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Kinetic scheme of the non-equilibrium discharge in nitrogen–oxygen mixtures

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Abstract. A kinetic scheme for non-equilibrium discharge in nitrogen–oxygen mixtures is developed, which almost wholly describes chemical transformations of particles in the cold ($200\,\mathrm{K} \leqslant T \leqslant 500\,\mathrm{K}$) vibrationally unexcited gas. The kinetic scheme includes processes of excitation of electronic states, destruction and ionization of heavy particles by electron impact, associative ionization, electron attachment and detachment, electron–ion and ion–ion recombination, chemical transformations of neutral particles (in ground and excited electronic states) and ion conversion. On the basis of kinetic modelling in the framework of the kinetic scheme proposed, the influence of the electronic excitations of nitrogen molecules and atoms on air composition dynamics is analysed.

1. Introduction

When solving numerous problems of electrophysics, gaseous lasers physics, plasma chemistry, atmospheric physics and so on, a detailed consideration of the kinetics of non-equilibrium plasma-chemical processes in nitrogen–oxygen mixtures is essential. Channels determining the balance of neutral and charged particles in a non-equilibrium plasma are highly diverse. A vast collection of experimental and theoretical information on separate elementary reactions has been accumulated, but in spite of this, the question of whether the description of physicochemical phenomena on the basis of available kinetic schemes is satisfactory has still not been clarified in a number of cases.

The desire to formulate the most complete variants of kinteic schemes of processes in non-equilibrium nitrogen–oxygen plasma is stimulated in many respects by the need to examine the ecological consequences of realization of expensive projects involving a prolonged influence of powerful electromagnetic radiation on the atmosphere. Specifically, the project of radiowave re-translation by artificial ionized regions [1,2] should be counted among such projects. It envisages a prolonged maintenance by rather intensive microwave radiation of discharges in the stratosphere which can result in a local degradation of the ozone layer [3]. The requirement for a complete non-equilibrium microwave discharge kinetic scheme for atmospheric air is also important in connection with the problem of electrode-free long-distance energy transfer [4,5].

The majority of authors have modelled plasma-chemical processes proceeding in electrical discharges in airlike mixtures on the basis of reactions with nitrogen and oxygen atoms being formed by electron impact dissociation of the initial molecules. In some cases (see, for instance, [6]) the appearance of electronically excited atoms N(^{2}D) effectively being oxidized by oxygen molecules is taken into account in reactions of the type $N_2 + e \Rightarrow 2N + e$. The influence of oxygen molecules in the state $a^1\Delta_g$ on the process of ozone component formation in the afterglow period was also considered. The role of electronically excited nitrogen molecules in an atmosphere with changing chemical composition is hardly being discussed, but in [7] it was shown for non-equilibrium pulsed discharge in an airlike mixture $[N_2]:[O_2] = 4:1$ that, under conditions close to breakdown, reactions with such excited species radically affect the physicochemical kinetics.

This work undertakes an attempt to form a kinetic scheme of non-equilibrium discharge in nitrogen–oxygen mixtures, which could almost wholly describe chemical transformations of particles in the cold ($220\,\mathrm{K} \leqslant T \leqslant 500\,\mathrm{K}$) vibrationally unexcited gas. When selecting experimental and theoretical data on various reactions' rate constants a preference was made, if possible, in favour of fundamental review articles containing a critical analysis of accumulated information and of the most recent publications, taking into account the prehistory of the question under consideration and performed on the basis of the latest achievements of modern knowledge. Results of calculations taking into account the influence of electronic excitations of nitrogen molecules and atoms on air composition dynamics under

pulsed discharge in the framework of the kinetic scheme proposed are also presented.

2. The kinetic scheme of the non-equilibrium discharge

2.1. Excitation of electronic states, destruction and ionization of neutral particles by electron impact

The inclusion of all the electron impact electronic–vibrational excitation reactions of the nitrogen–oxygen mixture particles in the discharge scheme is an original and very laborious task. Its full solution, considering chemical and ion kinetics, is believed to be unexpedient in many cases. I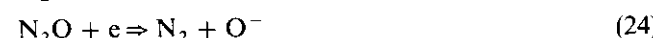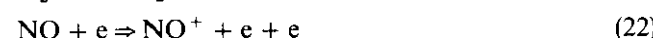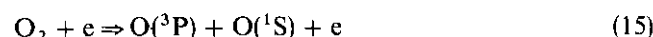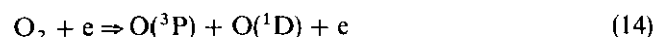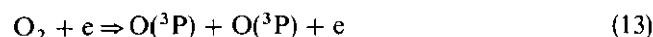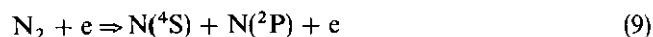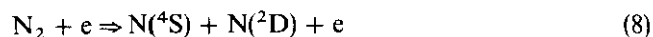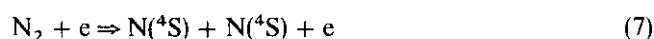ndeed, for the greater part, electronic states of particles are short-lived with respect to quenching processes, radiative transitions and predissociation processes. This circumstance permits to simplify the scheme of molecules and atoms excitation by electron impact, in not too rarefied media, without any noticable damage. In the framework of such a scheme, we propose considering only states sufficiently stable with respect to stepwise deactivation processes that they can play a noticeable role in the gas particles' chemical transformations balance. As the analysis has shown, the states $A^3\Sigma_u^+$, $B^3\Pi_g$, $a'^1\Sigma_u^-$ and $C^3\Pi_u$ for N_2 molecules, the states $a^1\Delta_g$ and $b^1\Sigma_g^+$ for O_2 molecules, the states ^2D and ^2P for N atoms and the states ^1D and ^1S for O atoms should be attributed to such states. Their population occurs not only by direct electron impact excitation but also due to quenching of near higher-lying states by unexcited molecules (see [8] for more details). According to the aforesaid, the kinetics of the electronic states' excitation and dissociation and ionization of the nitrogen–oxygen mixture neutral particles by electron impact can be described by the set of reactions

$$N_2 + e \longrightarrow N_2(A) + e, \tag{1}$$

$$N_2 + e \xrightarrow{\hspace{1cm}} N_2(B) + e \tag{2}$$
$$\longrightarrow N_2(W^3, B') + e$$
$$\xrightarrow{\text{st}} N_2(B)$$

$$N_2 + e \xrightarrow{\hspace{1cm}} N_2(a') + e \tag{3}$$
$$\longrightarrow N_2(a, w^1) + e$$
$$\xrightarrow{\text{st}} N_2(a')$$

$$N_2 + e \xrightarrow{\hspace{1cm}} N_2(C) + e \tag{4}$$
$$\longrightarrow N_2(E, a'') + e$$
$$\xrightarrow{\text{st}} N_2(C).$$
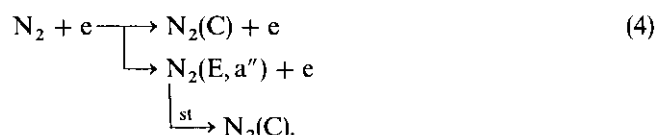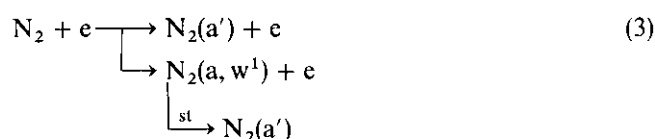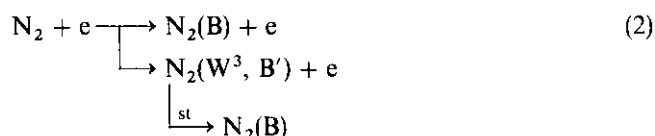
Higher resonant–radiative states of the N_2 molecule are strongly predissociated [9].

$$O_2 + e \Rightarrow O_2(a) + e \tag{5}$$

$$O_2 + e \Rightarrow O_2(b) + e \tag{6}$$

$$N_2 + e \Rightarrow N(^4S) + N(^4S) + e \tag{7}$$

$$N_2 + e \Rightarrow N(^4S) + N(^2D) + e \tag{8}$$

$$N_2 + e \Rightarrow N(^4S) + N(^2P) + e \tag{9}$$

$$N(^4S) + e \Rightarrow N(^2D) + e \tag{10}$$

$$N(^4S) + e \Rightarrow N(^2P) + e \tag{11}$$

$$N(^2D) + e \Rightarrow N(^2P) + e \tag{12}$$

$$O_2 + e \Rightarrow O(^3P) + O(^3P) + e \tag{13}$$

$$O_2 + e \Rightarrow O(^3P) + O(^1D) + e \tag{14}$$

$$O_2 + e \Rightarrow O(^3P) + O(^1S) + e \tag{15}$$

$$O(^3P) + e \Rightarrow O(^1D) + e \tag{16}$$

$$O(^3P) + e \Rightarrow O(^1S) + e \tag{17}$$

$$O(^1D) + e \Rightarrow O(^1S) + e \tag{18}$$

$$O_3 + e \Rightarrow O_2 + O + e \tag{19}$$

$$N_2 + e \Rightarrow N_2^+ + e + e \tag{20}$$

$$O_2 + e \Rightarrow O_2^+ + e + e \tag{21}$$

$$NO + e \Rightarrow NO^+ + e + e \tag{22}$$

$$O_2 + e \Rightarrow O^- + O \tag{23}$$

$$N_2O + e \Rightarrow N_2 + O^- \tag{24}$$

Here and after, for the purpose of shortening notation, the electronic states of molecules and atoms are designated by a single letter.

The rate constant values of reactions (1)–(24) are determined from kinetic calculations based on solving Boltzmann's equation for the electron energy distribution function. We will cite the results of such calculations for the airlike mixture $[N_2]:[O_2] = 4:1$, in a direct electric field. Conformably to the discharge scheme proposed, they can be represented according to [10] in the form of approximation formulae:

$$\log k_1 = -8.4 - 14/\vartheta$$

$$k_2 \simeq k_{e-B} + k_{e-W^3} + k_{e-B'}$$

$$\log k_{e-B} = -8.2 - 14.8/\vartheta$$

$$\log k_{e-W^3} = -8.3 - 15.4/\vartheta$$

$$\log k_{e-B'} = -8.7 - 16.8/\vartheta;$$

$$k_3 \simeq k_{e-a'} + k_{e-a} + k_{e-w^1}$$

$$\log k_{e-a'} = -8.8 - 16.7/\vartheta$$

$$\log k_{e-a} = -8.5 - 17.4/\vartheta$$

$$\log k_{e-w^1} = -8.7 - 17.5/\vartheta$$

$$k_4 \simeq k_{e-C} + k_{e-E} + k_{e-a''}$$

$$\log k_{e-C} = -8.2 - 21.1/\vartheta$$

$$\log k_{e-E} = -10.1 - 25.4/\vartheta$$

$$\log k_{e-a''} = -9.2 - 26.2/\vartheta$$

$$\log k_5 = \begin{cases} -9 - 5.2/\vartheta & \text{at } \vartheta < 4 \\ -10.2 - 0.35/\vartheta & \text{at } \vartheta > 4 \end{cases}$$

$$\log k_6 = \begin{cases} -9.5 - 6/\vartheta & \text{at } \vartheta < 3 \\ -11.2 - 0.72/\vartheta & \text{at } \vartheta > 3 \end{cases}$$

$$\log k_{13} \simeq \log k_{(X \to A + c' + C^3)} = -7.9 - 13.4/\vartheta$$

$$\log k_{14} \simeq \log k_{(X \to B^3 + {}^3\Pi_u)} = -8 - 16.9/\vartheta$$

$$\log k_{15} \simeq \log k_{(X \to 9.7 - 12.1 \text{ eV})} = -8.8 - 11.9/\vartheta$$

$\log k_{20} = -8.3 - 36.5/\vartheta$

$\log k_{21} = -8.8 - 28.1/\vartheta$

$\log k_{23} = \begin{cases} -9.3 - 12.3/\vartheta \text{ at } \vartheta > 8 \\ -10.2 - 5.7/\vartheta \text{ at } \vartheta > 8. \end{cases}$

The values of a parameter $\vartheta = E/n$ in these formulae are taken in units of $10^{-16}\,\text{V cm}^2$ (E is the electric field strength in V cm^{-1}, n is the concentration of N_2 and O_2 molecules in cm^{-3}); k_{e-a} is a rate constant of electron impact excitation of the αth electronic state of the N_2 molecule; $k_{(X \to A + c^1 + C^3)}$, $k_{(X \to B^3 + ^3\Pi_g)}$ and $k_{(X \to 9.7-12.1\,eV)}$ are rate constants of O_2 molecule dissociation through electronically excited levels higher than the $b^1\Sigma_g^+$ level. The approximations given in [10] are correct in the region $3 \leqslant \vartheta < 30$.

Rate constants values of the reactions (7)–(9) and (10)–(12) can be obtained by using data on these reactions' cross sections adduced correspondingly in [11] and [12]. This allows a correct description of discharge formation of the excited nitrogen atoms playing a significant role in the overall balance of the mixture particles' chemical transformations.

It should be noted that dissociation of the N_2 molecule by electron impact takes place in two stages: first electrons excite corresponding electronic–vibrational levels of the molecule, and then the particle may transfer from these levels to the decay electronic term. In the frame of the scheme indicated, the rate of the dissociation reaction is limited by the second stage of the process. Thus, if the gas is dense enough, then due to the quick quenching of electronically excited molecules, the efficiency of the N-atom production may be much lower than in the hypothetical case of instantaneously proceeding to the final stage of the predissociation. According to [9] this should be ascribed, on the whole, to reaction (7).

The rate constant of ozone dissociation [13] by electron impact (19) is approximately ten times the rate constant of molecular oxygen dissociation:
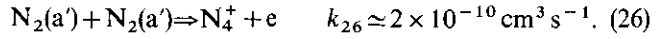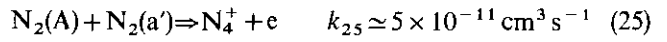
$$k_{19} \simeq 10(k_{13} + k_{14} + k_{15})$$

Rate constants of the oxygen atom excitation reactions (16)–(18) may be determined with the aid of the corresponding cross sections calculated in [12]. Cross sections of electron impact ionization of NO and electron dissociative attachment to N_2O are given in [14] and [15].

It should be taken into account that, in the case under consideration, threshold kinetic processes of electron interaction with neutral particles of the nitrogen–oxygen mixture are not exhausted by reactions (1)–(24). Conditions may be realized when this set of reactions must be supplemented with stepwise excitation and ionization processes, and also with processes of electron interaction with other components of the mixture.
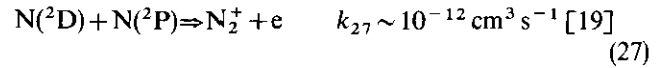
2.2. Associative ionization

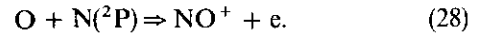Investigations devoted to the stability of the non-self-consistent discharge in pure nitrogen and in nitrogen with oxygen admixtures under high pressure [16, 17] have revealed the possibility of a determining influence of associative ionization processes of electronically excited metastable species on the discharge development (see [8]). In the proposed kinetic scheme, such processes are represented by the reactions [18]

$N_2(A) + N_2(a') \Rightarrow N_4^+ + e \qquad k_{25} \simeq 5 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1}$ (25)

$N_2(a') + N_2(a') \Rightarrow N_4^+ + e \qquad k_{26} \simeq 2 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1}.$ (26)

Additional channels of the associative ionization are

$N(^2D) + N(^2P) \Rightarrow N_2^+ + e \qquad k_{27} \sim 10^{-12}\,\text{cm}^3\,\text{s}^{-1}$ [19] (27)

and

$$O + N(^2P) \Rightarrow NO^+ + e. \qquad (28)$$

The rate constant of reaction (28) can be set equal in order of magnitude to the rate constant of the high-threshold reaction $O + N(^2D) \Rightarrow NO^+ + e$ [20], on condition that the activation barrier is absent. Then we get $k_{28} \sim 10^{-12}\,\text{cm}^3\,\text{s}^{-1}$.

2.3. Recombination of electrons and positive ions

The highest rate in this group of processes is usually characteristic of the dissociative recombination reactions

$N_4^+ + e \Rightarrow N_2 + N_2$

$\qquad k_{29} = 2 \times 10^{-6} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}.$ [21] (29)
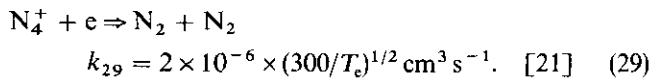
Here and after the electron temperature T_e means the quantity $(2\varepsilon_e)/(3k)$ (ε_e is the mean electron energy); T_e is in kelvin

$O_4^+ + e \Rightarrow O_2 + O_2$

$\qquad k_{30} = 1.4 \times 10^{-6} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}$ [21] (30)

$NO^+ \cdot NO + e \Rightarrow NO + NO$

$\qquad k_{31} = 1.3 \times 10^{-6} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}$ [21] (31)

$NO^+ \cdot N_2 + e \Rightarrow NO + N_2 \qquad k_{32} \to k_{31}$ (32)

$NO^+ \cdot O_2 + e \Rightarrow NO + O_2 \qquad k_{33} \to k_{31}$ (33)

$O_2^+ \cdot N_2 + e \Rightarrow O_2 + N_2 \qquad k_{34} \to k_{31}$ (34)

$NO_2^+ + e \Rightarrow NO + O$

$\qquad k_{35} = 2 \times 10^{-7} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}$ [22] (35)

$N_2O^+ + e \Rightarrow N_2 + O \qquad k_{36} \to k_{35}$ (36)

$N_3^+ + e \Rightarrow N_2 + N \qquad k_{37} \to k_{35}$ (37)
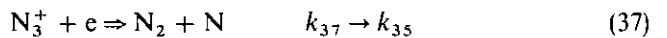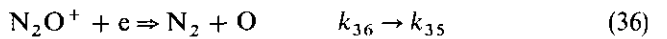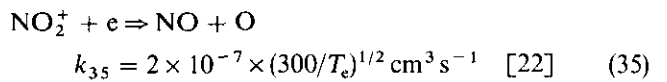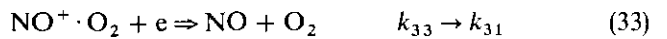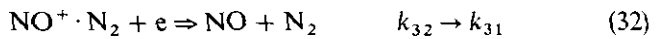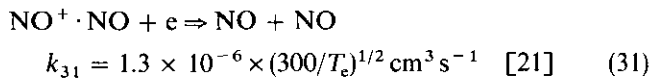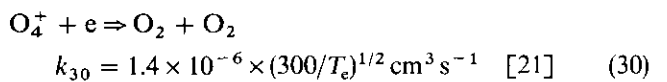
(according to [23] there should be fulfilled an inequality $k_{37} \ll 3 \times 10^{-6}\,\text{cm}^3\,\text{s}^{-1}$);

$N_2^+ + e \Rightarrow N + N$

$\qquad k_{38} = 2.8 \times 10^{-7} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}$ [22] (38)

$N_2^+ + e \Rightarrow N + N(^2D)$

$\qquad k_{39} = 2 \times 10^{-7} \times (300/T_e)^{1/2}\,\text{cm}^3\,\text{s}^{-1}$ [20] (39)

$O_2^+ + e \Rightarrow O + O$

$$k_{40} = 2 \times 10^{-7} \times (300/T_e)\,cm^3\,s^{-1} \quad [24] \quad (40)$$

$NO^+ + e \Rightarrow N + O$

$$k_{41} = 4 \times 10^{-7} \times (300/T_e)^{1.5}\,cm^3\,s^{-1} \quad [24] \quad (41)$$

$NO^+ + e \Rightarrow N(^2D) + O$

$$k_{42} = 3 \times 10^{-7} \times (300/T_e)\,cm^3\,s^{-1} \quad [20] \quad (42)$$
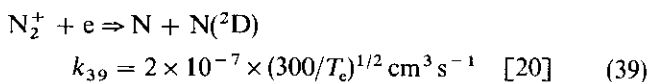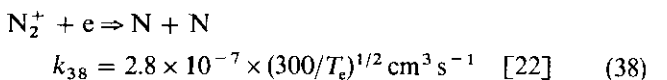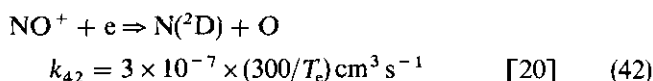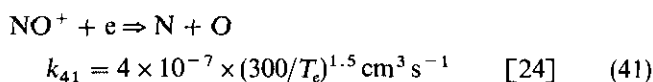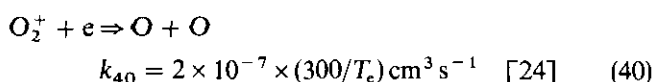
Electron–ion recombination is also possible in three-particle processes:

$$e + e + A^+ \Rightarrow e + A \quad (43)$$

$$e + A^+ + M \Rightarrow A + M \quad (44)$$
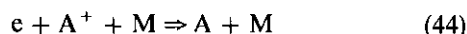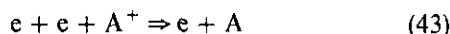
where $A^+ = N_2^+, O_2^+, NO^+, N^+, O^+$; $M = N_2, O_2$;

$$k_{43} = 10^{-19} \times (300/T_e)^{4.5}\,cm^6\,s^{-1} \quad [25]$$

$$k_{44} = 6 \times 10^{-27} \times (300/T_e)^{1.5}\,cm^6\,s^{-1} \quad [26]$$

2.4. Electron attachment and detachment processes

Under electric field the electron-loss processes with formation of negative ions are determined basically by the high-threshold reaction of electron dissociative attachment to oxygen (23) and reactions

$$e + O_2 + O_2 \Rightarrow O_2^- + O_2 \quad (45)$$

$$e + O_2 + N_2 \Rightarrow O_2^- + N_2 \quad (46)$$
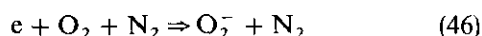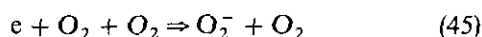
An approximation of experimental data adduced in [27] gives the following expressions for k_{45} and k_{46}:

$$k_{45} = 1.4 \times 10^{-29} \times \frac{300}{T_e} \times \exp\left(-\frac{600}{T}\right)$$
$$\times \exp\left(\frac{700 \times (T_e - T)}{T_e \times T}\right)\,cm^6\,s^{-1}$$

$$k_{46} = 1.07 \times 10^{-31} \times \left(\frac{300}{T_e}\right)^2 \times \exp\left(-\frac{70}{T}\right)$$
$$\times \exp\left(\frac{1500 \times (T_e - T)}{T_e \times T}\right)\,cm^6\,s^{-1}.$$

Since cross sections of reactions (45) and (46) have the greatest values in the low-energy region, the employment of the approximative dependences of their rate constants on the electron temperature holds under an electric field. From another point of view, three-body attachment rate constants can be determined by averaging these processes' cross sections over the electron energy distribution function. On the basis of this approach [10], an approximation formula for the nitrogen–oxygen mixture $[N_2]:[O_2] = 4:1$ has been derived:

$$k_{45} = (4.7 - 0.259) \times 10^{-31}\,cm^6\,s^{-1}$$

correct in the area $1 \leqslant \vartheta \leqslant 10$.

With the appearance of oxygen atoms, ozone and nitrogen oxides, an influence upon the negative-ion balance can be exerted by the following reactions:

$e + O + O_2 \Rightarrow O^- + O_2$

$$k_{47} = 10^{-31}\,cm^6\,s^{-1} \quad [28,29] \quad (47)$$

$e + O + O_2 \Rightarrow O + O_2^-$

$$k_{48} = 10^{-31}\,cm^6\,s^{-1} \quad [30] \quad (48)$$

$e + O_3 + O_2 \Rightarrow O_3^- + O_2$

$$k_{49} \leqslant k_{45} \quad [31] \quad (49)$$

$e + O_3 \Rightarrow O_2^- + O$

$$k_{50} = 10^{-9}\,cm^3\,s^{-1} \quad [32] \quad (50)$$

$e + O_3 \Rightarrow O^- + O_2$

$$k_{51} = 10^{-11}\,cm^3\,s^{-1} \quad [33] \quad (51)$$

$e + NO_2(+M) \Rightarrow NO_2^-(+M)$

$$k_{52} \sim 3 \times 10^{-11}\,cm^3\,s^{-1} \quad [31] \quad (52)$$
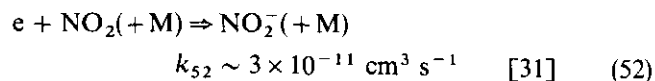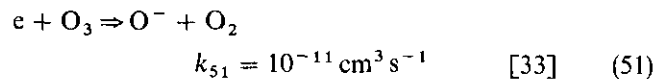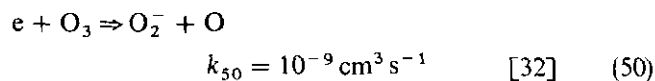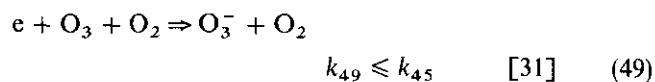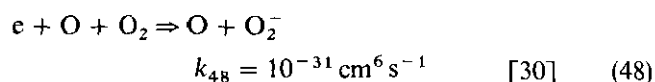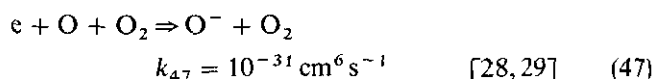
Electron attachment to the NO_2 molecule actually has a three-particle nature, but the intermediate state $(NO_2^-)^*$ has a long lifetime, so reaction (52) may be treated as a two-particle one over a wide range of gas pressure [27,31].

$$e + NO + M \Rightarrow NO^- + M. \quad (53)$$
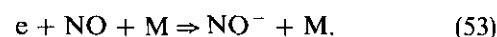
The rate constant of this reaction for $M = N_2, O_2$ is unknown. On the basis of data for other gases [27] one may accept the approximation $k_{53} \simeq 10^{-30}\,cm^6\,s^{-1}$. From [33],

$e + NO_2 \Rightarrow O^- + NO$

$$k_{54} = 10^{-11}\,cm^3\,s^{-1} \quad (54)$$

$e + N_2O + N_2 \Rightarrow N_2O^- + N_2$

$$k_{55} = [4.72(T_e(eV) + 0.412)^2 - 1.268] \times 10^{-31}\,cm^6\,s^{-1}. \quad (55)$$
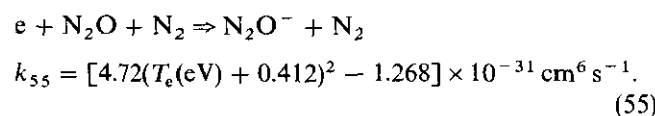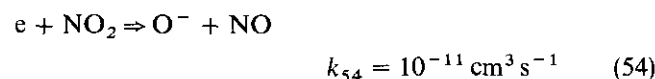
The detachment of electrons from the O^- ions by collisions with unexcited particles N_2 and O_2 under conditions interesting for us (when the gas temperature is not too high) practically does not occur (see [34]). As for the O_2^- ion, on account of lesser electron–O_2 affinity energy in comparison with the O atom reactions [24],

$O_2^- + N_2 \Rightarrow O_2 + N_2 + e$

$$k_{56} = 1.9 \times 10^{-12} \times (T/300)^{0.5} \times \exp(-4990/T)\,cm^3\,s^{-1} \quad (56)$$

$O_2^- + O_2 \Rightarrow O_2 + O_2 + e$

$$k_{57} = 2.7 \times 10^{-10} \times (T/300)^{0.5} \times \exp(-5590/T)\,cm^3\,s^{-1} \quad (57)$$
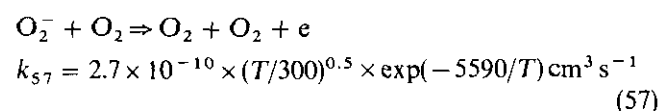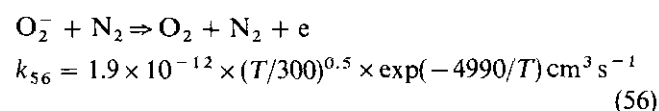
became noticable already at $T \simeq 400\,K$.

The electron detachment process effectively proceeds, when electronically excited molecules of nitrogen and oxygen are accumulated in the gas. In that case, the detachment mechanism is determined by the reactions

$O_2^- + O_2(a) \Rightarrow O_2 + O_2 + e$

$$k_{58} = 2 \times 10^{-10}\,cm^3\,s^{-1} \quad [24,25] \quad (58)$$

$O_2^- + O_2(b) \Rightarrow O_2 + O_2 + e$

$$k_{59} = 3.6 \times 10^{-10}\,cm^3\,s^{-1} \quad [35] \quad (59)$$

$O_2^- + N_2(A) \Rightarrow O_2 + N_2 + e$

$$k_{60} = 2.1 \times 10^{-9}\,cm^3\,s^{-1} \quad [35] \quad (60)$$

$O_2^- + N_2(B) \Rightarrow O_2 + N_2 + e$

$\qquad k_{61} = 2.5 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ [35] (61)

$O^- + O_2(a) \Rightarrow O_3 + e$

$\qquad k_{62} = 3 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [20] (62)

$O^- + O_2(b) \Rightarrow O + O_2 + e$

$\qquad k_{63} = 6.9 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [35] (63)

$O^- + N_2(A) \Rightarrow O + N_2 + e$

$\qquad k_{64} = 2.2 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ [35] (64)

$O^- + N_2(B) \Rightarrow O + N_2 + e$

$\qquad k_{65} = 1.9 \times 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ [35]. (65)
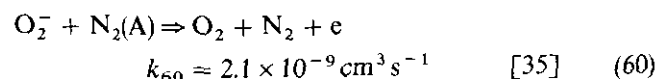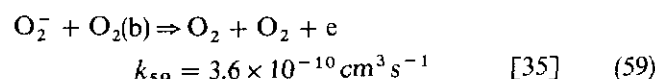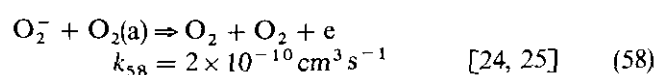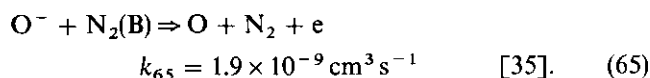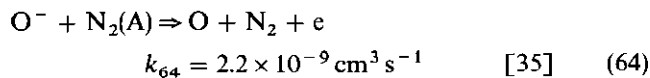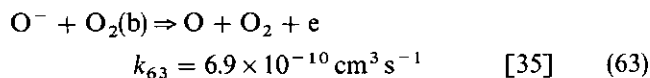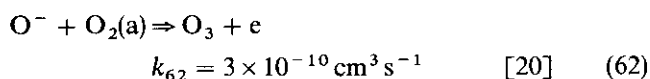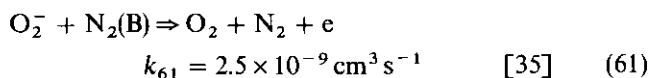
With formation of atomic oxygen and nitrogen in the discharge, associative detachment processes become a rather important channel of destruction of negative ions

$O_2^- + O \Rightarrow O_3 + e$

$\qquad k_{66} = 1.5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [20, 24, 25] (66)

$O_2^- + N \Rightarrow NO_2 + e$

$\qquad k_{67} = 5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [24] (67)

$O^- + O \Rightarrow O_2 + e$

$\qquad k_{68} = 5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [36] (68)

$O^- + N \Rightarrow NO + e$

$\qquad k_{69} = 2.6 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [22] (69)

$O_3^- + O \Rightarrow O_2 + O_2 + e$

$\qquad k_{70} = 3 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [37] (70)

$NO_2^- + O \Rightarrow NO_3 + e$

$\qquad k_{71} = 10^{-12}\,\mathrm{cm^3\,s^{-1}}$ [38]. (71)
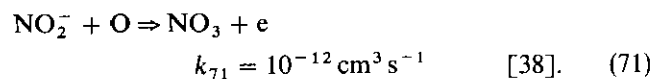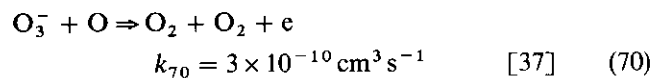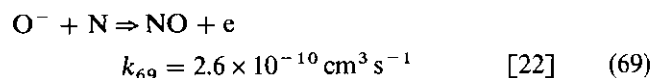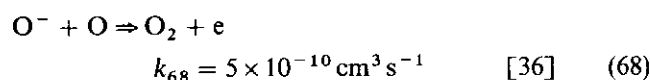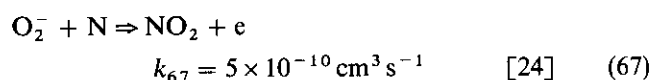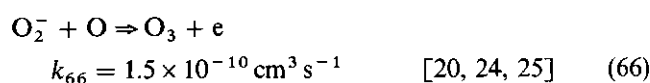
Reactions (66)–(71) can be supplemented by two additional reactions

$O^- + O_2 \Rightarrow O_3 + e$

$\qquad k_{72} = 5 \times 10^{-15}\,\mathrm{cm^3\,s^{-1}}$ [28, 29] (72)

$O^- + NO \Rightarrow NO_2 + e$

$\qquad k_{73} = 2.6 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ [22]. (73)
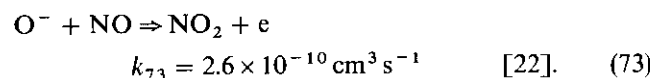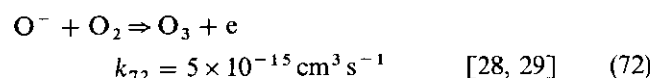
2.5. Chemical transformations of mixtures of neutral components

2.5.1. Processes with participation of ground electronic state particles.
The most detailed and reliable information on chemical reactions between unexcited neutral particles of the nitrogen–oxygen mixture is contained in [39]. In reference to our scheme it looks thus:

$N + O_2 \Rightarrow NO + O$

$$k_{74} \approx \begin{cases} 4.5 \times 10^{-12} \times \exp(-3220/T)\,\mathrm{cm^3\,s^{-1}} \\ \qquad\qquad\qquad 200\,\mathrm{K} \leqslant T \leqslant 300\,\mathrm{K} \\ 1.1 \times 10^{-14} \times T \times \exp(-3150/T)\,\mathrm{cm^3\,s^{-1}} \\ \qquad\qquad\qquad\qquad\qquad T > 300\,\mathrm{K} \quad (74) \end{cases}$$

$N + O_3 \Rightarrow NO + O_2$

$\qquad k_{75} \leqslant 2 \times 10^{-16}\,\mathrm{cm^3\,s^{-1}}$ (75)

$N + NO \Rightarrow N_2 + O$

$\qquad k_{76} = 1.05 \times 10^{-12} \times T^{0.5}\,\mathrm{cm^3\,s^{-1}}$ (76)

$N + NO_2 \Rightarrow N_2 + O_2$

$\qquad k_{77} = 7 \times 10^{-13}\,\mathrm{cm^3\,s^{-1}}$ (77)

$N + NO_2 \Rightarrow N_2 + O + O$

$\qquad k_{78} = 9.1 \times 10^{-13}\,\mathrm{cm^3\,s^{-1}}$ (78)

$N + NO_2 \Rightarrow N_2O + O$

$\qquad k_{79} = 3 \times 10^{-12}\,\mathrm{cm^3\,s^{-1}}$ (79)

$N + NO_2 \Rightarrow NO + NO$

$\qquad k_{80} = 2.3 \times 10^{-12}\,\mathrm{cm^3\,s^{-1}}$ (80)

$O + NO_2 \Rightarrow NO + O_2$

$\qquad k_{81} = 1.13 \times 10^{-11} \times (T/1000)^{0.18}\,\mathrm{cm^3\,s^{-1}}$ (81)

$O + O_3 \Rightarrow O_2 + O_2$

$\qquad k_{82} = 2 \times 10^{-11} \times \exp(-2300/T)\,\mathrm{cm^3\,s^{-1}}$ (82)

$O + NO_3 \Rightarrow O_2 + NO_2$

$\qquad k_{83} \approx 10^{-11}\,\mathrm{cm^3\,s^{-1}}$ (83)

$O + N_2O_5 \Rightarrow$ products

$\qquad k_{84} < 3 \times 10^{-16}\,\mathrm{cm^3\,s^{-1}}$ (84)

$NO + O_3 \Rightarrow O_2 + NO_2$

$\qquad k_{85} = 4.3 \times 10^{-12} \times \exp(-1560/T)\,\mathrm{cm^3\,s^{-1}}$ (85)

$NO + NO_3 \Rightarrow NO_2 + NO_2$

$\qquad k_{86} = 1.7 \times 10^{-11}\,\mathrm{cm^3\,s^{-1}}$ (86)

$NO_2 + O_3 \Rightarrow O_2 + NO_3$

$\qquad k_{87} = 1.2 \times 10^{-13} \times \exp(-2450/T)\,\mathrm{cm^3\,s^{-1}}$ (87)

$NO_3 + NO_3 \Rightarrow O_2 + NO_2 + NO_2$

$\qquad k_{88} = 5 \times 10^{-12} \times \exp(-3000/T)\,\mathrm{cm^3\,s^{-1}}$ (88)

$NO_2 + NO_3 \Rightarrow NO + NO_2 + O_2$

$\qquad k_{89} = 2.3 \times 10^{-13} \times \exp(-1600/T)\,\mathrm{cm^3\,s^{-1}}$ (89)

$N + N + M \Rightarrow N_2(X, A) + M \qquad M = N_2, O_2$

$\qquad k_{90} = 8.27 \times 10^{-34} \times \exp(500/T)\,\mathrm{cm^6\,s^{-1}}$ (90)

$O + O + N_2 \Rightarrow O_2(X, a, b, c^1, C^3, A) + N_2$

$\qquad k_{91} = 2.76 \times 10^{-34} \times \exp(720/T)\,\mathrm{cm^6\,s^{-1}}$ (91)

$O + O + O_2 \Rightarrow O_2(X, a, b, c^1, C^3, A) + O_2$

$\qquad k_{92} = 2.45 \times 10^{-31} \times T^{-0.63}\,\mathrm{cm^6\,s^{-1}}$† (92)

†When writing formulae (90)–(92), it was taken into account that the recombination of particles N and O should result in formation of molecules in electronic states with a dissociative limit corresponding to the taken combination of atoms. Values of partial rate constants of specified reactions may be approximately determined proceeding from the condition of the proportionality of the recombination stream to the statistical weight of the forming molecules' electronic states (see [40], Chapter 8, Section 1).

$$N + O + M \Rightarrow NO + M \qquad M = N_2, O_2$$

$$k_{93} = 1.76 \times 10^{-31} \times T^{-0.5} \, \text{cm}^6 \, \text{s}^{-1} \qquad (93)$$

$$O + O_2 + N_2 \Rightarrow O_3 + N_2$$

$$k_{94} = 6.2 \times 10^{-34} \times (300/T)^2 \, \text{cm}^6 \, \text{s}^{-1} \qquad (94)$$

$$O + O_2 + O_2 \Rightarrow O_3 + O_2$$

$$k_{95} = 6.9 \times 10^{-34} \times (300/T)^{1.25} \, \text{cm}^6 \, \text{s}^{-1} \qquad (95)$$

$$O + NO + M \Rightarrow NO_2 + M$$

$$M = N_2, O_2, NO, NO_2, N_2O \qquad (96)$$

$$O + NO_2 + M \Rightarrow NO_3 + M$$

$$M = N_2, O_2 \qquad (97)$$

$$NO_2 + NO_2 + M \Rightarrow N_2O_4 + M$$

$$M = N_2, O_2, N_2O_4, NO_2 \qquad (98)$$

$$NO_2 + NO_3 + M \Rightarrow N_2O_5 + M$$

$$M = N_2, O_2, N_2O_5, NO. \qquad (99)$$
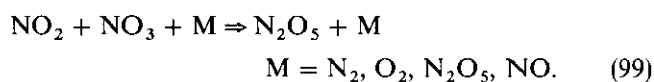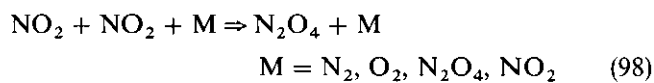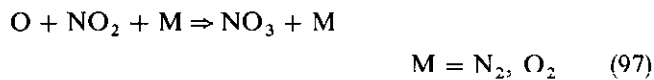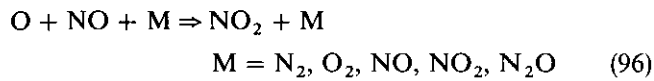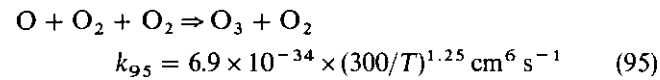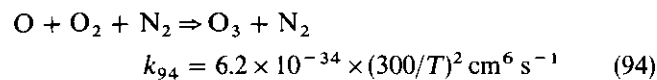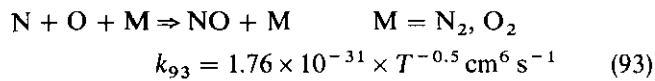
Rate constants of reactions (96)–(99) are determined with the help of the expressions

$$k_\alpha = \frac{k_\infty^{(\alpha)}(F_{(\alpha)})^{y_\alpha}}{[M] + k_\infty^{(\alpha)}/(k_0^{(\alpha)} \sum_i R_i^{(\alpha)} X_i)} \, \text{cm}^6 \, \text{s}^{-1}$$

$$F_{(\alpha)} = \exp(-T/T_{(\alpha)}) + \exp(-\tilde{T}_{(\alpha)}/T)$$

$$y_\alpha = [1 + \{[\log(k_0^{(\alpha)}[M] \sum_i R_i^{(\alpha)} X_i/k_\infty^{(\alpha)})]/v_\alpha\}^2]^{-1}$$

where $\alpha = 96, 97, 98, 99$; [M] is the total concentration of gas particles in cm^{-3}; X_i is the relative concentration of the ith component of the mixture.

For $\alpha = 96$

$$k_\infty^{(96)} = 3 \times 10^{-11} \times (T/300)^{0.3} \, \text{cm}^3 \, \text{s}^{-1}$$

$$k_0^{(96)} = 6.34 \times 10^{-32} \times (300/T)^{1.8} \, \text{cm}^6 \, \text{s}^{-1}$$

$$R_{N_2} = 1.6 \qquad R_{O_2} = 1.3 \qquad R_{NO} = 2.8$$

$$R_{NO_2} = 10 \qquad R_{N_2O} = 7$$

$$T_{(96)} = 1800 \, \text{K} \qquad \tilde{T}_{(96)} = 7200 \, \text{K} \qquad v_{96} = 1.$$

For $\alpha = 97$

$$k_\infty^{(97)} = 2.19 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1}$$

$$k_0^{(97)} = 8.08 \times 10^{-33} \times (1000/T)^2 \, \text{cm}^6 \, \text{s}^{-1}$$

$$R_{N_2} = R_{O_2} = 1 \qquad T_{(97)} = 1300 \, \text{K} \qquad \tilde{T}_{(97)} = 5200 \, \text{K}$$
$$v_{97} = 1.$$

For $\alpha = 98$

$$k_\infty^{(98)} = 8.3 \times 10^{-13} \times (T/300)^{1.7} \, \text{cm}^3 \, \text{s}^{-1}$$

$$k_0^{(98)} = 6.62 \times 10^{-34} \times (300/T)^{2.5} \, \text{cm}^6 \, \text{s}^{-1}$$

$$R_{N_2} = R_{O_2} = 0.5 R_{NO_2} = 0.5 R_{N_2O_4} = 1 \qquad T_{(98)} = 250 \, \text{K}$$

$$\tilde{T}_{(98)} = 1050 \, \text{K} \qquad v_{98} = 0.75 - \log F_{(98)}.$$

For $\alpha = 99$

$$k_\infty^{(99)} = 1.59 \times 10^{-12} \times (T/300)^{0.2} \, \text{cm}^3 \, \text{s}^{-1}$$

$$k_0^{(99)} = 3.69 \times 10^{-30} \times (300/T)^5 \, \text{cm}^6 \, \text{s}^{-1}$$

$$R_{N_2} = R_{O_2} = 1 \qquad R_{NO} = 1.3 \qquad R_{N_2O_5} = 4.4$$

$$T_{(99)} = 250 \, \text{K} \qquad \tilde{T}_{(99)} = 1050 \, \text{K}$$

$$v_{99} = 0.75 - \log F_{(99)}.$$

2.5.2. Processes with participation of electronically excited particles.

It was said above that a correct description of chemical transformations of the mixture's neutral components requires a consideration of the electronic kinetics of gas particles. Such consideration is especially necessary under conditions when $E_{\text{eff}}/n \geqslant 10^{-15} \, \text{V} \, \text{cm}^2$ (E_{eff} is the effective electric field strength). It is known [41] that in this case excitation of the N_2 and O_2 molecules' electronic states takes about half of the energy deposited in the discharge.

A comparatively complete analysis of the chemical kinetics stipulated by the presence of electronically excited particles in the gas can be realized on the basis of the following system of reactions

$$N_2(A) + O_2 \Rightarrow N_2(X) + O + O$$
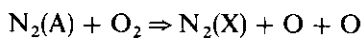
$$k_{100} = 2.54 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [42] \qquad (100)$$

$$N_2(A) + O_2 \Rightarrow N_2O + O$$
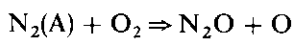
$$k_{101} = 7.8 \times 10^{-14} \, \text{cm}^3 \, \text{s}^{-1} \qquad [42] \qquad (101)$$

$$N_2(A) + O \Rightarrow NO + N(^2D)$$
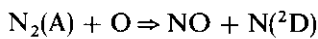
$$k_{102} \simeq 7 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [43] \qquad (102)$$

$$N_2(A) + N_2O \Rightarrow N_2 + N + NO$$
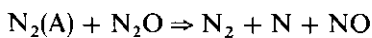
$$k_{103} = 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [44, 45] \qquad (103)$$

$$N_2(A) + N_2(A) \Rightarrow N_2(C) + N_2(X)\dagger \qquad (104)$$
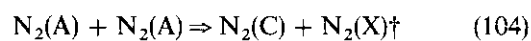
$$k_{104} \simeq 2 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [46]$$

$$k_{104} \simeq 1.6 \times 10^{-10} \times (300/T)^{2.64} \, \text{cm}^3 \, \text{s}^{-1} \qquad [47].$$

The former value of the quantity k_{104} was determined in [46] on the basis of the experimental data where ultraviolet radiation caused the $N_2(A)$ state excitation and did not affect the vibrational degrees of freedom. The higher value for k_{104} was obtained in [47] under conditions of strong vibrational non-equilibrium of the gas, when an intensive mixing of the molecules' excited electronic states could occur by interaction with the vibrational reservoir of the ground state.
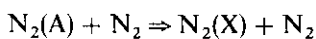
$$N_2(A) + N_2 \Rightarrow N_2(X) + N_2$$
$$k_{105} = 3 \times 10^{-18} \, \text{cm}^3 \, \text{s}^{-1} \qquad [48] \qquad (105)$$
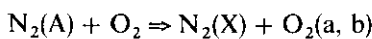
$$N_2(A) + O_2 \Rightarrow N_2(X) + O_2(a, b)$$
$$k_{106} = 1.29 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [42] \qquad (106)$$
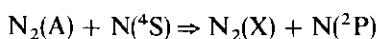
$$N_2(A) + N(^4S) \Rightarrow N_2(X) + N(^2P)$$
$$k_{107} = 5 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [40] \qquad (107)$$

† It was shown in [46] that, in vibrationally unexcited gas, excitation of the nitrogen molecules' electronic states in reactions of the type $N_2(A) + N_2(A) \Rightarrow N_2(Y) + N_2(X)$ (Y = B, W, B' and so on) must occur in the afterglow period, mainly by channel (104).

$N_2(A) + O \Rightarrow N_2(X) + O(^1S)$

$\qquad k_{108} = 2.1 \times 10^{-11} \, cm^3 \, s^{-1}$ [43]   (108)

$N_2(A) + NO \Rightarrow N_2(X) + NO$

$\qquad k_{109} = 7 \times 10^{-11} \, cm^3 \, s^{-1}$ [44]   (109)

$N_2(B) + N_2 \Rightarrow N_2(A) + N_2$

$\qquad k_{110} = 5 \times 10^{-11} \, cm^3 \, s^{-1}$ [40]   (110)

$N_2(B) \Rightarrow N_2(A) + h\nu$

$\qquad k_{111} = 1.5 \times 10^5 \, s^{-1}$ [49]   (111)

$N_2(B) + NO \Rightarrow N_2(A) + NO$

$\qquad k_{112} = 2.4 \times 10^{-10} \, cm^3 \, s^{-1}$ [44]   (112)

$N_2(B) + O_2 \Rightarrow N_2(X) + O + O$

$\qquad k_{113} \simeq 3 \times 10^{-10} \, cm^3 \, s^{-1}\dagger$ [40]   (113)

$N_2(a') + N_2 \overset{st}{\Rightarrow} N_2(B) + N_2$

$\qquad k_{114} \simeq 2 \times 10^{-13} \, cm^3 \, s^{-1}$ [50, 51]   (114)

$N_2(a') + O_2 \Rightarrow N_2(X) + O + O$

$\qquad k_{115} = 2.8 \times 10^{-11} \, cm^3 \, s^{-1}\dagger$ [51]   (115)

$N_2(a') + NO \Rightarrow N_2(X) + N + O$

$\qquad k_{116} = 3.6 \times 10^{-10} \, cm^3 \, s^{-1}$ [51]   (116)

$N_2(C) \Rightarrow N_2(B) + h\nu$

$\qquad k_{117} = 3 \times 10^7 \, s^{-1}$ [49]   (117)

$N_2(C) + N_2 \overset{st}{\Rightarrow} N_2(a') + N_2$

$\qquad k_{118} = 10^{-11} \, cm^3 \, s^{-1}$ [40]   (118)

$N_2(C) + O_2 \Rightarrow N_2(X) + O + O(^1S)$

$\qquad k_{119} \simeq 3 \times 10^{-10} \, cm^3 \, s^{-1}\dagger$ [40]   (119)

$O_2(a) + O_3 \Rightarrow O_2 + O_2 + O$

$k_{120} = 9.7 \times 10^{-13}$

$\qquad \times \exp(-1564/T) \, cm^3 \, s^{-1}$ [52]   (120)

$O_2(a) + N \Rightarrow NO + O$

$k_{121} = 2 \times 10^{-14} \times \exp(-600/T) \, cm^3 \, s^{-1}$ [53]   (121)

$O_2(a) + N_2 \Rightarrow O_2 + N_2$

$\qquad k_{122} = 3 \times 10^{-21} \, cm^3 \, s^{-1}$ [54]   (122)

$O_2(a) + O_2 \Rightarrow O_2 + O_2$

$k_{123} = 2.2 \times 10^{-18} \times (T/300)^{0.8} \, cm^3 \, s^{-1}$ [20]   (123)

$O_2(a) + O \Rightarrow O_2 + O$

$\qquad k_{124} = 7 \times 10^{-16} \, cm^3 \, s^{-1}$ [53]   (124)

$O_2(a) + NO \Rightarrow O_2 + NO$

$\qquad k_{125} = 2.5 \times 10^{-11} \, cm^3 \, s^{-1}$ [55]   (125)

$O_2(b) + O_3 \Rightarrow O_2 + O_2 + O$

$\qquad k_{126} = 1.8 \times 10^{-11} \, cm^3 \, s^{-1}$ [54]   (126)

$O_2(b) + N_2 \Rightarrow O_2(a) + N_2$

$k_{127} = 4.9 \times 10^{-15}$

$\qquad \times \exp(-253/T) \, cm^3 \, s^{-1}$ [56]   (127)

$O_2(b) + O_2 \Rightarrow O_2(a) + O_2$

$k_{128} = 4.3 \times 10^{-22} \times T^{2.4}$

$\qquad \times \exp(-241/T) \, cm^3 \, s^{-1}$ [56]   (128)

$O_2(b) + O \Rightarrow O_2(a) + O$

$\qquad k_{129} = 8 \times 10^{-14} \, cm^3 \, s^{-1}$ [54]   (129)

$O_2(b) + O \Rightarrow O_2(X) + O(^1D)$

$k_{130} = 3.39 \times 10^{-11} \times (300/T)^{0.1}$

$\qquad \times \exp(-4201/T) \, cm^3 \, s^{-1}$ [57]   (130)

$O_2(b) + NO \Rightarrow O_2(a) + NO$

$\qquad k_{131} = 4 \times 10^{-14} \, cm^3 \, s^{-1}$ [58]   (131)

$O_2(A, c, C) + O_2 \Rightarrow O_2(b) + O_2(b)$

$\qquad k_{132} = 2.9 \times 10^{-13} \, cm^3 \, s^{-1}$ [59]   (132)

$O_2(A, c, C) + N_2 \Rightarrow O_2(b) + N_2$

$\qquad k_{133} = 3 \times 10^{-13} \, cm^3 \, s^{-1}$ [60]   (133)

$O_2(A, c, C) + O \Rightarrow O_2(b) + O(^1D)$

$\qquad k_{134} = 9 \times 10^{-12} \, cm^3 \, s^{-1}$ [59]   (134)

$N(^2D) + O_2 \Rightarrow NO + O(^3P)$

$\qquad k_{135} = 1.5 \times 10^{-12} \times (T/300)^{0.5} \, cm^3 \, s^{-1}$ [20]   (135)

$N(^2D) + O_2 \Rightarrow NO + O(^1D)$

$k_{136} = 6 \times 10^{-12}$

$\qquad \times (T/300)^{0.5} \, cm^3 \, s^{-1}$ [20]   (136)

$N(^2D) + NO \Rightarrow N_2O$

$\qquad k_{137} = 6 \times 10^{-11} \, cm^3 \, s^{-1}$ [61]   (137)

$N(^2D) + N_2O \Rightarrow NO + N_2$

$\qquad k_{138} = 3 \times 10^{-12} \, cm^3 \, s^{-1}$ [44]   (138)

$N(^2D) + N_2 \Rightarrow N(^4S) + N_2$

$\qquad k_{139} = 6 \times 10^{-15} \, cm^3 \, s^{-1}$ [20]   (139)

$N(^2P) + O_2 \Rightarrow NO + O$

$\qquad k_{140} = 2.6 \times 10^{-12} \, cm^3 \, s^{-1}$ [62]   (140)

$N(^2P) + NO \Rightarrow N_2(A) + O$

$\qquad k_{141} = 3.4 \times 10^{-11} \, cm^3 \, s^{-1}$ [63]   (141)

$N(^2P) + N_2 \Rightarrow N(^2D) + N_2$

$\qquad k_{142} = 2 \times 10^{-18} \, cm^3 \, s^{-1}$ [64]   (142)

$N(^2P) + N \Rightarrow N(^2D) + N$

$\qquad k_{143} = 1.8 \times 10^{-12} \, cm^3 \, s^{-1}$ [40]   (143)

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†The analysis of the N_2 and O_2 molecules' electronic terms scheme shows that the channel of the dissociative quenching of the $N_2(B)$, $N_2(a')$ and $N_2(C)$ states corresponds to low values of the Messiah parameter. So reactions (113), (115) and (119) can be treated as the main channel of quenching of the $N_2(B)$, $N_2(a')$ and $N_2(C)$ states by unexcited oxygen molecules. The present suggestion seems to be quite probable because, in reference to the $N_2(A)$ state, it agrees with the known result (see [42]) on the principal role of channel (100) in the processes of quenching of the $N_2(A)$ molecules by unexcited oxygen molecules.

$O(^1D) + N_2 \Rightarrow O(^3P) + N_2$

$k_{144} = 1.8 \times 10^{-11}$
$$\times \exp(107/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [65] \qquad (144)$$

$O(^1D) + O_2 \Rightarrow O(^3P) + O_2(b)$

$k_{145} = 2.56 \times 10^{-11}$
$$\times \exp(67/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [65] \qquad (145)$$

$O(^1D) + O_2 \Rightarrow O(^3P) + O_2(X, v)$

$k_{146} = 6.4 \times 10^{-12}$
$$\times \exp(67/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [65] \qquad (146)$$

$O(^1D) + O_3 \Rightarrow O(^3P) + O(^3P) + O_2(X) \qquad (147)$

$O(^1D) + O_3 \Rightarrow O_2(X, v_1) + O_2(X, v_2) \qquad (148)$
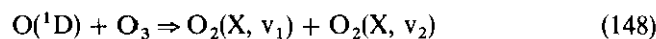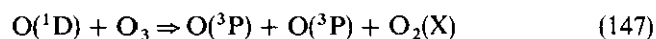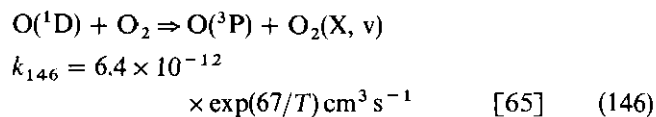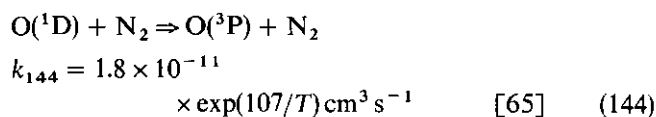
$$k_{147} = k_{148} = 1.2 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [52]$$

$O(^1D) + NO \Rightarrow N(^4S) + O_2(X)$

$$k_{149} = 1.7 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [61] \qquad (149)$$

$O(^1D) + N_2O \Rightarrow NO + NO$

$$k_{150} = 7.2 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [65] \qquad (150)$$

$O(^1D) + N_2O \Rightarrow N_2 + O_2$

$$k_{151} = 4.4 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [65] \qquad (151)$$

$O(^1S) + N_2 \Rightarrow \text{products}$

$$k_{152} = 5 \times 10^{-17}\,\text{cm}^3\,\text{s}^{-1} \qquad [61] \qquad (152)$$

$O(^1S) + O_2 \Rightarrow O(^3P) + O_2(A, c, C) \qquad (153)$

$O(^1S) + O_2 \Rightarrow O(^1D) + O_2(X, v) \qquad (154)$
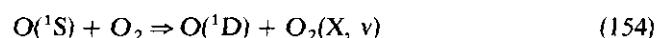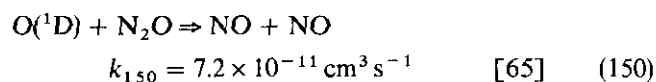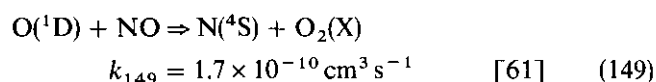
$k_{153} + k_{154} = 4.3 \times 10^{-12}$
$$\times \exp(-850/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [20]$$
$$k_{153} : k_{154} = 0.69 : 0.31 \qquad [66]$$

$O(^1S) + O_3 \Rightarrow O(^1D) + O(^3P) + O_2(X, v) \qquad (155)$

$O(^1S) + O_3 \Rightarrow O_2(X, v_1) + O_2(X, v_2) \qquad (156)$
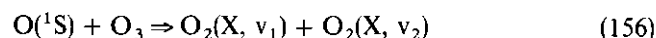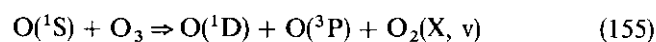
$k_{155} + k_{156} = 5.8 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [61]$
$$k_{155} \simeq k_{156}$$

$O(^1S) + NO \Rightarrow O(^3P) + NO \qquad (157)$

$O(^1S) + NO \Rightarrow O(^1D) + NO \qquad (158)$
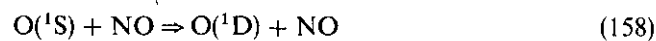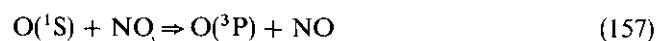
$k_{157} + k_{158} = 5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [61]$
$$k_{157} : k_{158} = 0.36 : 0.64 \qquad [67]$$

$O(^1S) + N_2O \Rightarrow O(^3P) + N_2O \qquad (159)$

$O(^1S) + N_2O \Rightarrow O(^1D) + N_2O \qquad (160)$
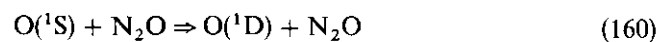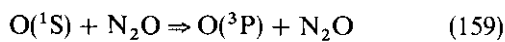
$k_{159} + k_{160} = 9.4 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1} \qquad [61]$
$$k_{159} : k_{160} = 0.67 : 0.33 \qquad [67]$$

$O(^1S) + O_2(a) \Rightarrow O(^1D) + O_2(b)$

$$k_{161} = 3.6 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [54] \qquad (161)$$

$O(^1S) + O_2(a) \Rightarrow 3O(^3P)$

$$k_{162} = 3.4 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [54] \qquad (162)$$

$O(^1S) + O_2(a) \Rightarrow O(^3P) + O_2(A)$

$$k_{163} = 1.3 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [54] \qquad (163)$$

$O(^1S) + O \Rightarrow O(^1D) + O$

$k_{164} = 5 \times 10^{-11}$
$$\times \exp(-301/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [68]. \qquad (164)$$
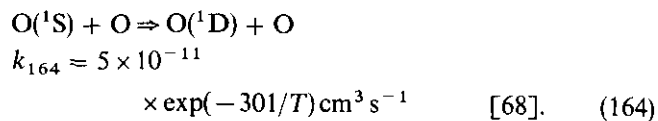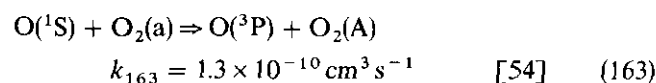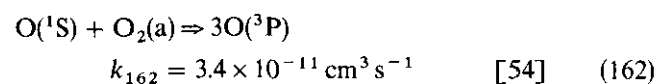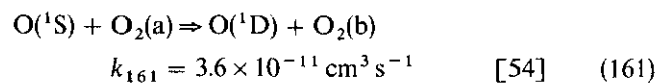
2.6. Ion conversion

The process of non-equilibrium discharge in nitrogen–oxygen mixtures is accompanied by the appearance of a wide spectrum of simple and complex ions. Incidentally, concentration of the complex ions increases as the total concentration of particles grows or the gas temperature decreases [21, 40]. The ionic composition depends also upon the electric discharge power.

In our conditions, the conversion of positive and negative ions is described by a system of reactions.

2.6.1. Positive ions

$N_2^+ + N_2 + N_2 \Rightarrow N_4^+ + N_2$
$$k_{165} = 5 \times 10^{-29}\,\text{cm}^6\,\text{s}^{-1} \qquad [20] \qquad (165)$$

$N_2^+ + N + N_2 \Rightarrow N_3^+ + N_2$
$k_{166} = 0.9 \times 10^{-29}$
$$\times \exp(400/T)\,\text{cm}^6\,\text{s}^{-1} \qquad [40] \qquad (166)$$

$O_2^+ + O_2 + O_2 \Rightarrow O_4^+ + O_2$
$k_{167} = 2.4 \times 10^{-30}$
$$\times (300/T)^{3.2}\,\text{cm}^6\,\text{s}^{-1} \qquad [24] \qquad (167)$$

$O_2^+ + N_2 + N_2 \Rightarrow O_2^+ \cdot N_2 + N_2$
$$k_{168} = 0.9 \times 10^{-30} \times (300/T)^2\,\text{cm}^6\,\text{s}^{-1} \qquad [20] \qquad (168)$$

$NO^+ + N_2 + N_2 \Rightarrow NO^+ \cdot N_2 + N_2$
$k_{169} = 2 \times 10^{-31}$
$$\times (300/T)^{4.4}\,\text{cm}^6\,\text{s}^{-1} \qquad [24] \qquad (169)$$

$NO^+ + O_2 + N_2 \Rightarrow NO^+ \cdot O_2 + N_2$
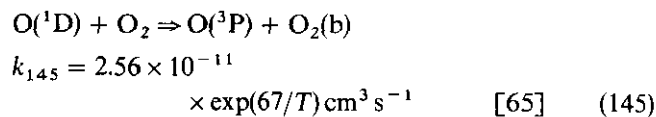$$k_{170} = 3 \times 10^{-31}\,\text{cm}^6\,\text{s}^{-1} \qquad [21] \qquad (170)$$

$NO^+ + O_2 + O_2 \Rightarrow NO^+ \cdot O_2 + O_2$
$$k_{171} = 0.9 \times 10^{-31}\,\text{cm}^6\,\text{s}^{-1} \qquad [21] \qquad (171)$$

$N^+ + N_2 + N_2 \Rightarrow N_3^+ + N_2$
$k_{172} = 0.9 \times 10^{-29}$
$$\times \exp(400/T)\,\text{cm}^6\,\text{s}^{-1} \qquad [40] \qquad (172)$$

$N^+ + O + M \Rightarrow NO^+ + M \qquad M = N_2, O_2$
$$k_{173} = 10^{-29}\,\text{cm}^6\,\text{s}^{-1} \qquad [22] \qquad (173)$$

$N^+ + N + M \Rightarrow N_2^+ + M \qquad M = N_2, O_2$
$$k_{174} = k_{173} \qquad [22] \qquad (174)$$

$O^+ + N_2 + M \Rightarrow NO^+ + N + M \qquad M = N_2, O_2$
$$k_{175} = 6 \times 10^{-29} \times (300/T)^2\,\text{cm}^6\,\text{s}^{-1} \qquad [20] \qquad (175)$$

$O^+ + O + M \Rightarrow O_2^+ + M \qquad M = N_2, O_2$
$$k_{176} = 10^{-29}\,\text{cm}^6\,\text{s}^{-1} \qquad [22, 30] \qquad (176)$$

$O^+ + N + M \Rightarrow NO^+ + M \qquad M = N_2, O_2$
$$k_{177} = 10^{-29}\,\text{cm}^6\,\text{s}^{-1} \qquad [22] \qquad (177)$$

$N^+ + O_2 \Rightarrow O_2^+ + N$
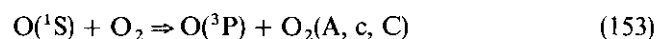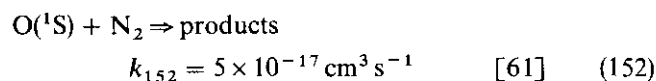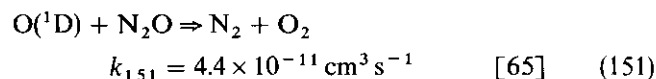$$k_{178} = 2.8 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20] \qquad (178)$$

$$N^+ + O_2 \Rightarrow NO^+ + O$$
$$k_{179} = 2.5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [53] \qquad (179)$$

$$N^+ + O_2 \Rightarrow O^+ + NO$$
$$k_{180} = 2.8 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [53] \qquad (180)$$

$$N^+ + O \Rightarrow N + O^+$$
$$k_{181} = 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (181)$$

$$N^+ + O_3 \Rightarrow NO^+ + O_2$$
$$k_{182} = 5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [57] \qquad (182)$$

$$N^+ + NO \Rightarrow N + NO^+$$
$$k_{183} = 8 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [20, 22] \qquad (183)$$

$$N^+ + NO \Rightarrow N_2^+ + O$$
$$k_{184} = 3 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (184)$$

$$N^+ + NO \Rightarrow O^+ + N_2$$
$$k_{185} = 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (185)$$

$$N^+ + N_2O \Rightarrow NO^+ + N_2$$
$$k_{186} = 5.5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (186)$$

$$O^+ + N_2 \Rightarrow NO^+ + N$$
$$k_{187} = 3 \times 10^{-12}$$
$$\times \exp(-0.00311T) \, \text{cm}^3 \, \text{s}^{-1} \qquad [24] \qquad (187)$$

$$O^+ + O_2 \Rightarrow O_2^+ + O$$
$$k_{188} = 3.3 \times 10^{-11}$$
$$\times \exp(-0.00169T) \, \text{cm}^3 \, \text{s}^{-1} \qquad [24] \qquad (188)$$

$$O^+ + O_3 \Rightarrow O_2^+ + O_2$$
$$k_{189} = 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [57] \qquad (189)$$

$$O^+ + NO \Rightarrow NO^+ + O$$
$$k_{190} = 2.4 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (190)$$

$$O^+ + NO \Rightarrow O_2^+ + N$$
$$k_{191} = 3 \times 10^{-12} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (191)$$

$$O^+ + N(^2D) \Rightarrow N^+ + O$$
$$k_{192} = 1.3 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [57] \qquad (192)$$

$$O^+ + NO_2 \Rightarrow NO_2^+ + O$$
$$k_{193} = 1.6 \times 10^{-9} \, \text{cm}^3 \, \text{s}^{-1} \qquad [38] \qquad (193)$$

$$O^+ + N_2O \Rightarrow N_2O^+ + O$$
$$k_{194} = 4 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (194)$$

$$O^+ + N_2O \Rightarrow NO^+ + NO$$
$$k_{195} = 2.3 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [38] \qquad (195)$$

$$O^+ + N_2O \Rightarrow O_2^+ + N_2$$
$$k_{196} = 2 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (196)$$

$$N_2^+ + O_2 \Rightarrow O_2^+ + N_2$$
$$k_{197} = 6 \times 10^{-11} \times (300/T)^{0.5} \, \text{cm}^3 \, \text{s}^{-1} \qquad [24] \qquad (197)$$

$$N_2^+ + O \Rightarrow NO^+ + N$$
$$k_{198} = 1.3 \times 10^{-10} \times (300/T)^{0.5} \, \text{cm}^3 \, \text{s}^{-1} \qquad [20] \qquad (198)$$

$$N_2^+ + O \Rightarrow O^+ + N_2$$
$$k_{199} = 10^{-11} \times (300/T)^{0.2} \, \text{cm}^3 \, \text{s}^{-1} \qquad [20] \qquad (199)$$

$$N_2^+ + O_3 \Rightarrow O_2^+ + O + N_2$$

$$k_{200} = 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [57] \qquad (200)$$

$$N_2^+ + N_2(A) \Rightarrow N_3^+ + N$$
$$k_{201} \leqslant 3 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [40] \qquad (201)$$

$$N_2^+ + N \Rightarrow N^+ + N_2$$
$$k_{202} = 2.4 \times 10^{-15} \times T \, \text{cm}^3 \, \text{s}^{-1} \qquad [40] \qquad (202)$$

$$N_2^+ + NO \Rightarrow NO^+ + N_2$$
$$k_{203} = 3.3 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [20] \qquad (203)$$

$$N_2^+ + N_2O \Rightarrow NO^+ + N_2 + N$$
$$k_{204} = 4 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (204)$$

$$N_2^+ + N_2O \Rightarrow N_2O^+ + N_2$$
$$k_{205} = 5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (205)$$

$$O_2^+ + N_2 \Rightarrow NO^+ + NO$$
$$k_{206} = 10^{-17} \, \text{cm}^3 \, \text{s}^{-1} \qquad [24] \qquad (206)$$

$$O_2^+ + N \Rightarrow NO^+ + O$$
$$k_{207} = 1.2 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [20] \qquad (207)$$

$$O_2^+ + NO \Rightarrow NO^+ + O_2$$
$$k_{208} = 4.4 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [24] \qquad (208)$$

$$O_2^+ + NO_2 \Rightarrow NO^+ + O_3$$
$$k_{209} = 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [22] \qquad (209)$$

$$O_2^+ + NO_2 \Rightarrow NO_2^+ + O_2$$
$$k_{210} = 6.6 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [38] \qquad (210)$$

$$O_2^+ + N_2O_5 \Rightarrow NO_2^+ + NO_3 + O_2$$
$$k_{211} = 8.8 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (211)$$

$$NO^+ + O_3 \Rightarrow NO_2^+ + O_2$$
$$k_{212} = 10^{-15} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (212)$$

$$NO^+ + N_2O_5 \Rightarrow NO_2^+ + NO_2 + NO_2$$
$$k_{213} = 5.9 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (213)$$

$$N_3^+ + O_2 \Rightarrow O_2^+ + N + N_2$$
$$k_{214} = 2.3 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (214)$$

$$N_3^+ + O_2 \Rightarrow NO_2^+ + N_2$$
$$k_{215} = 4.4 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (215)$$

$$N_3^+ + N \Rightarrow N_2^+ + N_2$$
$$k_{216} = 6.6 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [40] \qquad (216)$$

$$N_3^+ + NO \Rightarrow NO^+ + N + N_2$$
$$k_{217} = 7 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (217)$$

$$N_3^+ + NO \Rightarrow N_2O^+ + N_2$$
$$k_{218} = 7 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (218)$$

$$NO_2^+ + NO \Rightarrow NO^+ + NO_2$$
$$k_{219} = 2.9 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (219)$$

$$N_2O^+ + NO \Rightarrow NO^+ + N_2O$$
$$k_{220} = 2.9 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \qquad [33] \qquad (220)$$

$$N_4^+ + N_2 \Rightarrow N_2^+ + N_2 + N_2$$
$$\log k_{221} = -14.6 + 0.0036 \times (T - 300)$$
$$300 \, \text{K} \leqslant T \leqslant 900 \, \text{K} \qquad [40] \qquad (221)$$

$$N_4^+ + O_2 \Rightarrow O_2^+ + N_2 + N_2$$

$$k_{222} = 2.5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [36] \qquad (222)$$

$$N_4^+ + O \Rightarrow O^+ + N_2 + N_2 \qquad k_{223} \to k_{222} \qquad (223)$$

$$N_4^+ + N \Rightarrow N^+ + N_2 + N_2$$
$$k_{224} = 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [40] \qquad (224)$$

$$N_4^+ + NO \Rightarrow NO^+ + N_2 + N_2$$
$$k_{225} = 4 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [33] \qquad (225)$$

$$O_4^+ + N_2 \Rightarrow O_2^+ \cdot N_2 + O_2$$
$$k_{226} = 4.61 \times 10^{-12} \times (T/300)^{2.5}$$
$$\times \exp(-2650/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [20] \qquad (226)$$

$$O_4^+ + O_2 \Rightarrow O_2^+ + O_2 + O_2$$
$$k_{227} = 3.3 \times 10^{-6} \times (300/T)^4$$
$$\times \exp(-5030/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [24] \qquad (227)$$

$$O_4^+ + O_2(a,\,b) \Rightarrow O_2^+ + O_2 + O_2$$
$$k_{228} = 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20,\,24] \qquad (228)$$

$$O_4^+ + O \Rightarrow O_2^+ + O_3$$
$$k_{229} = 3 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [24] \qquad (229)$$

$$O_4^+ + NO \Rightarrow NO^+ + O_2 + O_2$$
$$k_{230} = 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [33] \qquad (230)$$

$$O_2^+ \cdot N_2 + N_2 \Rightarrow O_2^+ + N_2 + N_2$$
$$k_{231} = 1.1 \times 10^{-6} \times (300/T)^{5.3}$$
$$\times \exp(-2357/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [20] \qquad (231)$$

$$O_2^+ \cdot N_2 + O_2 \Rightarrow O_4^+ + N_2$$
$$k_{232} = 10^{-9}\,\text{cm}^3\,\text{s}^{-1} \qquad [20] \qquad (232)$$

$$NO^+ \cdot N_2 + N_2 \Rightarrow NO^+ + N_2 + N_2$$
$$k_{223} = 1.5 \times 10^6 \times T^{-5.4}$$
$$\times \exp(-2450/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [24]. \qquad (233)$$

2.6.2. Negative ions

$$O_2^- + O_2 + M \Rightarrow O_4^- + M \qquad M = N_2,\,O_2$$
$$k_{234} = 3.5 \times 10^{-31} \times (300/T)\,\text{cm}^6\,\text{s}^{-1} \qquad [20] \qquad (234)$$

$$O^- + O_2 + M \Rightarrow O_3^- + M \qquad M = N_2,\,O_2$$
$$k_{235} = 1.1 \times 10^{-30} \times (300/T)\,\text{cm}^6\,\text{s}^{-1}$$
$$[20,\,25] \qquad (235)$$

$$O^- + NO + M \Rightarrow NO_2^- + M \qquad M = N_2,\,O_2$$
$$k_{236} = 10^{-29}\,\text{cm}^6\,\text{s}^{-1} \qquad [22] \qquad (236)$$

$$O_2^- + O \Rightarrow O_2 + O^-$$
$$k_{237} = 3.3 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [25,\,30] \qquad (237)$$

$$O_2^- + O_3 \Rightarrow O_2 + O_3^-$$
$$k_{238} = 4 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20,\,25,\,29,\,30] \qquad (238)$$

$$O_2^- + NO_2 \Rightarrow NO_2^- + O_2$$
$$k_{239} = 8 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (239)$$

$$O_2^- + NO_3 \Rightarrow O_2 + NO_3^-$$
$$k_{240} = 5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [22] \qquad (240)$$

$$O_2^- + N_2O \Rightarrow O_3^- + N_2$$
$$k_{241} < 10^{-12}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (241)$$

$$O^- + O_2(a) \Rightarrow O_2^- + O$$
$$k_{242} = 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [29,\,30] \qquad (242)$$

$$O^- + O_3 \Rightarrow O + O_3^-$$
$$k_{243} = 5.3 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20,\,25] \qquad (243)$$

$$O^- + NO_2 \Rightarrow NO_2^- + O$$
$$k_{244} = 1.2 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (244)$$

$$O^- + N_2O \Rightarrow NO^- + NO$$
$$k_{245} = 2 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (245)$$

$$O^- + N_2O \Rightarrow N_2O^- + O$$
$$k_{246} = 2 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1} \qquad [22] \qquad (246)$$

$$O_3^- + O \Rightarrow O_2^- + O_2$$
$$k_{247} = 3.2 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20] \qquad (247)$$

$$O_3^- + NO \Rightarrow NO_3^- + O$$
$$k_{248} = 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (248)$$

$$O_3^- + NO \Rightarrow NO_2^- + O_2$$
$$k_{249} = 2.6 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1} \qquad [33] \qquad (249)$$

$$O_3^- + NO_2 \Rightarrow O_3 + NO_2^-$$
$$k_{250} = 7 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [69] \qquad (250)$$

$$O_3^- + NO_2 \Rightarrow O_2 + NO_3^-$$
$$k_{251} = 2 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [69] \qquad (251)$$

$$O_3^- + NO_3 \Rightarrow O_3 + NO_3^-$$
$$k_{252} = 5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [69] \qquad (252)$$

$$NO^- + O_2 \Rightarrow O_2^- + NO$$
$$k_{253} = 5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (253)$$

$$NO^- + NO_2 \Rightarrow NO_2^- + NO$$
$$k_{254} = 7.4 \times 10^{-16}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (254)$$

$$NO^- + N_2O \Rightarrow NO_2^- + N_2$$
$$k_{255} = 2.8 \times 10^{-14}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (255)$$

$$NO_2^- + O_3 \Rightarrow NO_3^- + O_2$$
$$k_{256} = 1.8 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (256)$$

$$NO_2^- + NO_2 \Rightarrow NO_3^- + NO$$
$$k_{257} = 4 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (257)$$

$$NO_2^- + NO_3 \Rightarrow NO_2 + NO_3^-$$
$$k_{258} = 5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [69] \qquad (258)$$

$$NO_2^- + N_2O_5 \Rightarrow NO_3^- + NO_3 + NO$$
$$k_{259} = 7 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [22] \qquad (259)$$

$$NO_3^- + NO \Rightarrow NO_2^- + NO_2$$
$$k_{260} = 3 \times 10^{-15}\,\text{cm}^3\,\text{s}^{-1} \quad T = 300\,\text{K} \quad [38] \qquad (260)$$

$$NO_3^{-*} + NO \Rightarrow NO_2^- + NO_2$$
$$k_{261} = 1.5 \times 10^{-11}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (261)$$

$$O_4^- + M \Rightarrow O_2^- + O_2 + M \qquad M = N_2,\,O_2$$
$$k_{262} = 10^{-10} \times \exp(-1044/T)\,\text{cm}^3\,\text{s}^{-1} \qquad [21] \qquad (262)$$

$$O_4^- + O \Rightarrow O_3^- + O_2$$
$$k_{263} = 4 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [20,\,22] \qquad (263)$$

$$O_4^- + NO \Rightarrow NO_3^{-*} + O_2$$
$$k_{264} = 2.5 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1} \qquad [38] \qquad (264)$$

$$O_4^- + O \Rightarrow O^- + O_2 + O_2$$
$$k_{265} = 3 \times 10^{-10}\,cm^3\,s^{-1} \qquad (265)$$
$$O_4^- + O_2(a, b) \Rightarrow O_2^- + O_2 + O_2$$
$$k_{266} = 10^{-10}\,cm^3\,s^{-1}\dagger. \qquad (266)$$

2.7. Recombination of positive and negative ions

One of the mechanisms for loss of charged particles in the non-equilibrium plasma is ion–ion recombination. Ion recombination in pair collisions predominates under rather low pressures. Under pressures higher than several Torr, the most essential mechanism of ion loss turns out to be their recombination with participation of a neutral particle [41, 70]. The mutual neutralization of positive and negative ions in the nitrogen–oxygen plasma is proposed to occur in the frame of the following kinetic scheme

I. $\quad A^- + B^+ \Rightarrow A + B$

$$k_I \simeq 2 \times 10^{-7} \times (300/T)^{0.5}\,cm^3\,s^{-1} \qquad [22, 25].$$

Here symbols A and B vary in accordance with the relations $A^- \rightarrow O_2^-$, O^-, O_3^-, NO^-, NO_2^-, NO_3^-, N_2O^- and $B^+ \rightarrow N_2^+$, O_2^+, N^+, O^+, NO^+, NO_2^+, N_2O^+,

II. $\quad A^- + (BC)^+ \Rightarrow A + B + C$

$$k_{II} \simeq 10^{-7}\,cm^3\,s^{-1} \qquad [22, 30].$$

The symbol A is varied in the same way as in the preceding case; $(BC)^+ \rightarrow N_2^+$, O_2^+, NO^+, NO_2^+, N_2O^+, N_3^+, N_4^+, O_4^+, $NO^+ \cdot N_2$, $NO^+ \cdot O_2$, $NO^+ \cdot NO$, $O_2^+ \cdot N_2$

III. $\quad (AB)^- + C^+ \Rightarrow A + B + C \qquad k_{III} \rightarrow k_{II}$.

Symbols A and B are correlated with particles entering combinations: $A \text{—} B \rightarrow O_2 \text{—} O_2$; $C^+ \rightarrow N_2^+$, O_2^+, N^+, O^+, NO^+, NO_2^+, N_2O^+.

IV. $\quad (AB)^- + (CD)^+ \Rightarrow A + B + C + D$

$$k_{IV} \simeq 10^{-7}\,cm^2\,s^{-1}.$$

For $\quad A \text{—} B \rightarrow O_2 \text{—} O_2$; $\quad C \text{—} D \rightarrow N \text{—} N_2$, $N_2 \text{—} N_2$, $O_2 \text{—} O_2$, $NO \text{—} N_2$, $NO \text{—} O_2$, $NO \text{—} NO$, $O_2 \text{—} N_2$.

V. $\quad A^- + B^+ + M \Rightarrow A + B + M$

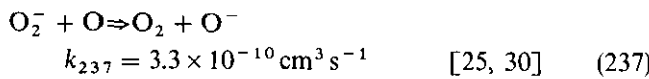For $M \rightarrow N_2, O_2$; $A \rightarrow O_2, O$;

and $B \rightarrow N_2, O_2, N, O, NO$.

VI. $\quad A^- + B^+ + M \Rightarrow AB + M$

For $M \rightarrow N_2, O_2$: (a) $A \rightarrow O_2$; $B \rightarrow N, O, NO$; and (b) $A \rightarrow O$; $B \rightarrow N_2, O_2, NO, O, N$. According to [22, 25] one may set

$$k_V \simeq k_{VI} \simeq 2 \times 10^{-25} \times (300/T)^{2.5}\,cm^6\,s^{-1}.$$

3. The influence of the electronic excitations of nitrogen molecules and atoms on the dynamics of the chemical composition of air under pulsed discharge

As an illustration of the kinetic scheme proposed, an electric discharge with the following parameters: mixture

†Unpublished data on the values of quantities k_{265} and k_{266} were kindly given to us by Dr J Zinn.

$[N_2]:[O_2] = 4:1$, $n = 10^{19}\,cm^{-3}$, $T = 300\,K$, $E_{eff}/n = 10^{-15}\,V\,cm^2$, pulse duration $\tau = 10^{-5}\,s$, was simulated. The parameters indicated approximately correspond to the conditions in the vicinity of the high-pressure microwave discharge channels [71]. Taking into account the fact that in this case free electrons are created, on the whole, with the aid of photo-ionization of the gas by ultraviolet radiation from the channel, the electron concentration was considered to be constant and equal to $4 \times 10^{11}\,cm^{-3}$.

Calculated time variations of concentrations of gas components are presented in figures 1–3; results of calculations for the same conditions, but with the aid of a kinetic scheme omitting reactions of electronically excited nitrogen molecules, are shown in figure 4. In both cases the specific energy deposited in the gas amounts to $0.23\,J\,cm^{-3}\,atm^{-1}$, which permits neglect of the vibrational excitation of gas molecules.

As one can see from figures 1 and 4, consideration of processes including electronically excited N_2 molecules essentially affects the accumulation of discharge chemical products. So production of atomic oxygen, subsequently converting to ozone, increases three times at the expense of the dissociation reactions of O_2 involving excited N_2 molecules (100), (113), (115), (119), the maximal contribution being connected with the $N_2(B^3\Pi_g)$ state.

Formation of the nitrogen oxide NO at small times is determined by the reactions

$$N_2(A) + O \Rightarrow NO + N(^2D)$$
$$N(^2D) + O_2 \Rightarrow NO + O$$
$$N(^2P) + O_2 \Rightarrow NO + O.$$

Figure 1. Time variation for the concentration of chemically active particles and chemical reaction products in a pulsed microwave discharge. Nitrogen–oxygen mixture $[N_2]:[O_2] = 4:1$, $n = 10^{19}\,cm^{-3}$; $T = 300\,K$; $E_{eff}/n = 10^{-15}\,V\,cm^2$.
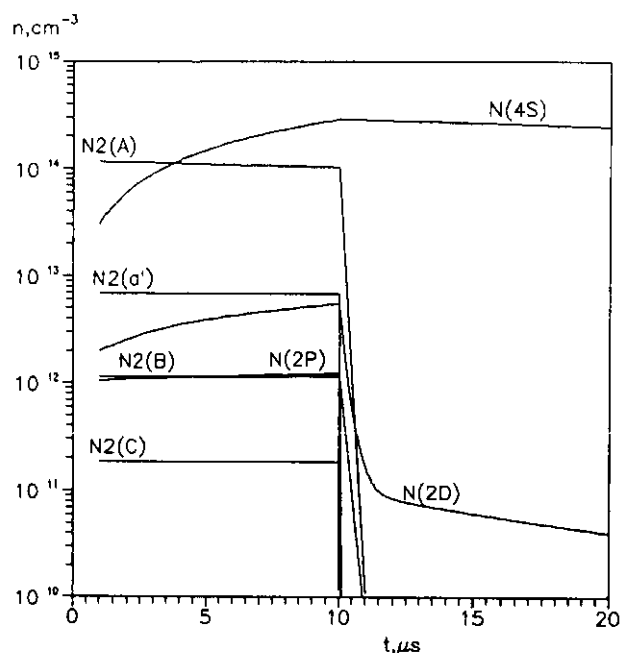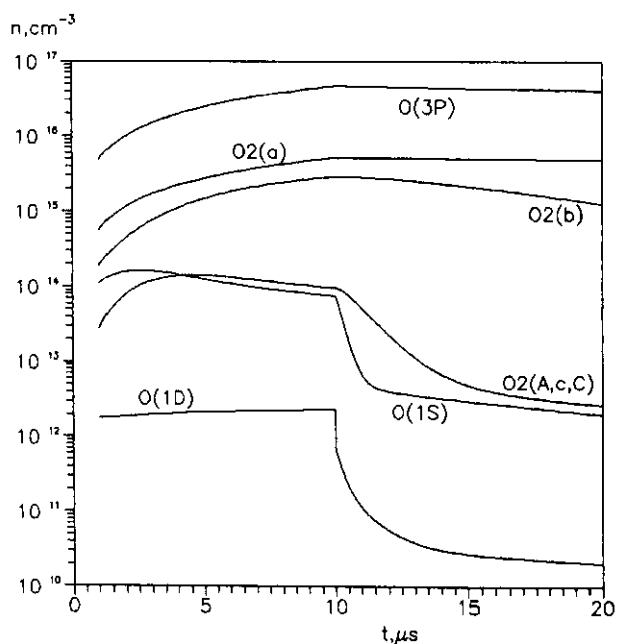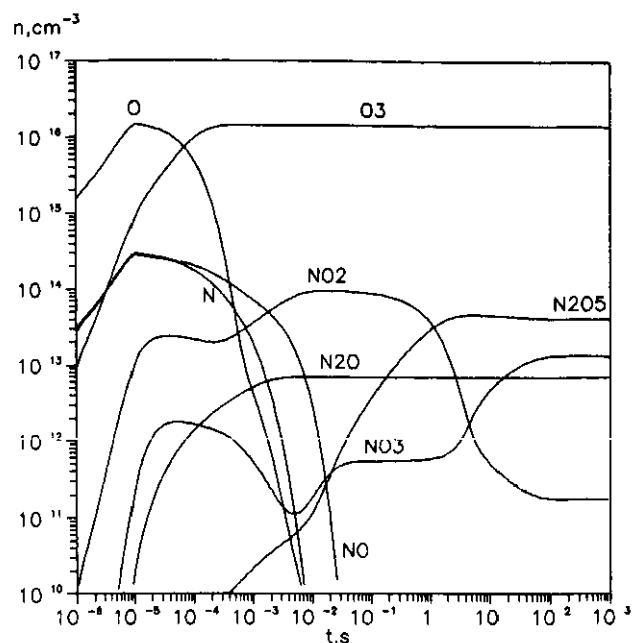
Figure 2. Time variation for the concentration of electron-excited nitrogen molecules and atoms in a pulsed microwave discharge. Nitrogen–oxygen mixture $[N_2] : [O_2] = 4 : 1$; $n = 10^{19}$ cm^{-3}; $T = 300$ K; $E_{eff}/n = 10^{-15}$ V cm^2.

Figure 4. Time variation for the concentration of chemically active particles and chemical reaction products in a pulsed microwave discharge (calculations without taking into account reactions with electron-excited molecules of nitrogen).

Figure 3. Time variation for the concentration of electron-excited oxygen molecules and atoms in a pulsed microwave discharge. Nitrogen–oxygen mixture $[N_2] : [O_2] = 4 : 1$; $n = 10^{19}$ cm^{-3}; $T = 300$ K; $E_{eff}/n = 10^{-15}$ V cm^2.

Excited atoms $N(^2D)$ and $N(^2P)$ are obtained in reactions (8) and (9) of the N_2 molecule dissociation by electron impact and are converted almost entirely to NO. Because the effectiveness of the process (7) of N_2 dissociation with production of two ground state nitrogen atoms is low, with process (102) switched off, concen-

trations of $N(^4S)$ and NO components should be equal by the end of the discharge, which is confirmed by the calculations. Further dynamics of the quantities $[N(^4S)]$ and $[NO]$ is conditioned by the reactions

$$N(^4S) + O_2 \Rightarrow NO + O$$
$$N(^4S) + NO \Rightarrow N_2 + O$$
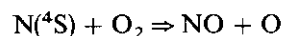
which lead to the complete disappearnace of N atoms and to partial decrease of the NO concentration.

The interaction of the excited molecules $N_2(A)$ with oxygen atoms ensures a doubling of the concentration of NO produced during the discharge. Incidentally, the final level of the concentration of all NO_x oxides increases by a factor of five. It should be noted that every interaction leads to the formation of two NO molecules, because the second product of the reaction, namely $N(^2D)$, quickly interacts with molecular oxygen, yielding another NO molecule.

Electronically excited nitrogen molecules determine also the main mechanism of N_2O production:

$$N_2(A) + O_2 \Rightarrow N_2O + O.$$
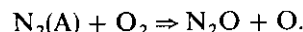
In the absence of $N_2(A)$ particles, the formation of N_2O proceeds only by the reaction

$$N + NO_2 \Rightarrow N_2O + O$$
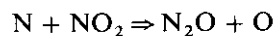
whose effectiveness under the conditions considered is 25 times lower.

Thus, neglecting the role of electronically excited nitrogen molecules and atoms in formation of chemical products in non-equilibrium nitrogen–oxygen plasmas may lead to crude errors.

4. Conclusion

A kinetic scheme for non-equilibrium discharge in nitrogen-oxygen mixtures is proposed. It is formed from an impressive set of reactions (about 450), with the help of which it is possible to describe the main part of the available experimental data on the chemical and ion composition of cold ($T \leqslant 500$ K) vibrationally unexcited gas in the discharge and after-discharge periods. In spite of this, however, the question of the role of various mechanisms of excitation, ionization and chemical (ion) transformation in the nitrogen-oxygen plasma cannot be considered to be completely clarified (see [19, 39]). At the same time, the formulated kinetic model, even with all its imperfection, will allow, for instance, more realistic characterization of a wide range of physicochemical phenomena arising from the impact upon the atmosphere of powerful microwave radiation.

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