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We present the results of experimental and theoretical studies of the component content of active particles in the volume barrier discharge in wet ($RH\approx80\%$) air. To describe the plasma kinetics, a new numerical model, in which the power introduced into a discharge gap is immediately averaged over the entire discharge volume, is proposed. The numerical dependences of the component content of particles formed in the discharge on the gas medium temperature, transient time of the gas mixture in a discharge gap, and specific power are obtained. The concentrations of O_3 , HNO_3 , and HNO_2 at specific power values of $W_d = 1.5$ and 0.75 W/cm^3 are measured experimentally. The rotational temperature of nitrogen molecules $T_{\rm rot}$ is measured as well. The comparison of experimental data with the results of calculations shows that the O_3 concentration is in quantitative agreement with the calculations, whereas the HNO_3 concentration exhibits just a qualitative agreement. Experimentally, the measured HNO₂ concentration essentially exceeds the theoretically calculated value. The main reasons for this discrepancy are presented. It is also shown that the experimental data are in better agreement with the calculations under the increase of both the specific power and the transient time of gas mixture in a discharge gap.

1. Introduction

In the last decade, the dielectric barrier discharge attained broad technological applications. It is used for the surface modification [1], in the creation of excimer lamps [2] and flat plasma panels [3], for the purification of exhaust gases [4], sterilization of medical instruments [5], and removal of volatile organic components [6]. One of the actual tasks for now is the development of a numerical model for the description of the kinetics of plasma-chemical reactions occurring in the barrier discharge [7]. Usually [8], in numerical calculations of the concentrations of particles in the discharge, the plasma kinetics in separate current channels of microdischarges is calculated at first, and then, after the time interval of order of the diffusion time ($\sim 10^3$ s), the averaging of the concentrations of all components is performed over the entire discharge gap. In such an approach, there are several parameters (the dimensions of microdischarges, their density over the square unit of

they are commonly considered as the fitting ones. The calculations performed in the present paper are based on another approach, in which the power introduced into a discharge is immediately averaged over the entire discharge volume. With such an approach, the processes that possess a linear behavior with respect to the electron concentration, as well as non-linear ones with the reaction time being greater than the diffusion time, are described correctly. An advantage of this approach consists in the absence of fitting parameters. In the present paper, we calculate the component content of active particles formed in plasma in air with 80% relative humidity. The numerical dependences of the concentrations of gas medium particles formed in the discharge on the gas mixture temperature, transient time of a gas mixture in the discharge gap, and specific power in the discharge are obtained. The concentrations of O₃, HNO₃, and HNO_2 are measured experimentally. The comparison of experimental data with the results of calculations has shown that the O_3 concentration quantitatively agrees with the calculations, whereas the HNO_3 concentration exhibits just a qualitative agreement. The experimentally measured HNO₂ concentration essentially exceeds the theoretically calculated value. The main reasons of this discrepancy are presented. It is also shown that the experimental data are in better agreement with the calculations under the increase of both the specific power and the transient time of the gas mixture in a discharge gap.

discharge electrodes, and the frequency of the occurrence

of microdischarges) that are not definitely known, and

2. Description of the Setup and the Methods of Experimental Measurements

The experimental researches were performed at a setup shown schematically in Fig. 1. A quartz tube having 368 mm length, 26.5 mm external diameter, and 1.5 mm



Fig. 1. Scheme of the experimental setup. 1 -quartz tube, 2 -high voltage electrode, 3 -grounded electrode, 4 -discharge gap, 5 -Teflon cap, 6 -windows of KU-1 quartz for optical diagnostics

wall thickness served as a dielectric barrier. A profiled metal high-voltage electrode with 21 mm external diameter, which formed four discharge gaps, was placed inside the tube. The lengths and widths of the discharge gaps comprised 50 and 1.25 mm, respectively. A metal foil put on the quartz tube at locations of the discharge gaps served as ground electrodes. The ends of the quartz tube were tightly closed by Teflon tubes having windows made of KU-1 quartz glass with 3 mm diameter and 2 mm thickness intended for optical diagnostics (the low transmission band wavelength for the windows of KU-1 quartz comprised about 170 nm). The system for desiccation/wetting enabled to supply the ambient air to the discharge gaps with 20-90% relative humidity and 20-22 °C temperature. The volume pumping rate through each of the discharge gaps was varied in the range from 1 to 8 cm^3/s , correspondingly to average values of the transient time of particles in the discharge gap $\tau = 2.4 \div 0.3$ s. (The average transient time of particles in the discharge $\tau = V/2v$, where V is the volume of the discharge gap). For powering the discharge, an AC source with a voltage of 15 kV and a frequency of 400 Hz was used. The specific power W_d introduced into the discharge was varied in the range $0.75 \div 2.5 \text{ W/cm}^3$.

For optical measurements, a monochromator of the MDR-23 type with a base of 0.6 m was used. A DDS-30 deuterium lamp and an OR-33-03 incandescent lamp were used as radiation sources of continuous spectra in the wavelength ranges 200÷400 and 400÷1200 nm, respectively. Photoelectric multipliers of the FEU-100 and FEU-39A types were used as radiation detectors.

The concentration of particles inside the discharge gap was calculated on the basis of the Lambert—Bouguer law

 $F = F_0 \exp(-\sigma nl),$

where F_0 and F are the light fluxes incident on and transmitted through the studied object, respectively;

n is the concentration of absorbing particles; σ is the absorption cross section; and l is the optical path length.

The NO₃ concentration was calculated from the absorption of the lamp radiation at wavelengths $\lambda = 662$ and 623 nm. The concentrations of O₃, HNO₃, HNO₂, N₂O₅, and H₂O₂ were calculated on the basis of the curve of integral absorption by all the particles in the wavelength range 200–300 nm by means of the automated fit routine.

The concentrations of particles were fitted by this routine until the coincidence of the experimental and calculated absorption curves with a pre-defined precision. The possibility to use this method is justified by the fact that the spectrum dependences of the absorption cross sections for these particles are essentially different in this wavelength range.

In the calculation of the concentrations of particles, the absorption cross sections were taken from [9]. We did not succeed in measuring the concentrations of H_2O_2 , N_2O_5 , and NO_3 in any regime of the discharge glowing. Thus, the concentrations of these particles were below the sensitivity thresholds of the used method ($\approx (5 \div 10) \times 10^{14}$ cm³ for H_2O_2 and N_2O_5 and $\approx 1 \times 10^{13}$ cm³ for NO_3).

3. Discharge Model

In the calculation of the component content of the plasma and the concentrations of molecules and radicals formed in the barrier discharge volume, the following kinetic equations were used:

$$\frac{dN_i}{dt} = S_{ei} + \sum_j k_j N_j + \sum_{j,l} k_{jl} N_j N_l + \dots$$
(1)

Here, N_i are the concentrations of molecules and radicals; k_j , k_{jl} are the rate constants of molecular processes; S_{ei} is the formation rate for the products of electron-molecular reactions calculated from the equation

$$S_{ei} = \frac{W}{V} \frac{1}{\varepsilon_{ei}} \frac{W_{ei}}{\sum_{j} W_{ej} + \sum_{j} W_{j}},\tag{2}$$

W is the power introduced into the barrier discharge; V is the barrier discharge volume; W_{ej} is the specific power spent for the electron-molecular processes of inelastic scattering with threshold energy ε_{ei} ;

$$W_{ei} = \sqrt{\frac{2q}{m}} n_e N_i \varepsilon_{ei} \int_0^\infty \varepsilon Q_{ei}(\varepsilon) f(\varepsilon) d\varepsilon, \qquad (3)$$

where $q = 1.602 \cdot 10^{-12}$ erg/eV; *m* and n_e are the electron mass and concentration, respectively; Q_{ei} is the cross section of the corresponding inelastic process; $f(\varepsilon)$ is the electron energy distribution function;

 W_i is the specific power spent for heating the gas,

$$W_i = \frac{2m}{M_i} \sqrt{\frac{2q}{m}} n_e N_i \int_0^\infty \varepsilon^2 Q_i(\varepsilon) f(\varepsilon) d\varepsilon, \qquad (4)$$

where M_i is the mass of molecules of the corresponding type, and Q_i is the transport scattering cross section.

The electron distribution function was calculated from the Boltzmann equation in the two-term approximation [10, 11]:

$$\frac{1}{n_e N} \left(\frac{m}{2e}\right)^{1/2} \varepsilon^{1/2} \frac{\partial(n_e f(\varepsilon))}{\partial t} - \frac{1}{3} \left(\frac{E}{N}\right)^2 \frac{\partial}{\partial \varepsilon} \left(\frac{\varepsilon}{\sum_i \frac{N_i}{N} Q_i} \frac{\partial f(\varepsilon)}{\partial \varepsilon}\right) - \frac{\partial}{\partial \varepsilon} \left[2\sum_i \frac{m}{M_i} \frac{N_i}{N} Q_i \varepsilon^2 \left(f(\varepsilon) + T \frac{\partial f(\varepsilon)}{\partial \varepsilon}\right)\right] = S_{eN}.$$
 (5)

Here, ε is the energy (eV); T is the gas temperature (eV); e is the electron charge; E is the electric field strength; N is the total concentration of molecules; N_i is the concentration of molecules of the corresponding type; m is the electron mass; and S_{eN} is the integral of inelastic collisions of electrons with neutral particles.

The integral of inelastic collisions of electrons with gas molecules was chosen as

$$S_{eN} = \sum_{i} \frac{N_j}{N} [(\varepsilon - \varepsilon_i) Q_{ei}(\varepsilon + \varepsilon_i) f(\varepsilon + \varepsilon_i) - \varepsilon Q_i(\varepsilon_i) f(\varepsilon)], \qquad (6)$$

where Q_{ei} are the cross sections of excitation and ionization of O₂ and N₂ molecules with threshold energy ε_i .

The electron-electron scattering was not taken in consideration, because our trial calculations showed that if $n_e/N \leq 10^{-6}$, which is well obeyed in the experiment, then the e-e scattering provides no essential influence on the rate constants of electron-molecular processes (the electron concentration in separate current channels $\approx 10^{13}$ cm⁻³ [12, 13]).

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It was assumed in the calculations that the electric field in a discharge did not vary in space and time. It was taken to be 20 kV/cm which is the mean field in the barrier discharge in air, as follows from [14]. In the solution of Eqs. (1), the elementary processes listed in Tables 1 and 2 were taken into consideration. The rates of excitation, dissociation, and ionization of N₂ and O_2 by electron hits were calculated with the use of the cross sections of these reactions taken from [15-22]. Unfortunately, the cross sections of dissociation of other components are unknown at present. However, it was shown in [32] that the decomposition of a molecule by the electron hit occurs via its excitation to the repulsive level with energy of about twice the dissociation energy. In the calculations of the dissociation rates with unknown cross sections, we used the cross section of oxygen dissociation biased by the doubled threshold energy of the process. It is worth to note that these processes do not influence essentially the electron energy distribution function, since the concentrations of secondary products of the reactions are essentially less than those of N_2 and O_2 . In the calculations, it was assumed that a gas mixture is always inside the discharge gap during the discharge glowing. The processes occurring at electrodes of the barrier discharge were not considered in the calculations.

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N⁰	Reactions	Rate	Reference
1	$O_2 + e \rightarrow O + O + e$	1.38×10^{-9}	[16]
2	${ m O}_2+{ m e} ightarrow { m O}_2({ m 1}\Delta_g)+{ m e}$	1.81×10^{-9}	[17]
3	$N_2 + e \rightarrow N_2(A^3\Sigma_u^+) + e$	3.56×10^{-10}	[18]
4	$N_2 + e \rightarrow N_2(a^1\Pi_q) + e$	2.08×10^{-10}	[19]
5	${ m O}_2+{ m e} ightarrow{ m O}_2({ m v})+{ m e}$	5.4×10^{-9}	[20]
6	$\mathrm{N}_2 + \mathrm{e} ightarrow \mathrm{N}_2(\mathrm{v}) + \mathrm{e}$	1.73×10^{-7}	[21]
7	$\rm N_2 + e \rightarrow \rm N + \rm N + e$	1.01×10^{-10}	[22]
8	$O_2 + e \rightarrow O_2^+ + e$	6.2×10^{-12}	[22]
9	$N_2 + e \rightarrow N_2^{\mp} + e$	5.29×10^{-13}	[22]
10	$H_2O + e \rightarrow OH + H + e$	1.09×10^{-10}	*
11	${ m O}_2+{ m e} ightarrow{ m O}+{ m O}({ m d})+{ m e}$	4.74×10^{-10}	*
12	$O_3 + e \rightarrow O_2 + O + e$	5.88×10^{-9}	*
13	$\rm N_2O + e \rightarrow \rm N_2 + O + e$	3.95×10^{-9}	*
14	$NO_2 + e \rightarrow NO + O + e$	1.13×10^{-9}	*
15	$N_2O_4 + e \rightarrow NO_2 + NO_2 + e$	7.75×10^{-9}	*
16	$\rm N_2O_5 + e \rightarrow \rm NO_2 + \rm NO_3 + e$	6.16×10^{-9}	*
17	$\rm HO_2 + e \rightarrow OH + O + e$	1.67×10^{-9}	*
18	$\rm HO_2 + e \rightarrow \rm H + \rm O_2 + e$	3.10×10^{-9}	*
19	$H_2O_2 + e \rightarrow OH + OH + e$	2.36×10^{-9}	*
20	$OH + e \rightarrow O + H + e$	2.84×10^{-10}	*
21	$\rm N_2O + e \rightarrow \rm NO + \rm N + e$	1.28×10^{-10}	*
22	$\rm NO + e \rightarrow N + O + e$	1.45×10^{-11}	*
23	$\rm HNO + e \rightarrow \rm NO + \rm H + e$	2.85×10^{-9}	*
24	$NO_3 + e \rightarrow NO_2 + O + e$	2.92×10^{-9}	*
25	$\mathrm{HNO}_2 + \mathrm{e} \rightarrow \mathrm{NO} + \mathrm{OH} + \mathrm{e}$	2.88×10^{-9}	*
26	$\mathrm{HO_2NO_2} + \mathrm{e} \rightarrow \mathrm{NO_2} + \mathrm{HO_2} + \mathrm{e}$	2.88×10^{-9}	*
27	$\rm HNO_3 + e \rightarrow OH + NO_2 + e$	2.88×10^{-9}	*
28	$HNO_3 + e \rightarrow HO_2 + NO + e$	8.26×10^{-10}	*

Table 2

No	Beactions	Bate	Beference
1	$O(d) + H_2 O \rightarrow OH + OH$	2.2×10^{-10}	[92]
1	$O(d) + H_2O \rightarrow OH + OH$	2.2×10	[23]
2	$O(d) + N_2 \rightarrow O + N_2$	$1.8 \times 10^{-11} e^{-11}$	[10]
3	$O(d) + O_2 \rightarrow O + O_2$	3.8×10^{-11}	[23]
4	$O(d) + H_2O \rightarrow O + H_2O$	1.2×10^{-11}	[23]
5	$\rm N + HO_2 \rightarrow \rm NO + OH$	2.2×10^{-11}	[23]
6	$NO_3 + OH \rightarrow NO_2 + HO_2$	2.3×10^{-11}	[23]
7	$\mathrm{OH} + \mathrm{OH} + \mathrm{M} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{M}$	$6.9 \times 10^{-31} (300/T)^{0.8}$	[10]
8	$\mathrm{OH} + \mathrm{O}_3 o \mathrm{HO}_2 + \mathrm{O}_2$	$1.7 \times 10^{-12} e^{-940/T}$	[10]
9	$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} e^{250/T}$	[23]
10	$O + HO_2 \rightarrow OH + O_2$	$2.9 \times 10^{-11} e^{200/T}$	[23]
11	$H + O_2 \rightarrow OH + O_2$	$1.4 \times 10^{-10} e^{-480/T}$	[23]
10	$H + UO \rightarrow OH + OU$	2.0×10^{-10} $c^{-500/T}$	[20]
12	$H + HO_2 \rightarrow OH + OH$	$3.0 \times 10^{-23} T = 2.6$	[23]
13	$H + OH + M \rightarrow H_2O + M$	$1.1 \times 10^{-20} I^{-210}$	[23]
14	$OH + OH \rightarrow H_2O + O$	$6.2 \times 10^{-14} (T/298)^{2.0} e^{934/1}$	[10]
15	$\mathrm{OH} + \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \mathrm{HO_2}$	$2.9 \times 10^{-12} e^{-160/T}$	[10]
16	$O + O + M \rightarrow O_2 + M$	$2.76 \times 10^{-31}/T$	[23]
17	$\mathrm{HO}_2 + \mathrm{HO}_2 ightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	$2.2 \times 10^{-13} e^{600/T}$	[23]
18	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$1.9 \times 10^{-33} e^{980/T}$	[23]
19	$N + N + M \rightarrow N_2 + M$	$8.3 \times 10^{-34} e^{500/T}$	[23]
20	$O + H_0 O_0 \rightarrow OH + HO_0$	$1.4 \times 10^{-12} e^{-2000/T}$	[=0]
20	$O + H_2O_2 \rightarrow OH + HO_2$	1.4×10 c 1.45×10^{-15}	[20]
21	$O + \Pi_2 O_2 \rightarrow \Pi_2 O + O_2$ $O(d) + O_2 \rightarrow O + O + O_2$	1.45×10 2.22×10^{-10}	[22]
22	$O(d) + O_3 \rightarrow O + O + O_2$	2.55×10^{-10}	[25]
23	$O(d) + O_3 \rightarrow O_2 + O_2$	2.33×10	[25]
24	$H + HO_2 \rightarrow H_2O_2$	9×10^{-16}	[26]
25	$N + O_3 \rightarrow NO + O_2$	1×10^{-10}	[27]
26	$\mathrm{N} + \mathrm{NO}_2 ightarrow \mathrm{N}_2 + \mathrm{O}_2$	7×10^{-13}	[28]
27	$N + NO_2 \rightarrow N_2 + O + O$	9.1×10 ⁻¹³	[28]
28	$\mathrm{O} + \mathrm{O}_3 ightarrow \mathrm{O}_2 + \mathrm{O}_2$	$8 \times 10^{-12} e^{-2060/T}$	[10]
29	$\mathrm{O} + \mathrm{NO}_3 ightarrow \mathrm{O}_2 + \mathrm{NO}_2$	1×10^{-11}	[28]
30	$\mathrm{NO}_3 + \mathrm{NO}_3 \rightarrow \mathrm{O}_2 + \mathrm{NO}_2 + \mathrm{NO}_2$	$7.5 \times 10^{-12} e^{-3000/T}$	[10]
31	$\rm N + OH \rightarrow \rm NO + H$	$3.8 \times 10^{-11} e^{85/T}$	[12]
32	$N + \Omega_2 \rightarrow N\Omega + \Omega$	$4.4 \times 10^{-12} e^{-3220/T}$	12
33	$N + O + M \rightarrow NO + M$	$1.8 \times 10^{-31} (T)^{-1/2}$	[19]
34	$N O M \rightarrow NO M$	3.4×10^{-32}	[12]
25	$NO + II + M \rightarrow HNO + O$	$0.1 \times 10^{-19} \cdot 2819/T$	[12]
30 20	$NO + HO_2 \rightarrow HNO + O_2$	9.1×10 e	[12]
30	$NO + HO_2 + M \rightarrow HNO_3 + M$	$3.0 \times 10^{-0.0}$	[12]
37	$\rm NO + HO_2 \rightarrow NO_2 + OH$	$3.7 \times 10^{-12} e^{240/1}$	[12]
38	$\rm NO + N ightarrow N_2 + O$	3.1×10^{-11}	[12]
39	$\mathrm{NO} + \mathrm{NO}_3 ightarrow \mathrm{NO}_2 + \mathrm{NO}_2$	$1.6 \times 10^{-11} e^{150/T}$	[12]
40	$\rm NO + O + M \rightarrow \rm NO_2 + M$	$1.0 \times 10^{-31} (T/300)^{-1.6}$	[12]
41	$\mathrm{NO} + \mathrm{O}_3 ightarrow \mathrm{NO}_2 + \mathrm{O}_2$	$9.0 \times 10^{-13} e^{-1200/T}$	[12]
42	$\rm NO + OH + M \rightarrow HNO_2 + M$	$7.4 \times 10^{-31} (T/300)^{-2.4}$	[12]
43	$NO_2 + HO_2 + M \rightarrow HO_2NO_2$	$1.5 \times 10^{-31} (T/300)^{-3.2}$	[12]
44	$NO_2 + N \rightarrow N_2O + O$	2.4×10^{-12}	[12]
45	$NO_2 + N \rightarrow NO + NO$	6.0×10^{-12}	27
46	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	$1.4 \times 10^{-33} (T/300)^{-3.8}$	[12]
47	$NO_2 + NO_2 + M \rightarrow N_2O_5 + M$	$3.6 \times 10^{-30} (T/300)^{-4.1}$	[10]
48	$NO_2 + NO_2 \rightarrow N_2O_7$	11×10^{-12}	[27]
40	$NO_2 + O_3 + NO_2 + O_2$	$5.5 \times 10^{-12} \cdot 188/T$	[2+]
49	$NO_2 + O \rightarrow NO + O_2$	1.0×10^{-18}	[10]
50	$NO_2 + O_3 \rightarrow NO + O_2 + O_2$ $NO_3 + O_3 + M_3 + NO_3 + M_3$	$1.0 \times 10^{-31} (\pi / 200) = 1.5$	[10]
51	$NO_2 + O + M \rightarrow NO_3 + M$	$1.3 \times 10^{-0.1} (1/300)^{-1.0}$	[10]
52	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{-2450/1}$	[12]
53	$NO_2 + OH + M \rightarrow HNO_3 + M$	$2.2 \times 10^{-30} (T/300)^{-2.9}$	[12]
54	$\rm N_2O_5+M\rightarrow NO_3+NO_2+M$	$1.75 \ e^{-11100/T}(T)^{-1.83}$	[27]
55	$N_2O_5 \rightarrow NO_3 + NO_2$	$5.49 \times 10^{14} e^{-11100/T} (T)^{0.1}$	[27]
56	$N_2O_5 + H_2O \rightarrow HNO_3 + HNO_3$	5.0×10^{-21}	[12]
57	$HNO + O_2 \rightarrow NO + HO_2$	$5.25 \times 10^{-12} e^{-1510/T}$	[12]
58	$HNO_2 + OH \rightarrow NO_2 + H_2O$	$1.8 \times 10^{-11} e^{-390/T}$	[12]
59	$HNO_2 + OH \rightarrow NO_2 + H_2O$	$1.5 \times 10^{-14} e^{650/T}$	[19]
60	$HNO_3 + NO \rightarrow HNO_2 + NO_2$	7.37×10^{-21}	[12]
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N⁰	Reactions	Rate	Reference
61	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$5.0 \times 10^{-6} e^{-10000/T}$	[12]
62	$\mathrm{O} + \mathrm{O}_2 + \mathrm{M} ightarrow \mathrm{O}_3 + \mathrm{M}$	$5.6 \times 10^{-34} (T/300)^{-2.6}$	[10]
63	$\rm O + OH \rightarrow O_2 + H$	$2.3 \times 10^{-11} e^{110/T}$	[10]
64	$\rm H + \rm O_2 + \rm M \rightarrow \rm HO_2 + \rm M$	$5.4 \times 10^{-32} (T/300)^{-1.8}$	[10]
65	$NO_2 + NO_3 \rightarrow NO + NO + O_2$	$2.3 \times 10^{-13} e^{-1600/T}$	[9]
66	$\mathrm{O} + \mathrm{N_2O_5} ightarrow \mathrm{O_2} + \mathrm{N_2O_4}$	3.0×10^{-16}	[28]
67	$\rm O+HNO_3 ightarrowOH+NO_3$	3.0×10^{-17}	[29]
68	$\mathrm{O} + \mathrm{HO}_2\mathrm{NO}_2 \rightarrow \mathrm{HO}_2 + \mathrm{NO}_3$	8.6×10^{-16}	[30]
69	$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$	$1.3 \times 10^{-12} e^{380/T}$	[31]
70	${ m O}({ m d}) + { m N}_2{ m O} ightarrow { m N}_2 + { m O}_2$	4.9×10^{-11}	[27]
71	$O(d) + N_2O \rightarrow NO + NO$	6.7×10^{-11}	[27]
72	$\mathrm{HO}_2 + \mathrm{O}_3 \rightarrow \mathrm{OH} + \mathrm{O}_2 + \mathrm{O}_2$	$2.03 \times 10^{-16} (T/300)^{4.57} e^{693/T}$	[10]
73	$\rm NO+~NO~+~O_2 \rightarrow NO_2~+~NO_2$	1.4×10^{-38}	[27]
74	$\rm NO + O ightarrow O_2 + N$	$1.39 \times 10^{-37} e^{-19400/T}$	[27]
75	$O + N_2 \rightarrow NO + N$	$1.06 \times 10^{-6} e^{-38400/T}/T$	[27]
76	$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$	$2.71 \times 10^{-11} e^{-947/T} T^{-0.23}$	[27]
77	$O_2 + O_3 \rightarrow O + O_2 + O_2$	2.8×10^{-15}	[32]

Continues of Table 2

4. Results of Numerical Modeling of the Component Content of Particles in the Plasma of Volume Barrier Discharge

The calculation of the component content of particles in a discharge gap was performed for the specific power in the discharge $W_d = 0.75$ and 1.5 W/cm^3 , the transient time of the gas mixture in a discharge gap up to 4.8 s, and the temperature range from 300 to 500 K. The known experimental temperature dependences of the rates of reactions in the range 200–450 K were extrapolated to 500 K, when it was required.

In Fig. 2, the calculated maximum concentrations of the components of a gas mixture are presented for the specific power $W_d = 1.5$ W/cm³, gas mixture temperature 425 K, air relative humidity 80%, and various transient times of the gas mixture in a discharge gap -0.3, 1.2, and 2.4 s (the time increases from top to bottom). The concentrations of the H and HNO components are not shown in the figure, because their values do not exceed 10^8 cm⁻³. One can see from the figure that

- components O₃, N₂O, N₂O₄, and HNO₃ exhibit the highest concentrations $\approx (1 \div 5) \times 10^{16} \text{ cm}^{-3}$;

- concentrations of HNO₂, NO, and NO₂ reach about $10^{14} - 10^{15} \text{ cm}^3;$

 concentrations of the majority of components exhibit a weak dependence on the transient time of a gas mixture in a discharge gap;

- only the concentrations of N₂O₄, HNO₃, and N₂O possess the essential dependence on the transient time of a gas mixture - at the time increase from 0.3 to 2.4 s, their concentrations grow up practically by one order of magnitude.

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Fig. 2. Concentrations of components of the gas mixture calculated for the specific power $W_d = 1, 5 \text{ W/cm}^3$, gas mixture temperature 425 K, air relative humidity 80%, and transient time of the gas mixture in a discharge gap of 0.3, 1.2, and 2.4 s (the time increases from top to bottom)

In Fig. 3, the dependences of the concentrations of components on the transient time of the gas mixture in a discharge gap are presented for $W_d = 1.5 \text{ W/cm}^3$ and the gas mixture temperature 425 K. One can see from the figure that, at the initial time moment of the discharge development (up to $\sim 10^{-4} \div 10^{-3} \text{ s}$), the concentrations of all components grow up linearly with time. Then the character of the dependences begins to change. Whereas the concentrations of N₂O₄, N₂O, HNO₃, and HNO₂ still possess a monotonous growth with time, those of NO, N,



Fig. 3. Calculated dependences of the concentrations of different components on the transient time of the gas mixture in a discharge gap. The specific power in the discharge $W_d = 1.5 \text{ W/cm}^3$, gas mixture temperature 425 K, and air relative humidity 80%

O, OH, and HO₂ reach their maximum values, and then their decrease occurs, so that quasi-stationary values are reached after about 0.1 s. The concentrations of O₃, NO₃, and N₂O₅ reach their maxima in about 0.5 - 1.0 s after the appearance of the mixture in the discharge gap. Then their decrease begins. The concentrations of the other components, such as H₂O₂ and NO₂, reach their quasi-stationary values in 0.01 - 0.1 s. The decrease of the specific power down to 0.75 W/cm³ has practically no influence on the temporal dependence of the concentrations of gas mixture components; it just leads to some increase of the typical durations required for reaching the maximum values, and to some decrease of quasi-stationary values of the concentrations.

In Fig. 4, the numerically obtained dependences of the concentrations of O_3 , HNO₃, HNO₂, N₂O₅, H₂O₂, and NO₃ components on the gas medium temperature for various transient times in a discharge gap at the specific power $W_d = 1.5$ W/cm³ are presented. One can see that the behavior of the concentrations does not depend on the transient time of a gas medium in the discharge. One can see also that the HNO₃ concentration possesses a weak dependence on temperature, as compared with the other components. At the same time, due to the efficient oxidation of NO in reaction 41 (Table 2), the O₃ concentration decreases by more than two orders of magnitude with the temperature growth. A greater decrease rate (by 4–5 orders) with the temperature growth is exhibited by the N₂O₅



Fig. 4. Calculated dependences of the concentrations of O₃, H₂O₂, NO₃, N₂O₅, HNO₃, and HNO₂ components on the gas medium temperature for different transient times of a gas mixture in the discharge: a - 0.3 s, b - 1.2, c - 2.4. Specific power in the discharge $W_d = 0.75$ W/cm³, and the air relative humidity is 80%

concentration. The main process which results in the decomposition of N_2O_5 to NO_3 and NO_2 is reaction 54 (Table 2). The hydrogen peroxide concentration also decreases as temperature grows. The temperature dependence of the H_2O_2 concentration is mainly determined by the competition of the following processes of birth and death of particles (Table 2). The rates of birth and death of hydrogen peroxide in those reactions decrease with increase in temperature.

The HNO₂ concentration is practically independent of the gas medium temperature and the transient time of a gas mixture in the discharge and, at $T \approx 425$ K, approximately equals 10^{14} cm⁻³ for $W_d = 1.5$ W/cm³ and 7×10^{13} cm⁻³ for $W_d = 0.75$ W/cm³.

5. Experimental Results and Their Discussion

Prior to the description of the experimental results and their discussion, it is worth to determine the difference in the statement of the problems in theory and in experiment and to formulate conditions, under which the comparison of experimental and theoretical results is correct. The most essential difference between the conditions of the experiment and those accepted in the calculation consists in the fact that, under experimental conditions, a gas mixture is permanently pumped through the discharge, whereas it is assumed in the theory that the mixture is permanently located at the discharge space. Due to this difference, it is impossible to experimentally reproduce the theoretical dependences of the concentrations of active particles on the transient time of a gas mixture in the discharge (Fig. 3). As was already mentioned, the experiments were performed for three values of volume pumping rates which corresponded to the mean transient times of particles in the discharge gap $\tau = 0.3, 1.2, \text{ and } 2.4 \text{ s.}$ Thus, we can compare the experimental and theoretical results only at separate points in Fig. 3 which correspond to the time intervals mentioned above. Taking into account the fact that an uncertainty in the calculated rates for the majority of reactions could influence the temporal dependence behavior, it would be reasonable to compare the stationary values of concentrations obtained in the experiment and in calculations. For that purpose, it would be necessary that the concentrations of particles reach their stationary values for the transient time of a gas mixture in the discharge. As one can see from Fig. 3, this condition is fulfilled for the majority of components of the gas mixture. However, this condition is not fulfilled for HNO₃, N₂O₂, and N₂O, and thus one could expect that the experimentally determined concentrations of three these components would be less than their theoretical values.

Another essential difference between the theory and the experiment consists in that the reactions at the surface of the discharge electrodes are not taken into account in the calculations. However, some reactions at the electrode surface can be rather efficient, and this can result in a significant mismatch between the theoretical and experimental values for certain components.



Fig. 5. Dependence of the nitrogen rotational temperature on the discharge glowing duration for different transient times of a gas mixture in the discharge gap τ . The specific power in a discharge $W_d = 1.5 \text{ W/cm}^3$, and the air relative humidity is about 80%

The essential mismatch between the theory and the experiment may be due to incorrect calculations of the rates of certain reactions. As was noted above, the cross sections for many reactions were unknown. For this reason, they were calculated by the authors using certain assumptions.

Finally, it should be also noted that the gas mixture temperature in the calculations was introduced as a fitting parameter, whereas, in the experiment, depended on the discharge glowing duration. it To estimate the gas mixture temperature, the rotational temperature of nitrogen molecules $T_{\rm rot}$ was experimentally measured, because this value is close to the translational temperature of the mixture [33]. For that purpose, the 0–0 transition of the second positive system of nitrogen $N_2(C^3\Pi_u \rightarrow B^3\Pi_g), \lambda =$ 337.13 nm, was used. The measurements of rotational temperature were performed for different values of the transient time of a gas mixture in the discharge gap τ and the discharge glowing duration t. The results of measurements performed at the specific power W_d = 1.5 W/cm^3 and the transient time of the gas mixture in a discharge gap $\tau \approx 0.3$, 1.2, and 2.4 s are presented in Fig. 5 (each point in the figure represents the data averaged for three measurements). One can see from the figure that the dependence of $T_{\rm rot}$ on the discharge glowing duration t does not differ essentially for the measurements with different transient times in the discharge. Particularly, the glowing rotational temperature reaches its maximum value ≈ 430 K in all



Fig. 6. Experimental dependences of O₃, HNO₃, and HNO₂ concentrations on the discharge glowing duration t for different transient times of a gas mixture in the discharge τ : a - 0.3 s, b - 1.2, c - 2.4

three regimes approximately at the 25-th minute of the discharge. (At the specific power $W_d = 0.75 \text{ W/cm}^3$, the dependence has the same form, but the maximum rotational temperature is somewhat lower).

It should be noted that the typical time of $T_{\rm rot}$ coming to a stationary level essentially exceeds the typical transient time of a mixture in the discharge. This, at first sight, the mismatch is due to the influence of electrodes of the discharge which provide a significant thermal inertia to the system. Accordingly to this consideration, the temperature of the electrodes measured by us possesses the same dependence on the discharge glowing duration t and is close by its value to the rotational temperature.

Such temporal dependence of the temperature of a mixture can also result in the corresponding temporal dependences of the concentrations of active particles. Indeed, the experimentally measured dependences of the O₃, HNO₃, and HNO₂ concentrations on the discharge glowing duration at $W_d = 1.5$ W/cm³ (Fig. 6, each point represents the data averaged for three measurements) possess the same behavior as the temporal dependence of the rotational temperature $T_{\rm rot}$: the time of approaching the stationary regime for all three components coincides with the typical time of heating of the gas mixture.

The comparison of experimental dependences (Fig. 6) with theoretically obtained ones (Fig. 4) shows that the behavior of these dependences is the same for HNO_3 and HNO_2 . But, in case of O_3 , these dependences are different: the ozone concentration decreases with the temperature growth in the theory and is practically independent of it in experiment.

Let us now proceed to our main task, the comparison of the experimentally obtained concentrations of active particles with the corresponding theoretical values. One can see from Figs.4 and 6 that the best qualitative and quantitative agreement between the experiment and the calculation is observed for a gas mixture temperature of about 425 K. Correspondingly to the calculation, the measured O_3 concentration is practically independent of the transient time of the mixture in a discharge and has a mismatch of no more than 50% with the calculated value. The experimental dependence of the HNO₃ concentration on the transient time of the mixture in a discharge also agrees with the calculation. However, the numerical value of the concentration in the first case is notably less than that in the second one. The best agreement is observed for the transient time of the mixture in a discharge $\tau = 2.4$ s: in this regime, $n_{\rm theor}/n_{\rm exp} \approx 3$. With decrease in the transient time in a discharge down to 0.3 s, the ratio $n_{\rm theor}/n_{\rm exp}$ becomes worse and comprises ≈ 4.5 . Such a mismatch between the experiment and the theory is, first of all, explained by the fact that the approach time of the HNO_3 concentration to the stationary regime exceeds the typical transient time of the mixture in a discharge. This consideration is approved by the fact that the mismatch between the experiment and the calculation decreases with increase in the transient time of the mixture in a discharge. The worst agreement between the experiment and the calculation is observed for the HNO_2 component. In this case, the experimentally measured concentrations significantly exceed the theoretical values. Particularly, for the transient time of the mixture in a discharge $\tau = 0.3$ s, the ratio $n_{\rm exp}/n_{\rm theor}$ is about 27, and it

comprises about 150 for $\tau = 2.4$ s. It is possible to list the most probable reasons for such strong mismatch:

- The HNO_2 decay rate in reaction R25 (Table 1) obtained by means of calculations may be significantly overestimated;

— It is possible that, in addition to reaction R42 (Table 2) in the discharge volume which is taken into account in the theory, the same reaction occurs at the surface of the discharge electrodes. Such a possibility is evidenced by the fact that a mismatch between the theory and the experiment increases with increase in the transient time of the mixture in a discharge.

The decrease of the specific power W_d from 1.5 to 0.75 W/cm³ does not lead to a change of the experimentally measured dependences of the O_3 , HNO_3 , and HNO_2 concentrations on the discharge glowing duration. Accordingly to the calculation, the concentrations of these components diminish with decrease in the specific power. However, the mismatch between the theoretical and experimental values of the concentrations increases in this case. As in the case of a higher power, the strongest mismatch is observed for the HNO₂ component. The most probable reason for such an increase of the mismatch between the theory and the experiment is as follows. With decrease in the specific power in the discharge, the number of microdischarges is simultaneously decreased, and our model provides a less correct description of the kinetics of the processes running in the discharge plasma.

6. Conclusions

We have proposed a new approach to the calculation of the component content of active particles in filamentary volume barrier discharge. In the a conventional calculational model, the plasma kinetics is calculated firstly for separate current channels of microdischarges. Then, after a delay of about the diffusion time (~ 10^{-3} s), the averaging of the concentrations of all components over the entire volume of a discharge gap is performed. Unlike the conventional model, the main idea of our approach consists in the immediate averaging of the power introduced into the discharge over the entire discharge volume. The advantage of this approach is due to the absence of fitting parameters related to the filamentary nature of the barrier discharge and the correct description of the processes possessing a linear behavior with respect to the electron concentration, as well as of the non-linear processes with the reaction time being greater than the diffusion time.

The results of numerical simulations are in a quantitative agreement with the experiment for O_3 and in a qualitative one for HNO_3 and HNO_2 . From our viewpoint, the possible reasons for the mismatch between the theoretical and experimental values of the HNO_3 and HNO_2 concentrations are:

 neglecting the processes running at the surface of the discharge electrodes;

— the absence of experimental data for most cross sections of elementary processes, which leads to the error upon the use of calculated cross sections.

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ДОСЛІДЖЕННЯ КОМПОНЕНТНОГО СКЛАДУ АКТИВНИХ ЧАСТИНОК У БАР'ЄРНОМУ РОЗРЯДІ У ВОЛОГОМУ (RH≈80%) ПОВІТРІ

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Резюме

Наведено результати експериментального та теоретичного дослідження компонентного складу активних частинок об'ємного бар'єрного розряду у вологому (RH≈80%) повітрі. Для опису кінетики плазми запропоновано нову чисельну модель, в якій потужність, що надходить у розрядний проміжок, відразу усереднюється по всьому розрядному об'єму. Отримано чисельні залежності компонентного складу частинок, що утворюються в розряді, від температури газового середовища, часу перебування газової суміші в розрядному проміжку і питомої потужності. Експериментально виміряно концентрації О3, HNO3 і HNO2 при питомих потужностях $W_d = 1,5$ та 0,75 Вт/см³. Виміряно також обертальну температуру молекул азоту $T_{\rm rot}$. Порівняння експериментальних даних із розрахунком показало, що кількісного узгодження досягнуто для концентрації О3, для концентрації HNO₃ узгождження лише якісне. Концентрація $\mathrm{HNO}_2,$ виміряна експериментально, суттєво перевищує теоретично розраховану. Вказано основні причини такої неузгодженості. Показано також, що експериментальні дані краще узгоджуються з розрахунком при підвищенні питомої потужності та збільшенні часу перебування газової суміші в розрядному проміжку.