Calculation of electron-molecule reactions of NO decomposition in pulsed corona discharges

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Abstract In recent years there has been increasing research interest in the removal of nitrogen-oxides from exhaust gases using a pulsed corona discharge reactor. The pulsed streamer corona produces energetic electrons that excite, ionize and dissociate gas molecules, and by forming radicals that enhance the gas-phase chemical reactions which reduce the pollutant’s concentration. The decomposition ratio of these substances is dependant on the gas composition, concentration, energy distribution of fast electrons, and other parameters. For a detailed analysis of the phenomena, knowledge of chemical reaction mechanisms is essential. The reaction rates of possible molecule-molecule reactions can in most cases be found in the literature, but the rates of the electron-molecule collision reactions depend on the energy of free electrons. With the knowledge of the field distribution, the energy of the free electrons and the reaction rates can be found. In this paper the authors present a method, in which the reaction rates of the electron-molecule collision are determined. The model is based on a calculation of: the energy of free electrons in the time and space varying field, considering the mean free path and the energy-dependent reaction cross sections of molecules. Knowing the rates, it is possible to solve the reaction kinetic equations, and to get the time-evolution of by-products, and the decomposition ratio of the pollutant gases.

1. Introduction

The air pollution caused by the combustion of fossil fuels in industrial boilers, power generation and diesel engines is a serious problem. The nitrogen oxides are the cause of acid rain and photochemical smog, sulphur-dioxide gas is also the origin of acid rain which is responsible for the degradation of forests historic buildings and monuments. The pulsed corona discharge process (PCDP) is an effective method to remove hazardous chemicals from exhaust gases [1], [2], [3]. The unipolar corona discharge is a stable, self-maintaining gas discharge, characterized by low gas temperature, and high electron temperature. During the discharge, the free electrons are accelerated by the electric field, and during their drift they can lose the energy by inelastic collision. The collision of energetic electrons with gas molecules causes the formation of chemically active species to initiate chemical reactions, leading to the removal of gaseous pollutants. Compared to the other non-thermal plasma technology, PCDP is more efficient, because a large part of input energy goes into the production of energetic electrons, rather than into gas heating. (Mizuno et. al., 1986)
2. The corona reactor

The reactor is a 120 cm long wire-to-cylinder system filled with the mixture of air or nitrogen and 100-300 ppm NO at atmospheric pressure (figure 1). The inner wire, with a radius of \( a = 0.1 \text{ mm} \), is subjected to high voltage pulses, whereas the outer electrode, with a radius of \( b = 3 \text{ cm} \), is grounded. The wire is made of tungsten and the outer cylinder is made of stainless steel. The electric field is determined by the space charge density and the electric charge accumulated on the electrodes. The space and time-dependent electric field is determined by solving the Laplace-Poisson, and the continuity equations. [4] Figure 2. shows the electric field distribution: the time dependence of the field corresponds with the pulse shape of the voltage and current, and the intensity is inversely proportional to the distance from the corona electrode.

3. Determination of reaction rates of the electron-molecule collision reactions

The calculation is based on the Townsend-theory. This theory is founded on two conditions [5], [6]:

1. The free electrons gain relatively high energies from the electric field because of their long mean-free path between collisions with gas molecules. Until their energy is less than the ionization or excitation energy, the electrons retain virtually all their kinetic energy in elastic collisions. When they gain sufficient energy in their paths through the electric field for ionization or excitation, they are capable of transferring all their energy by inelastic collision.

2. The ions can not accelerate significantly because their mass is large compared to the electrons mass, and during the collision with each other, they lose approximately the half of their energy by inelastic collisions.

To calculate the number of gas molecules subjected to electron-molecule reactions during the corona pulse, a number of electrons which have at least the binding energy of gas molecules have to be found. In order to solve the problem the volume of the reactor is divided into \( n \) equal space interval, the examined time period is divided into \( m \) equal time interval. The path taken by an electron starting from the optional \( r_p \) interval at \( t_q \) time during \( \Delta t \):

\[
\Delta r_i(r_p, t_q) = \frac{e}{m_e} \int_{t_q}^{t_q+\Delta t} E(r_p, t) \cdot t dt
\]
Where $E(r,t)$ is the space and time dependent field strength, $m$ is the mass, $e$ is the charge of the electron. During this time the energy gained from the electric field can be estimated as:

$$\Delta W_1 \cong \Delta r_1 \cdot e \cdot \frac{E(r_p, t_q) + E(r_p + \Delta r_1, t_q + \Delta t)}{2}$$

(2)

The velocity of the electron after $\Delta t$ time is:

$$\Delta v_1 = \int_{t_q}^{t_q + \Delta t} a(r_p, t) dt = \frac{e}{m} \int_{t_q}^{t_q + \Delta t} E(r_p, t) dt$$

(3)

Generalized: the path of the electron during the $i$-th $\Delta t$ interval is:

$$\Delta r_i(r_p, t_q) = \frac{e}{m} \int_{t_q}^{t_q + i \Delta t} \int_{t_q}^{t_q + (i-1) \Delta t} E(r_p + \sum_{j=1}^{i-1} \Delta r_j, t) \cdot t dt + \sum_{j=1}^{i-1} \Delta v_j \cdot \Delta t$$

(4)

The energy gained by the electron during this interval is:

$$\Delta W_i = \Delta r_i \cdot e \cdot \frac{E(r_p + \sum_{j=1}^{i-1} \Delta r_j, t_q, (i-1) \Delta t) + E(r_p + \sum_{j=1}^{i} \Delta r_j, t_q + i \Delta t)}{2}$$

(5)

After $k \Delta t$ time acceleration, the total kinetic energy of the electron can be given as:

$$W(k)_{pq} \cong \sum_{i=1}^{k} \Delta W_i = e \cdot \sum_{i=1}^{k} \Delta r_i \cdot \frac{E(r_p + \sum_{j=1}^{i-1} \Delta r_j, t_q, (i-1) \Delta t) + E(r_p + \sum_{j=1}^{i} \Delta r_j, t_q + i \Delta t)}{2}$$

(6)

If $W(k)_{pq} \geq W_0$ where $W_0$ is the activation energy of the chemical reaction, but

$$W(k-1) < W_0$$

(7)

then the electron reach the necessary activation energy after $k \Delta t$ time and

$$r(k)_{pq} = \sum_{i=1}^{k} \Delta r_i = r_{pq}$$

(8)

path. According to the kinetic gas theory, the probability of the electron can make $r_{pq}$ distance without collision is:

$$P(r \geq r_{pq}) = e^{\frac{-r_{pq}}{\lambda}}$$

(9)

where $\lambda$ is the mean-free path. The number of free electrons can be estimated in $t_q$ as:

$$n(t_q) = \frac{i(t_q)}{e \cdot n}$$

(10)

The number of electron starting at $t_q$ in the $p$-th space interval, having the energy of $W \geq W_0$:

$$N_p(t_q) = n(t_q) \cdot e^{\frac{-r_{pq}}{\lambda}} = \frac{i(t_q)}{e \cdot n} \cdot e^{\frac{-r_{pq}}{\lambda}}$$

(11)
Summing these values for each time and space interval, the total number of electrons having the energy of \( W \geq W_0 \) can be obtained:

\[
N^* = \sum_{p=1}^{n} \sum_{q=1}^{m} N_p(t_q)
\]  

(12)

The probability of chemical transformation during a collision with an electron of given energy can be characterized by the energy dependent reaction cross-section. For the i-th elementary reaction the cross-section is:

\[
\sigma_i
\]

The sum of the individual reaction cross-section yields the total reaction cross-section:

\[
\sum_i \sigma_i = \sigma_t
\]  

(13)

The fraction of the total number of events for the i-th process is the relative cross-section [7]:

\[
\sigma_{i,rel} = \frac{\sigma_i}{\sigma_t}
\]  

(14)

As the reaction cross-section is energy dependent, a more sophisticated model can be given by considering the cross-sections as a function of energy of the colliding electrons. An analytical expression for the energy dependence of cross section is not available in the literature, only tabulated or graphically data can be found [8], [9]. For this reason the considered electron energy range has been divided into \( l \) small energy ranges, which correspond to the energy characteristics of the relative cross section of the given range:

\[
W_i - W_{i+1} \quad i = 1, \ldots, l
\]  

(15)

Calculating the number of electrons \( N_i^* \) having the energy of \( W \geq W_i \) and composed the

\[
\tilde{N}_i = N_i^* - N_{i+1}^* \quad \text{for} \ i = 1, \ldots, l
\]  

(16)

the energy distribution of the electrons can be obtained for the corresponding energy ranges of the cross-section. To calculate the number of effective collisions resulting the given chemical reaction, the number of collisions must be weighed by the relative cross-section, and the relative number of reactant molecules in each energy ranges:

\[
N_i' = \sigma_{i,rel} \cdot \tilde{N}_i \cdot \frac{C_i}{C} \quad \text{for} \ i = 1, \ldots, l
\]  

(17)

Where \( C_j \) is the concentration of the molecules taking part in the j-the reaction, \( C \) is the concentration of all molecules. The total number of the given reactions in the whole reactor can be obtained as:

\[
N' = \sum_{i=1}^{l} N_i'
\]  

(18)

The reaction rate of a given chemical transformation is the quantity of reactant substance subjected to the reaction in unit volume during unit time. The electron-molecule collision is a second order chemical reaction, so:

\[
k = \frac{V_r}{N' \cdot \tau} \cdot \left[ \frac{cm^3}{molecules \cdot sec} \right]
\]  

(19)

Where \( \tau \) is the duration of corona pulse, and \( V_r \) is the volume of the reactor.
4. Results

The calculated rate coefficients were checked by the minimum reaction set for modelling the transformations of the nitrogen oxides in nitrogen. This reaction set model was developed by first considering the behaviour of NO in N₂: several authors have examined this system [10-13]:

**Table 1. The main reactions and rates for transformation of nitrogen-oxides in nitrogen**

| Chemical reactions | k \left( \frac{cm^3}{molecules \cdot sec} \right) | References |
|--------------------|-----------------------------------------------|------------|
| 1. \( N_2 + e \rightarrow N_2^+ + 2e \) | \( k_1 = 4.66 \cdot 10^{-16} \) | Present work |
| 2. \( N_2 + e \rightarrow 2N + e \) | \( k_2 = 9.02 \cdot 10^{-17} \) | Present work |
| 3. \( N_2^+ + e \rightarrow 2N \) | \( k_3 = 2.61 \cdot 10^{-15} \) | Present work |
| 4. \( N_2O^+ + e \rightarrow N_2 + O \) | \( k_4 = 7.65 \cdot 10^{-16} \) | Present work |
| 5. \( N + NO \rightarrow N_2 + O \) | \( k_5 = 3.40 \cdot 10^{-11} \) | \[11\], \[13\] |
| 6. \( NO + O \rightarrow NO_2 \) | \( k_6 = 2.33 \cdot 10^{-12} \) | \[12\], \[13\] |
| 7. \( O + O \rightarrow O_2 \) | \( k_7 = 1.7 \cdot 10^{-13} \) | \[11\], \[12\] |
| 8. \( NO_2 + N \rightarrow N_2O + O \) | \( k_8 = 3 \cdot 10^{-12} \) | \[10\], \[12\] |
| 9. \( NO_2 + O \rightarrow NO + O_2 \) | \( k_9 = 9.7 \cdot 10^{-12} \) | \[12\], \[13\] |
| 10. \( N_2^+ + N_2O \rightarrow N_2O^+ + N_2 \) | \( k_{10} = 5 \cdot 10^{-12} \) | \[12\], \[13\] |

**Figure 3. The time evolution of species of NO decomposition**
- ■: NO
- ▲: N₂O
- □: O
- ▼: O₂
- +: NO₂
The reaction equation system was solved by a computer program developed by Gábor Peintler [14].

In the experiment the peak value of voltage pulses was 35 kV, the pulse repetition was 50 pulse per second, the flow rate was 50 l/h. The concentration of NO (392 ppm), NO₂ (0 ppm) and N₂O (0 ppm) was measured and compared to the outlet of the reactor values: 90% decrease in NO (40 ppm) and 80 ppm of N₂O, less than 5 ppm of NO₂ were measured by using an FTIR device.

5. Conclusions
The reaction rates of electron-molecule collision can be determined by calculating the energy of free electrons in the space and time varying electric field, considering the relative collision cross-section. In this way a direct relation can be given between the reaction rate coefficients and the physical and chemical characteristics of the system.

The model is not perfect: the minimum reaction set of NO decomposition (10 equations) is not enough for the correct description of the phenomena. In case of NO and decomposition, considering pulse repetition, there is a good agreement between the experimental data and the model, but for N₂O production there is a difference between them. It has to be completed by additional equations.

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