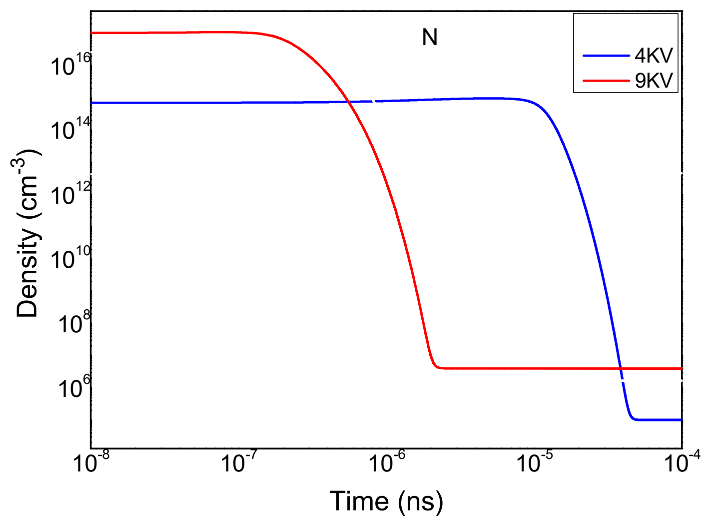

Figure III.2: Temporal variation of the density of species (N)

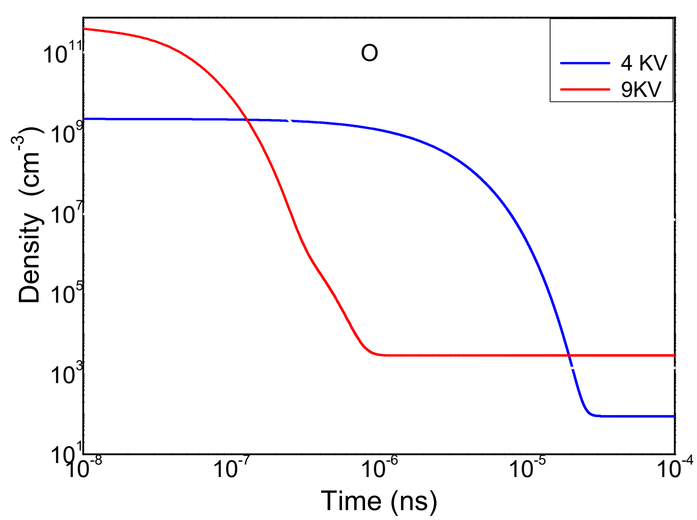

Figure III.3: Temporal variation of the density of species (O)

Following the application of the electrical discharge, electron impacts with the particles in the gas mixture occur within a time frame considered by our simulation, ranging from 10^{-8} ns to 10^{-4} ns. During this period, we observe the onset of the formation of (N) and (O) species from the dissociation of (N_2) and (O_2) molecules. As the applied voltage increases to 9 kV, the density of these two primary radicals becomes significantly higher.

The formation of (N) and (O) from the initial $N_2/O_2/NO$ mixture is promoted by the reaction mechanisms described in reactions [47] and [48] below:

N°	The reactions	Reaction rate K ($cm^3\ s^{-1}$)
R_1	$e + N_2 \rightarrow e + N + N$	$K_1 = 0.830\ 10^{-33}$
R_2	$e + N_2 \rightarrow N^- + N$	$K_2 = 0.830\ 10^{-33}$
R_3	$e + O_2 \rightarrow e + O + O$	$K_3 = 5.276\times10^{-11}$
R_4	$e + O_2 \rightarrow O^- + O$	$K_4 = 4.8\times10^{-9}$
R_5	$N_2 + O_2 \rightarrow 2\ N + O_2$	$K_5 = 0.830\ 10^{-33}$

Table III.1: Reactions involved in the formation of (N) and (O)

The decline or consumption of (N) and (O) begins around 10^{-8} ns, and is significantly more pronounced at higher voltage. This consumption contributes to the formation of secondary radicals such as ozone (O_3) and nitrogen oxides (NO_2, N_2O, and NO_3).

During this phase, nitric oxide (NO) plays a key role in the formation of these species, thereby reducing its own concentration, which is beneficial since (NO) is considered one of the most harmful pollutants.

The following chemical reactions [48] and [49] summarize the consumption of (N) and (O) in favour of the formation of (O_3, NO_2, N_2O, and NO_2).

---

[47] Capitelli.M,.M.Ferreira. C, Gordiets. B.F, Osipov. A.I, "PlasmaKinetic*s*Atmospheric Gases", Springer, (2000).

[48] MirokinI. Y,.Mallard.W.G, "The NIST Chemical Kinetics" Database-Version 2q98",(1998).

[49] Soria.C , Pontiga.F, Castellanos.A : " Plasma Chemical and Electrical Modeling of a Negative DC Corona in Pure Oxygen", Plasma Sources Science and Technology, 2004, Vol.13, pp. 95-107, (USA).

N°	The reactions	Reaction rate K ($cm^3\ s^{-1}$)
R$_6$	$O + O_2 + N_2 \rightarrow O_3 + N_2$	$K_6 = 0.300\ 10^{-27}$
R$_7$	$O + 2\ O_2 \rightarrow O_3 + O_2$	$K_7 = 0.300$ 10-27
R$_8$	$N + 2\ O \rightarrow NO_2$	$K_8 = 0.660\ 10^{-30}$
R$_9$	$2O + N + O_2 \rightarrow NO_2 + O_2$	$K_9 = 0.175\ 10^{-27}$
R$_{10}$	$N_2 + 3O \rightarrow N_2O + O_2$	$K_{10} = 0.175\ 10^{-27}$
R$_{11}$	$2\ N + O \rightarrow N_2O$	$K_{11} = 0.660\ 10^{-30}$

Table III.2: Reactions involved in the formation of (O_3).

Figure (III.4**)** shows the temporal variation of the O_3 species density. A significant difference in densities is observed for the two applied voltages: less than 10^{+19} m^{-3} at 4 kV and more than 10^{+21} m^{-3} at 9 kV. This clearly indicates that ozone formation is highly sensitive to the increase in voltage, and consequently, to the strength of the applied electric field.

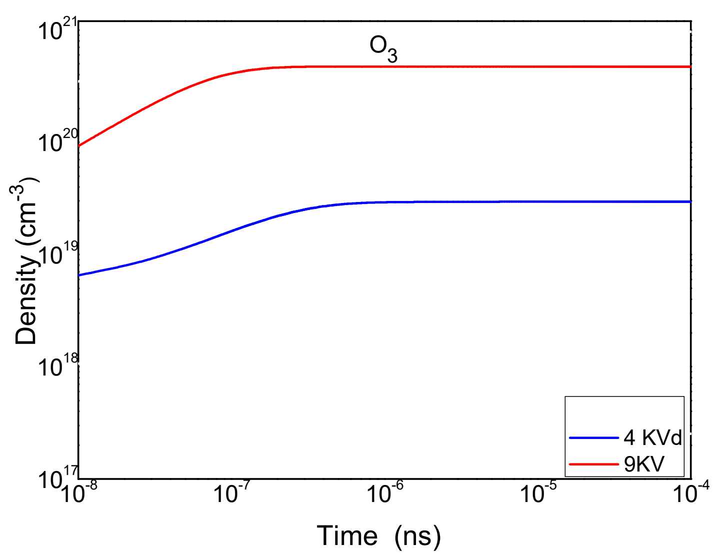

Figure III.4: Temporal Variation of (O_3) Species Density

After its formation, ozone actively reacts with NO to produce NO_2, according to the following reaction pathway [50]:

N°	The reactions	Reaction rate K ($cm^3 s^{-1}$)
R$_{12}$	$O_3 + NO \rightarrow O_2 + NO_2$	$K_{12} = 0.180\ 10^{-11}$
R$_{13}$	$2\ NO + O_2 \rightarrow 2\ NO_2$	$K_{13} = 0.140\ 10^{-37}$
R$_{14}$	$O + NO + O_2 \rightarrow NO_2 + O_2$	$K_{14} = 0.175\ 10^{-27}$

Table III.3: Reactions involved in the formation of (NO_2)

Figures (III.5) and (III.6) illustrate the regeneration of nitrogen oxides (NO_2) and (NO_3). The densities of these species initially increase and then begin to decline beyond 10^{-7} ns. This behaviour is primarily due to their simultaneous production and mutual consumption through ongoing chemical reactions.

[50] Graves.D.B, Lieberman. M.A, Hess. D.W. "Global Model of Plasma Chemistry in a High Density Oxygen Discharge." J.Electrochem. Soc. 141(6),1546-1555 (1994).

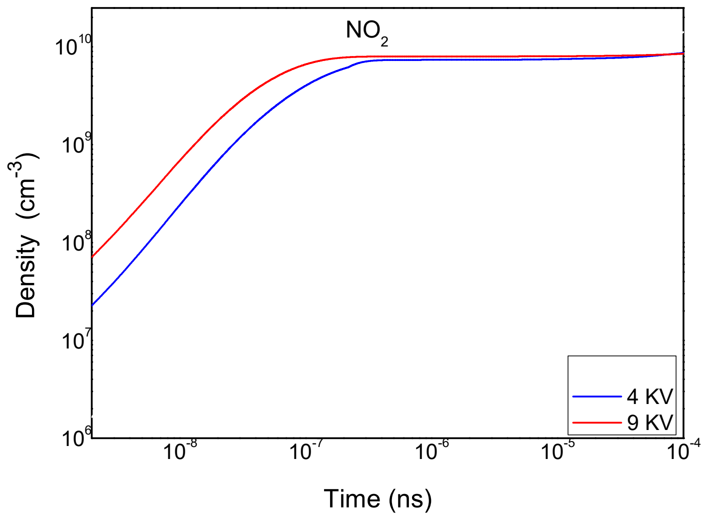

Figure III.5: Temporal Variation of (NO_2) Species Density

The following reaction table[8] presents the formation of (NO_3à, which occurs through the presence of NO_2 as well as through the interaction with pre-existing (O_2) and (O_3) molecules.

N°	The reactions	Reaction rate K (cm^3 s^{-1})
R_{15}	$NO + NO_2 \longrightarrow 2NO_3$	$K_{15} = 0.300\ 10^{-10}$
R_{16}	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	$K_{16} = 0.120\ 10^{-12}$
R_{17}	$2\ NO_2 + O_2 \longrightarrow 2\ NO_3$	$K_{17} = 0.750\ 10^{-11}$
R_{18}	$2\ NO + O_2 \longrightarrow NO + NO_3$	$K_{18} = 0.271\ 10^{-10}$

Table III.4: Reactions involved in the formation of (NO_3)

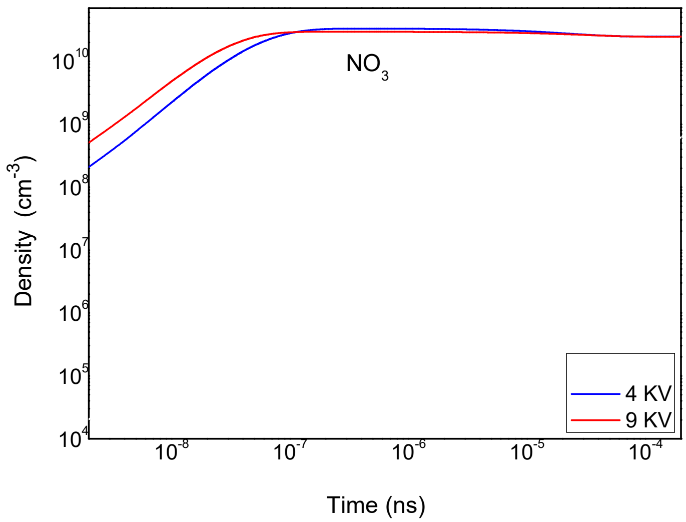

Figure III.6: Temporal Variation of (NO_3) Species Density

Figure (III.7) shows the evolution of the (N_2O) species**.** We first observe the production of this compound within the time range $10^{-9} < t < 10^{-8} ns$. This production is mainly promoted by the presence of (NO), but also by (NO_2) and (NO_3).

The favourable reactions [51] are:

N°	The reactions	Reaction rate K ($cm^3\ s^{-1}$)
***R*$_{19}$**	$N + NO + O_2 \rightarrow N_2O + O_2$	$K_{19} = 0.175\ 10^{-27}$
***R*$_{20}$**	$N + NO_2 \rightarrow N_2O + O$	$K_{20} = 0.240\ 10^{-11}$
***R*$_{21}$**	$NO_2 + NO_3 \rightarrow N_2O + 2O_2$	$K_{21} = 0.230\ 10^{-12}$

Table III.5: Reactions involved in the formation of (N_2O)

However, this is also accompanied by an initial rapid decrease down to $\mathbf{10^{-6}}$, followed by a second decline to $\mathbf{10^{-4}}$, as this is a highly unstable species. It leads to the regeneration of (NO), (O_2), and N_2 through the following reactions [52]:

[51] MirokinI. Y, Mallard. W.G,"The NIST Chemical Kinetics Database-Version 2q98",(1998).

N°	The reactions	Reaction rate K (cm^3 s^{-1})
***R**$_{22}$*	$O + N_2O \rightarrow N_2 + O_2$	$K_{22} = 0.500\ 10^{-16}$
***R**$_{23}$*	$O + N_2O \rightarrow 2\ NO$	$K_{23} = 0.600\ 10^{-11}$

Table III.6: Reactions involved in the formation of (N_2), (O_2) and (NO)

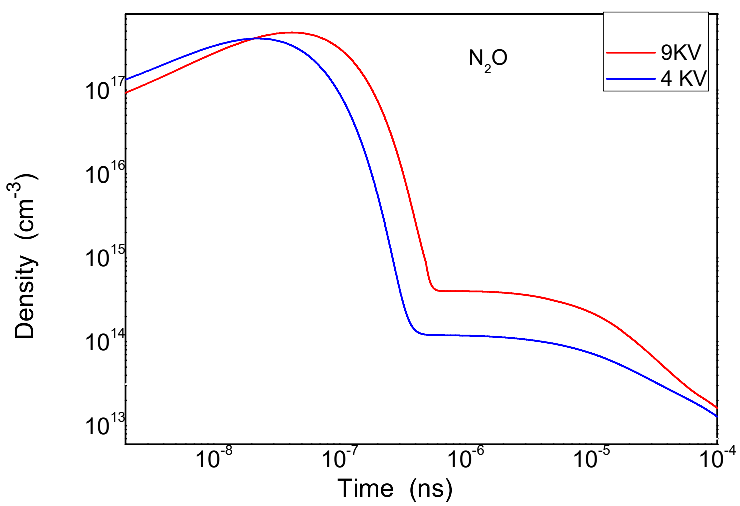

Figure III.7: Temporal Variation of (N_2O) Species Density

Figure (III.8) shows the temporal variation of the (NO) species density**,** which is one of the most dangerous oxides to human health. Its density is seen to decrease significantly, as (NO) is involved in the majority of reactions contributing either to the formation or consumption of other oxides, according to the previously mentioned reactions (R12, R13, R14, R15, R18, and R19).

[52] Graves. Lee,D.B, Lieberman. M.A, and Hess. D.W. "Glo,bal Model of Plasma Chemistry in a High Density Oxygen Discharge." J.Electrochem. Soc. 141(6),1546-1555 (1994).

At a voltage of 4 kV, this species takes some time before it decomposes in favour of the previously mentioned compounds.

In contrast, at 9 kV, (NO) is efficiently destroyed, indicating that high voltage plays a key role in the specific reduction of NO and the overall reduction of nitrogen oxides (NO_x).

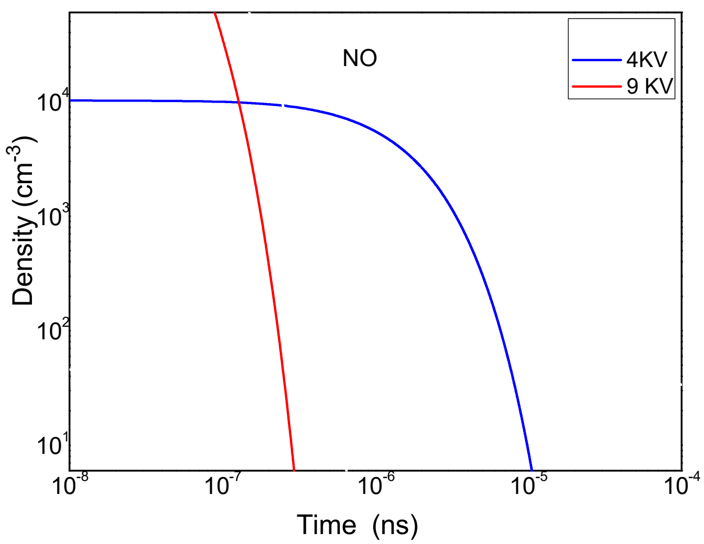

Figure III.8: Temporal Variation of (NO) Species Density

Conclusion

In this Master's research work, we conducted a numerical simulation of the evolution of species density in a gas mixture composed of 75% nitrogen (N_2) and 25% oxygen (O_2), initially contaminated with 350 ppm of nitric oxide (NO). The mixture is subjected to a corona discharge with a point-to-plane geometry, under atmospheric pressure and ambient temperature, in order to investigate the behavior of nitrogen oxides (NO_x) and analyze the effect of increasing the applied voltage. The duration of the discharge spans from 10^{-8} ns to 10^{-4} ns.

The chemical kinetics of the gas phase involves 10 reactive species undergoing 23 chemical reactions, selected from a larger set of over 150 possible interactions, based on their fast reaction rates. The gas dynamics are modeled by accounting for the diffusion of each chemical species throughout the entire reactor domain.

The simulation results show that the conversion of the $N_2 + O_2 +$ NO mixture following the passage of the electrical discharge "Corona" , which ionizes the gas and generates neutral species such as N and O, plays a key role in the formation of various secondary species such as ozone (O_3), nitrogen dioxide (NO_2), nitrate radical (NO_3), and nitrous oxide (N_2O), and in the depletion of NO. These effects are examined under the influence of two distinct voltage conditions: a low voltage of 4 kV and a higher voltage of 9 kV.

The main findings obtained from this Master's thesis can be summarized as follows:

- ✓ The formation mechanism of NO_x primarily occurs through the reaction between N_2 and O_2, but also in the presence of the (NO) species, which is a toxic oxide with numerous harmful effects on both health and the environment.
- ✓ The reduction mechanism of (NO) is mainly attributed to the high voltage applied, which enables the immediate degradation of this species.
- ✓ (NO_2) and (NO_3) particles appear in significant quantities but subsequently participate in the formation of another species, (N_2O).
- ✓ Nitrous oxide (N_2O) exhibits two points of regression due to its instability and its involvement in the reformation of (O_2) and (N_2).
- ✓ It is also observed that high voltage plays a crucial role in the synthesis of various species, influencing both their production and consumption in favour of one another.

These results open up numerous opportunities for further research aimed at improving both the efficiency and selectivity of the gas and target species. To achieve this, we propose the following:

- **Continue model/experiment comparisons**: These comparisons should be extended to a variety of conditions, including inter-electrode distance, tip curvature radius, and gas composition. Such comprehensive comparisons are essential for validating the numerical code.
- **Conduct tests under DC voltage conditions**: These should be carried out with carefully chosen initial conditions, based on the hypotheses developed.
- **Further increase the complexity of the gas mixture**: This involves approximating the composition of a polluted gas more closely by introducing additional components such as (CO_2) and water vapour (H_2O).
- **Perform an interferometric study of the discharge**: This will provide a spatial mapping of all species present within the discharge.

Mémoire de Master en Physique de l'Université Abou bekr Belkaïd – Tler
Spécialité : Physique des Plasmas
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ABSTRACT

This research is part of a comprehensive approach to modeling the chemical kinetics of a gaseous $N_2/O_2/NO$ mixture subjected to a corona discharge in a point-to-plane configuration. This technique is considered one of the most promising for the generation or abatement of nitrogen oxides. To this end, we conducted simulations on a gas mixture composed of 75% nitrogen (N_2) and 25% oxygen (O_2), initially contaminated with 350 ppm of nitric oxide (NO), under applied voltages of 4 kV and 9 kV. The mathematical model employed is based on the classical hydrodynamic equations of fluid motion, assuming that diffusive transport phenomena are predominant. The equations are discretized using the finite volume method, and numerical diffusion is mitigated through the Flux Corrected Transport (FCT) technique.
The simulation results indicate that the degradation of NO is accompanied by the formation and subsequent disappearance of other chemical species, such as nitrogen dioxide (NO_2), ozone (O_3), and nitrous oxide (N_2O). Furthermore, the applied high voltage plays a crucial role in determining the overall efficiency of the process.

INDEX TERMS

Gaseous mixture $N_2/O_2/NO$ – Corona discharge – Chemical kinetics – FCT method – NOx synthesis

RÉSUMÉ

Cette recherche rentre dans le cadre global de modélisation de la cinétique chimique d'un mélange gazeux $N_2/O_2/NO$ traversé par une décharge électrique de type couronne et de géométrie point –plan, cette technique est actuellement l'une des dispositions les plus prometteuses pour la création ou la destruction des oxydes d'azote. Pour cette raison, nous avons effectué la simulation d'une mixture 75% N_2 et 25% O_2 initialement pollué par 350 ppm (NO) sur la quelle est appliquée une tension d de 4 KV et 9KV. Le modèle mathématique utilisé repose sur les équations classiques de l'hydrodynamique d'un fluide dans l'hypothèse où seuls les phénomènes de transport diffusifs sont prédominants. Les équations sont discrétisées par la méthode des volumes finis et les flux de diffusion sont corrigés par la méthode F.C.T. (Flux Corrected Transport) pour limiter la diffusion numérique.
Les résultats obtenus montrent que la destruction de l'oxyde d'azote (NO)est accompagnée par l'apparition et la disparition d'autres espèces, tels que le dioxyde d'azote (NO_2), l'ozone (O_3), le (N_2O), etc… et l'influence de la haute tension joue un rôle important dans l'efficacité du processus.

MOTS CLÉS

Mélange gazeux $N_2/O_2/NO$ - Décharge corona- cinétique chimique - Méthode FCT. Synthese des NO_X

ملخص

تندرج هذه الدراسة ضمن الإطار العام لنمذجة الحركية الكيميائية لخليط غازي مكوَّن من $N_2/O_2/NO$ الذي يمر بتفريغ كهربائي من نوع "كورونا" وبنموذج هندسي من نوع نقطة-مستوى. تُعتبر هذه التقنية واحدة من أكثر الأساليب الواعدة حاليًا لتوليد أو إزالة أكاسيد النيتروجين .في هذا السياق، تم إجراء محاكاة لخليط غازي يتكون من 75% من النيتروجين (N_2) و25% من الأوكسجين (O_2) ملوث في البداية بـ 350 جزء في المليون (ppm) من أكسيد النيتروجين(NO) ، والذي يتم تطبيق عليه جهد كهربائي مقداره 4 كيلو فولت و9 كيلو فولت. النموذج الرياضي المُستخدم يعتمد على المعادلات التقليدية للهيدروديناميكا الخاصة بالمائع، حيث يفترض أن ظواهر النقل بواسطة الانتشار هي السائدة. تم تفكيك المعادلات باستخدام طريقة الحجوم المنتهية(Finite Volume Method) ، بينما تم تعديل تدفقات الانتشار باستخدام طريقة النقل المصحَّح للتدفق (F.C.T.) للحد من الأخطاء العددية الناتجة عن الانتشار.
أظهرت النتائج المستخلصة أن عملية تدمير أكسيد النيتروجين (NO) تترافق مع ظهور واختفاء مركبات أخرى مثل ثاني أكسيد النيتروجين(NO_2) ، والأوزون(O_3) ، وأكسيد النيتروس (N_2O) ، وغيرها من الجزيئات. و من هذا تبين أن الجهد الكهربائي العالي يلعب دورًا حاسمًا في تحسين كفاءة العملية.

الدالة الكلمات

خليط غازي $N_2/O_2/NO$ – تفريغ إكليلي – حركية كيميائية – طريقة FCT – تكوين NOx