

Negative Ions, Ozone, and Metastable Components in dc e + O₃ Glow Discharge

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*The 18 typos were fixed by
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3 July 2016

Abstract

In a dc glow discharge in oxygen, the concentrations of minor components of O₂(*a*¹A_g), O₂(*b*¹Σ_g), O₃, O(¹D), as well as negative ions and electrons have been measured. Balance equations have been derived which describe satisfactorily the stationary concentrations of these components as functions of gas pressure and discharge current. For the first time, the rate constants of important aeronomical reactions (a) O⁻ + O₂(*a*¹A_g) → O₃ + e, (b) O₂⁻ + O₂(*a*¹A_g) → 2O₂ + e and (c) e + O₃ → O₂⁻ + O have been measured as functions of gas temperature *T* and mean energies of ions *E_i* and electron *E_e*: $K_a = (2.5 \pm 0.5) \cdot 10^{-9} \cdot (T/300)^{4 \pm 0.4} \cdot (E_i/0.04)^{-2.6 \pm 0.4} \text{ cm}^3/\text{s}$ for $T = 385\text{--}605 \text{ K}$ and $E_i = 0.10\text{--}0.66 \text{ eV}$; $K_b = (1.0 \pm 0.3) \cdot 10^{-10} \cdot (T/300)^{-2 \pm 0.5} \cdot (E_i/0.04)^{0.23 \pm 0.05} \text{ cm}^3/\text{s}$ for $T = 330\text{--}605 \text{ K}$ and $E_i = 0.09\text{--}1.5 \text{ eV}$; K_c for $E_e = 0.8\text{--}5 \text{ eV}$.

1. Introduction

In recent years, the stationary dc glow discharge in oxygen at low pressure has drawn great interest, since the results of its investigation have important applications (aeronomy, lasers, plasma chemistry, etc.).

The range of pressures $p < 2$ Torr in discharge tubes with the radius $R = 1\text{--}3$ cm has been studied in detail. Under these conditions, the discharge at dc ($i = 30\text{--}300$ mA), as a rule, is not contractional (H-form) and only slightly disturbed (the low frequency noise amplitude is small, strata are absent). Langmuir probe methods make it possible to measure the concentrations of electrons [e] and positive ions n_+ [1–4 et al.] Numerous recent measurements and calculations of the form of the nonmaxwellian electron energy distribution function (EEDF) show good conformity [5, 6]. After theoretical investigations [7, 8], the first systematic measurements of concentrations of metastable atoms and molecules of oxygen have been made [9–11] at $p = 0.1\text{--}10$ Torr. Measurements of the oxygen atom concentrations O(³P) have been made many times and using different methods [12–14]. The energy characteristics of the O₂ discharge at low pressures have been considered. It has been shown that under stationary conditions the mean kinetic energies of electrons *E_e*, ions *E_i* and neutrals *E_n* are mostly different, $E_e \gg E_i \gg E_n$, the thermalization of ions takes place only for $p > 3\text{--}5$ Torr [15, 16]. The temperature $T = 2E_n/3$ is one of the basic characteristics of the discharge (the accuracy of determining the parameter E/n depends on it), and it has been measured in discharge tubes of a similar size using different methods [17, 18]. An interesting peculiar feature has been revealed there at $p = 2\text{--}10$ Torr: the gas temperature on the axis of the cylindrical discharge tube $T(O)$ goes up considerably as the gas pressure increases, in spite of the

usual decrease of E_e . The experimental material obtained has made it possible in [10] to pass over from theoretical discharge models to the measurement of the reaction rate constants which are important in aeronomy, and also to reveal the mechanism of the population of singlet levels $a^1\Delta_g$ and $b^1\Sigma_g^+$ of O_2 at $p > 2$ Torr and to determine more precisely the balances for $O(^1D)$ and $O(^1S)$ which have initially been examined in [19] without accounting for metastable molecules of oxygen. For the pressure interval $p = 0.1-2$ Torr, analysis of experimental data on the kinetic mechanism of the formation and destruction of metastable components of $O(^1D)$, $O(^1S)$, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in a glow discharge is presented in [20, 21].

As has been shown by numerous researchers during the recent decade, the role of ozone in kinetic mechanisms is very important, but it has not been adequately studied so far. SABADIL in [8] has shown for the first time that the mechanism of ozone formation in a discharge includes negative ions and excited molecules of oxygen. Later, on the basis of experimental data of [10], it has been shown that in the pressure interval $p = 2-9$ Torr, the dominant deactivation process of the level $a^1\Delta_g$ is the reaction $O_2(a^1\Delta_g) + O^- \rightarrow O_3 + e$, and of the level $b^1\Sigma_g^+$ is the reaction $O_2(b^1\Sigma_g^+) + O_3 \rightarrow O_2^\# + O_3^\#$, and the main process of electron attachment is characterized by $O_3 + e \rightarrow O_2^- + O$ followed by a fast reexchange reaction $O_2^- + O \rightarrow O_2 + O^-$.

The present paper develops the results obtained in [10, 11, 15, 18-21] and deals with the kinetics of the processes with negative ions in a stationary oxygen glow discharge, with direct current ($i = 50-150$ mA) in the gas pressure interval of $p = 0.1-2$ Torr. The purpose of the investigation is to estimate the rate constants of some inadequately studied reactions, depending on the mean energies of reagents, viz.:



Section 2 presents the description of the experiments conducted, section 3 formulates the problem of kinetic analysis of elementary processes with the participation of negative ions, ozone and metastable atoms and molecules of oxygen; for pressures $p = 2-9$ Torr (section 3a), the description is based on the results of [10]. Sections 4, 5 show a solution of the kinetic problem. Section 6 contains an analysis of temperature dependences of the reaction rate constants (1).

2. Experimental Results

A positive column of the stationary dc glow discharge in O_2 has been investigated in our experiment. The conditions of filling the discharge tube with oxygen were quasi-flowing. One portion of O_2 was used for 20-50 minutes and was then replaced by another one. Oxygen was obtained by warming-up chemically pure $KMnO_4$; additional refinement of O_2 was made on traps cooled by liquid nitrogen (77°K). The purity of gas in the discharge tube with the radius $R = 3$ cm and length of 50 cm made from molybdenum glass was checked spectroscopically. The content of impurities (H_2 and H) did not exceed $\gamma = 3 \cdot 10^{-5}\%$. The degree of evacuation was tested by a thermocouple vacuummeter. The O_2 gas pressure was measured by a capacitance manometer, which made it impossible for the vapours of oil and for other gases to penetrate into the vacuum system. Tungsten electrodes were transferred to side branches. The training of the installation was conducted at increased pressures of oxygen (up to 25 Torr) during 600-800 hours with periodical changing of the polarity of the discharge tube electrodes.

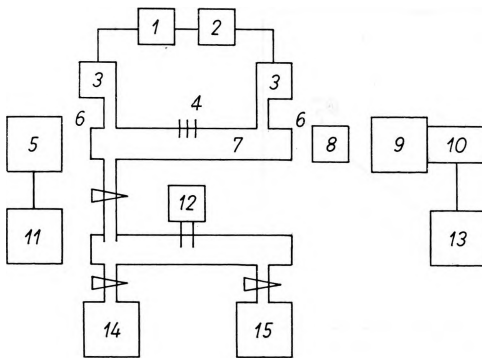


Fig. 1. Scheme of experimental installation: 1 — high-voltage dc source, 2 — load resistor, 3 — electrodes, 4 — probes, 5 — standard radiation source, 6 — optical windows, 7 — discharge tube, 8 — condenser, 9 — monochromator MSD, 10 — photomultiplier PM-79, 11 — low-voltage dc source P4103, 12 — vacuum-meters, 13 — registration system, 14 — container with pure O_2 , 15 — system of vacuum pumping of the installation. For measurement of the intensity of the band λ 1270 nm, instead of 8–10, a photoresistor FSG with a modulator and synchronous detection amplifier U2-8 were used.

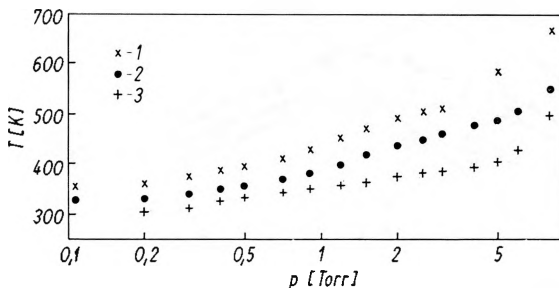


Fig. 2. Results of measurement of gas temperature on the axis of glow discharge in oxygen. Discharge current: 150 mA — 1, 100 mA — 2, 50 mA — 3.

The scheme of the experimental installation is presented in Fig. 1. The discharge was analyzed using the Langmuir probe method and spectroscopically. The deviation from the mean measured values did not exceed 20% in a series of experiments.

The axial electric field intensity E was measured on the discharge axis by the method of two probes, the temperature of the discharge tube $T(R)$ wall being determined by the thermocouple.

The probe method was used to measure on the discharge axis the values of $[e]$, n_+ , E_e at $p = 0.1 - 1.5$ Torr. Tungsten probes 0.02 and 0.2 mm in diameter were used.

The gas temperature on the discharge axis $T(0)$ has been identified with the rotational temperature of the λ 762 nm O_2 band ($b^1\Sigma_g^+$, $v' = 0 \rightarrow X^3\Sigma_g^+$, $v'' = 0$), for which we have obtained spectra resolved over the rotational structure in the entire investigated range of pressures and currents of the discharge ($p = 0.1 \div 9$ Torr, $i = 50 - 250$ mA) (Fig. 2, [18]). The measurement error for $T(0)$ was not worse than 3%. The mean energies of ions (Fig. 3) have been calculated from the VANIE formula [22] on the basis of experimental data for E and $T(0)$ [15].

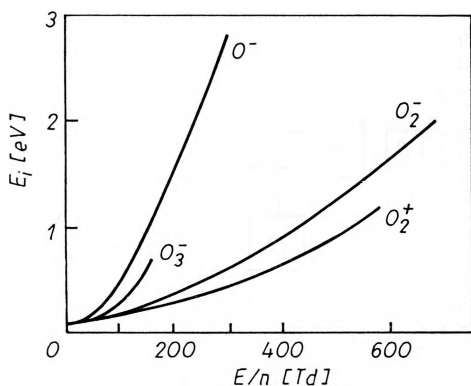


Fig. 3. Mean energies of ions on the axis of glow discharge in oxygen as functions of the values of a reduced electric field ($1 \text{ Td} = 10^{-17} \text{ V} \cdot \text{cm}^2$).

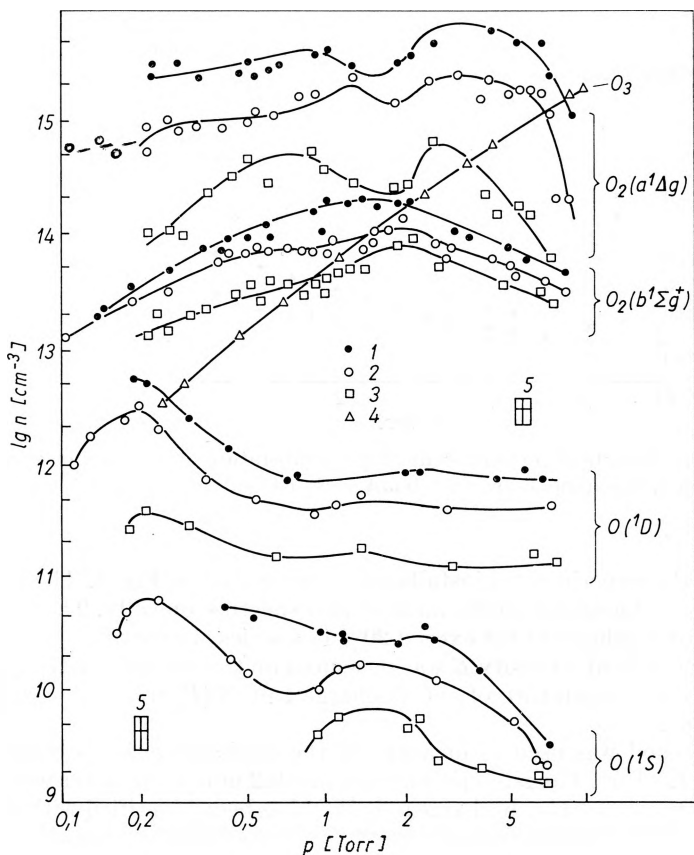


Fig. 4. Concentrations of $O(^1D)$, $O(^1S)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, O_3 , as measured experimentally on the axis of glow discharge in oxygen as functions of gas pressure in the discharge. Discharge current: 150 mA — 1, 100 mA — 2, 50 mA — 3, 50–150 mA — 4; for ozone, no dependence on current has been observed. Index 5 designates measurement error intervals.

Optical spectra in the range of λ 400–850 nm have been obtained with the MSD monochromator. The photomultiplier PM-79 has also been used, as well as, in the registration scheme, the digital electrometric amplifier B7-30 and recorder H306. From the absolute line intensity of λ 630 and 558 nm OI, the concentrations of atoms of O(1D) and O(1S) in the axial zone of the discharge have been determined [19]. The concentration of the molecules O₂($b^1\Sigma_g^+$) has been determined from the absolute intensity of the band λ 762 nm [11]. With the help of an interference filter with the transmission center at λ 1270 nm (100 nm FWHM) and photoresistor FSG cooled by liquid nitrogen, the population of the level $a^1\Delta g$ of O₂ [11] has been measured (Fig. 4). The concentration of ozone has been determined from the UV radiation absorption in the Hartley continuum [10, 23]. All optical characteristics of the trained discharge were stable during 0.8–1 hour (up to 2 hrs at higher gas pressures). Plasma noises (low-frequency oscillations) $f = 1 - 20$ kHz and strata were observed only at $i > 100$ mA and $p \cong 1.4 - 2.5$ Torr. It has been found that the noise level is in correlation with γ — the relative value of impurity content in oxygen. At $\gamma > 10^{-30}\%$, the duration of stable burning of the discharge decreases to 20–40 minutes.

3. Processes of Ozone Formation and Conversion of Negative Ions in Oxygen Glow Discharge

3a. Kinetic problem in the Pressure Range of $p = 2 - 9$ Torr

Let us consider the kinetic mechanisms for negative ions of oxygen and ozone on the basis of experimental data presented above (section 2). The presently accepted kinetic mechanisms for excited and a number of ion components have been formed, to a great extent, under the influence of traditional theoretical views on the composition and properties of the plasma of the discharge in O₂. For instance, in 1972 systematic measurements of the ozone concentration were made for the first time [23].

The experiment has shown that [O₃] is approximately proportional to p^2 in the interval $p = 0.6 - 9$ Torr (Fig. 4) and is independent of the discharge current in the interval $i = 50 - 150$ mA. The simplest model satisfying the experimental data has been proposed:



(the complete list of processes taken into account in this paper and the values for reaction rate constants are presented in Tab. 1). From (2) we obtain $[\text{O}_3] = [\text{O}_2]^2 K_{02}/K_{03} \propto [\text{O}_2]^2$. However, subsequent precisioning of the values of K_{02} and K_{03} , as well as the accounting for the temperature dependence of the rate constants of these reactions have revealed that the mechanism (2) can ensure only 2–4% of the ozone concentration observed in the discharge. An important achievement in this regard has become paper [24] where an effective process of ozone formation has been examined



whose rate constant has been very uncertain $K_{36} = (0.3 - 30) \cdot 10^{-10}$ cm³/s [25]. In [10] we have measured the concentrations of O₂($a^1\Delta g$) and O₂($b^1\Sigma_g^+$) and shown that the

Table 1

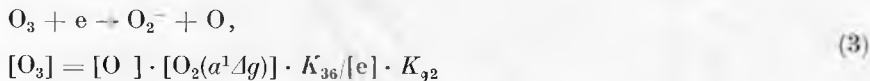
Reaction rate constants for reactions with participation of minor components for oxygen glow discharge

Process	Reaction code	Rate constant K in cm^3/s or cm^6/s and cross-section σ	Reference
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	02	$6.9 \cdot 10^{-34}(T/300)^{-1.25}$, $T = 220-370 \text{ K}$	25
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	03	$1.5 \cdot 10^{-11} \exp(-2300/T)$, $T = 220-400 \text{ K}$	25
$\text{O} + \text{O}^- \rightarrow \text{O}_2 + \text{e}$	04	$1.9 \cdot 10^{-10}$	22
$\text{O} + \text{O}_2^- \rightarrow \text{O}^- + \text{O}_2$	05	$3.0 \cdot 10^{-10}$	22
$\text{O} + \text{O}_3^- \rightarrow \text{O}_2^- + \text{O}_2$	06	$2.5 \cdot 10^{-10}$	22
$\text{O}(^1D) + \text{O}_3 \rightarrow 2\text{O}_2$	14	$2.4 \cdot 10^{-10}$	25
$\text{O}(^1D) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	15	$2.0 \cdot 10^{-34}$	44
$\text{O}(^1S) + \text{O}_3 \rightarrow 2\text{O}_2$	24	$5.8 \cdot 10^{-10}(T/300)^{-2}$ $T = 300-550 \text{ K}$	10
$\text{O}_2(a^1\Delta_g) + \text{O}_3 \rightarrow 2\text{O}_2 + \text{O}$	35	$5.2 \cdot 10^{-11} \exp(-2840/T)$, $T = 280-360 \text{ K}$	25
$\text{O}_2(a^1\Delta_g) + \text{O}^- \rightarrow \text{O}_3 + \text{e}$	36	$(0.3-30) \cdot 10^{-10}$ $4 \cdot 10^{-9}$, $T = 440-550 \text{ K}$	25 10,20
$\text{O}_2(a^1\Delta_g) + \text{O}_2^- \rightarrow 2\text{O}_2 + \text{e}$	37	$(0.2-20) \cdot 10^{-10}$ $4.5 \cdot 10^{-11}$, $T = 440-550 \text{ K}$	25 20
$\text{O}_2(b^1\Sigma_g^+) + \text{O}_3 \rightarrow \text{O}_2^* + \text{O}_3^*$	43	$2.0 \cdot 10^{-11}$	25
$\text{O}_2(b^1\Sigma_g^+) + \text{O} \rightarrow \text{O}_3 + \text{e}$	44	$K_{44} = 2.3 \cdot K_{36}$ from [25]	43
$\text{O}_2(b^1\Sigma_g^+) + \text{O}_2^- \rightarrow 2\text{O}_2 + \text{e}$	45	$K_{45} = 1.8 \cdot K_{37}$ from [25]	43
$\text{O}_3(A^2\Sigma_u^+) + \text{O}_2(a^1\Delta_g) \rightarrow \text{O}_3 + \text{O}$	55		38
$\text{O}_3 \rightarrow \text{diffusion}$	60	$(n \cdot D)_0 = 6.2 \cdot 10^{18} (\text{cm} \cdot \text{s})^{-1}$	39
$\text{O}_3 + \text{O}^- \rightarrow \text{O}_3^- + \text{O}$	61	$8 \cdot 10^{-10}$	22
$\text{O}_3 + \text{O}_2^- \rightarrow \text{O}_3 + \text{O}_2 + \text{e}$	62	$6 \cdot 10^{-10}$	22
$\text{O}_3 + \text{O}_3^- \rightarrow 3\text{O}_2 + \text{e}$	63	$3 \cdot 10^{-10}$	22
$\text{O}_3 + \text{O}^+ \rightarrow \text{O}_2 + \text{O}_2^+$	64	very slow	45
$\text{O}_k^- \rightarrow \text{ambipolar diffusion}$, $k = 1, 2, 3$	70		22,29
$\text{O}^- + \text{O}_2 \rightarrow \text{O} + \text{O}_2^-$	71a	$K_{71}(E_i)$	22
$\rightarrow \text{O} + \text{O}_2 + \text{e}$	71b		22
$\text{O}^- + \text{O}_2 + \text{M} \rightarrow \text{O}_3^- + \text{M}$	73	$\leq 9 \cdot 10^{-31}$	22
$\text{O}_2^- + \text{O}_2 \rightarrow 2\text{O}_2 + \text{e}$	74	$K_{74}(E_i), \sigma(E_i)$	22
$\text{O}_2^- + \text{O}_2 + \text{M} \rightarrow \text{O}_4^- + \text{M}$	75	$5 \cdot 10^{-31}$	22
$\text{O}_k^- + \text{O}_n^+ \rightarrow \text{products}$	78	$\simeq 6 \cdot 10^{-8}$, $k, n = 1, 2, 3$	22
$\text{O}_k^- + \text{O}_n^+ + \text{M} \rightarrow \text{products}$	79	$\simeq 3 \cdot 10^{-25}(T/300)^{-2.5}$	46
$\text{O}_3^- + \text{O}_2 \rightarrow \text{O}_3 + \text{O}_2 + \text{e}$	76	$2.3 \cdot 10^{-11}$	39
$\text{e} + \text{O}_2 \rightarrow \text{O}^- + \text{O}$	87a	$K_{87a}(E_e, T), \sigma(E_e, T)$	22
$\rightarrow \text{O}^- + \text{O}^+ + \text{e}$	87b	estimate	24
$\text{e} + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2$	91	$\leq 5 \cdot 10^{-31}$	22
$\text{e} + \text{O}_3 \rightarrow \text{O}_2^- + \text{O}$	92a	$K_{92a}(E_e = 0.01-0.4 \text{ eV}), \sigma(E_e)$ $K_{92a}(E_e = 0.8-2.1 \text{ eV})$	22 10,20
$\rightarrow \text{O} + \text{O}_2 + \text{e}$	92b	estimate	24
$\rightarrow \text{O}_3^+ + 2\text{e}$	92c	estimate	24
$\text{e} + \text{O}_3 + \text{M} \rightarrow \text{O}_3^- + \text{M}$	93	$K_{93} = K_{91}$	24
$\text{e} + \text{O}_2(a^1\Delta_g) \rightarrow \text{O}^- + \text{O}$	94a	$K_{94a}(E_e)$	5
$\rightarrow \text{O}^- + \text{O}^+ + \text{e}$	94b	estimate	24
$\text{e} + \text{O}_2(b^1\Sigma_g^+) \rightarrow \text{O}^- + \text{O}$	95	$K_{95}(E_e)$	5
$\text{e} + \text{O}^- \rightarrow \text{O} + 2\text{e}$	96	$K_{96}(E_e)$	5

Notes: In cases when the temperature interval is not given $T = 300 \text{ K}$.

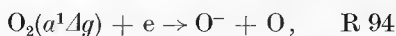
A complete summary of reactions for oxygen components is presented in [47].

measured values of $[O_3]$ at $p = 2-9$ Torr are described satisfactorily by the reactions of formation (R 36) and destruction (R 92) of ozone:

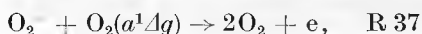
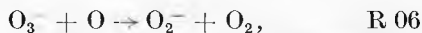
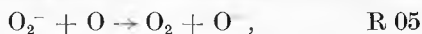
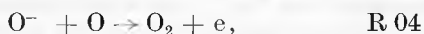


It should be noted that reaction R 43 $O_3 + O_2(b^1\Sigma_g^+) \rightarrow$ has appeared to be far less effective for the destruction of ozone than (R 92). The calculated from (3) values of $[O_3]$ were close to the experimental data and only slightly dependent on the discharge current. Under these conditions, on the discharge axis $T \simeq 400-600$ K, $E_i = 0.08$ to 0.11 eV and $E_e = 0.9-2.0$ eV (Figs. 2, 3).

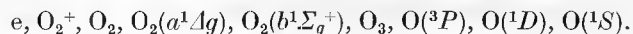
In [10, 26] it has been shown that (R 92) at $p = 2-9$ Torr is a more effective process of electron attachment than the traditionally considered one



This can be accounted for by the relatively small threshold energy of dissociation in ozone (1.0 eV) in comparison with the O_2 molecule (5.1 eV). The kinetic analysis in [10] was not based on a certain, previously proposed mechanism of ozone formation; it was based on the quantitative analysis of the contributions of all known processes presented in Tab. 1 (see below Figs. 6-9). The accounting for mean energies of all of the reagents was made in successive order. An important part in the conversion of negative ions play the ion-molecular reactions of the recharge and deattachment of electrons, with the participation of "minor components" of plasma:



For correct analysis of the role of these and other reactions, experimentally controlled components have been used in [10]:



A summary of the analysis of the negative ion kinetics in a discharge in O_2 has been comprehensively outlined in [26], where, for example, partial pressures of each of the ions O^- , O_2^- , O_3^- have been calculated as functions of the gas pressure in the discharge (Fig. 5). The situation obtained is in good conformity with the results of mass-spectrometric studies of the plasma of the O_2 discharge if the comparison is made according to the scale of the E/n parameter [8, 16, 27, 29, etc.]. It should be emphasized that in our case all measurements have been made on the axis of the cylindrical discharge tube where for most components the volume processes dominate and not the probability of the diffusive departure of the components to the walls up to $p \lesssim 0.1$ Torr (Figs. 6-9). That is why the problem of the effectiveness of wall deactivation of active components is not very important in our analysis.

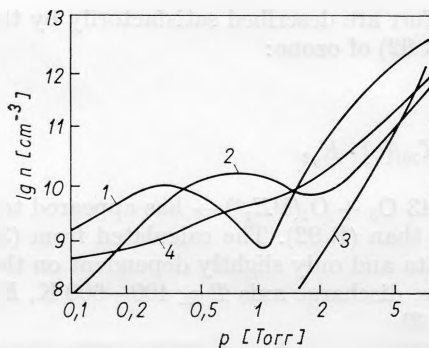


Fig. 5. Calculated values of concentrations of charged components on the axis of glow discharge in oxygen as functions of gas pressure. Discharge current — 100 mA. Designations: 1 — $[O_2^-]$, 2 — $[O^-]$, 3 — $[O_3^-]$, 4 — $[e]$ (experiment [40]).

3b. Kinetic Problem in the Pressure Range of $p = 0.1 - 2$ Torr

Studies of the mechanisms of the formation of negative ions of oxygen at low pressures have been carried out during the recent 30 years [2, 27, 31–35]. These studies have revealed: a) the special role of “minor components” $O(^3P)$, O_3 , $O_2(a^1\Delta g)$, $O_2(b^1\Sigma_g^+)$; b) considerable exceeding of the mean energies of ions E_i over the gas temperature T .

This paper is the first investigation where, in the analysis of the ion conversion, experimentally measured values of $[O_3]$, $[O_2(a^1\Delta g)]$, $[O_2(b^1\Sigma_g^+)]$ have been used, and the error of determining the mean energies of ions (within the Vanie theory) did not exceed 10%.

By making use of the summary of reactions from Tab. 1, we derive kinetic equations for O^- , O_2^- , O_3^- and O_3 in the form of a statistical balance between the production and loss processes:

$$\begin{aligned} \frac{d[O^-]}{dt} = & V_{05} + V_{87} + V_{94} + V_{95} - V_{04} - V_{36} - V_{44} - V_{61} - V_{70} \\ & - V_{71} - V_{73} - V_{78} - V_{79} - V_{96}, \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{d[O_2^-]}{dt} = & V_{06} + V_{71} + V_{91} + V_{95} - V_{37} - V_{45} - V_{62} - V_{70} \\ & - V_{74} - V_{75} - V_{78} - V_{79} - V_{05}, \end{aligned} \quad (5)$$

$$\frac{d[O_3^-]}{dt} = V_{61} + V_{73} + V_{93} - V_{06} - V_{63} - V_{70} - V_{76} - V_{78} - V_{79}, \quad (6)$$

$$\begin{aligned} \frac{d[O_3]}{dt} = & V_{02} + V_{15} + V_{36} + V_{44} + V_{55} + V_{76} - V_{03} - V_{14} - V_{24} \\ & - V_{35} - V_{43} - V_{60} - V_{61} - V_{62} - V_{63} - V_{64} - V_{92} - V_{93} \end{aligned} \quad (7)$$

where V is the volume reaction rate in $\text{cm}^{-3}\text{s}^{-1}$ (the product of the reagent concentrations by the reaction rate constant). It should be noted that Tab. 1 does not give reactions with the participation of O_4^- , since these ions are formed in three-body collisions which are inefficient in our conditions ($n \leq 6 \cdot 10^{16} \text{ cm}^{-3}$).

In the stationary regime, the set of differential equations (4–7) is reduced to an algebraic one, which must be complemented by an equation for plasma quasi-neutrality:

$$[O^-] + [O_2^-] + [O_3^-] + [e] = n_+ \quad (8)$$

where n_+ is the total concentration of positive ions measured by the probe method (Fig. 5). The concentrations of all of the reacting components, except $[O^-]$, $[O_2^-]$ and $[O_3^-]$, are known from the experiments. The rate constant of the majority of reactions embraced by (4–7) are known at present to a sufficient accuracy. Thus, the set of equations (4–8) can be solved, i.e. the unknown dependences of the concentrations of the O^- , O_2^- and O_3^- ions upon the conditions in the discharge can be found. The error of this solution will be limited by the indeterminacy of the rate constants of a number of poorly studied reactions, for instance, (R 36) and (R 92).

Solutions obtained in this way make it possible to calculate the volume rate values of all reactions considered and thus to estimate their relative contribution to the total balance. The results of such a calculation, as a function of pressure (for $i = 100$ mA), are presented in Figs. 6–9.

As in the case of high pressures [Section 3a of this paper], at $p < 2$ Torr the reaction (R 43) must be excluded from the channels of the O_3 loss, since the volume rate of this

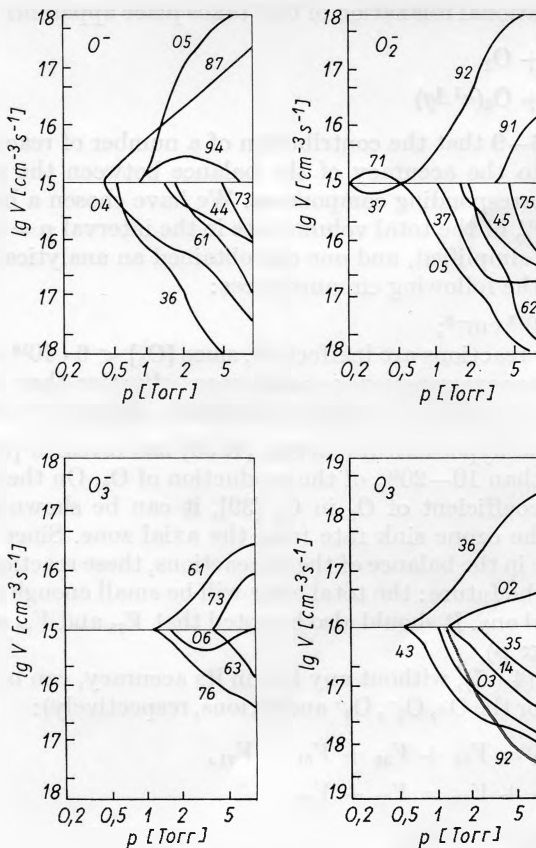
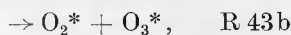


Fig. 6–9. Volume reaction rates for the formation (top) and loss (bottom) of components shown in the Figures, as functions of gas pressure on the discharge axis. Discharge current — 100 mA. Reaction numbers have been taken from Tab. 1.

reaction V_{43} exceeds by 1.5 orders of magnitude all possible channels of ozone formation (Fig. 9). It can be shown that $V_{43} \propto 2 \cdot 10^{17} p^3 \text{ cm}^{-3} \text{ s}^{-1}$, whereas the total ozone formation rate in the O_2 discharge has even a different dependence on the gas pressure ($V_{02} + V_{36}$) $\propto 10^{16} \cdot p^2 \text{ cm}^{-3} \text{ s}^{-1}$. In these estimates, the value $K_{43} = 2 \cdot 10^{11} \text{ cm}^3/\text{s}$ measured in [36] from the rate of the loss of $\text{O}_2(b^1\Sigma_g^+)$. However, it does not follow from the above that the loss of O_3 in this reaction takes place at the same high rate, since the intermediate products of (R 43) are active reagents whose behaviour is determined by the micro-component composition of a concrete experiment. It is possible that, when determining the probability of various channels in the reaction (R 43),

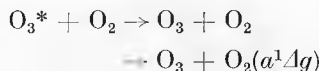


from the output of $\text{O}(^3P)$, the authors of [36] have not taken into account that the vibrationally excited ozone can dissociate rapidly:



and, as a result, they overestimate the efficiency of the reaction (R 43a). In [36] it is He and nitrogen oxides that have been taken as M and that are titration reagents.

In our conditions, the vibrational relaxation of $\text{O}_3^{\#}$ takes place apparently:



It can be seen from Figs. 6–9 that the contribution of a number of reactions can be ignored without any harm to the accuracy of the balance between the processes of production and loss of the corresponding components. We have chosen a boundary for the reactions: less than 1–5% of the total volume rate in the interval $p = 0.1 \div 2$ Torr. In this case, the set (4–8) is simplified, and one can obtain an analytical solution of the set, taking into account the following circumstances:

- at $p < 0.6$ Torr, $[\text{O}_3] < 10^{13} \text{ cm}^{-3}$;
- at $p < 2$ Torr, three-body reactions are ineffective, since $[\text{O}_2] < 6 \cdot 10^{16} \text{ cm}^{-3}$;
- the loss of ions in homogeneous reactions is much more effective than their loss in heterogeneous reactions considered as a result of ambipolar diffusion [17, 29, 37].

Maximum estimation of the hypothetical reaction (R 55) has revealed [38] that this reaction can yield not more than 10–20% of the production of O_3 . On the basis of the estimation of the diffusion coefficient of O_3 in O_2 [39], it can be shown that (R 60) provides less than 20% of the ozone sink rate from the axial zone. Since (R 55) and (R 60) are mutually exclusive in the balance of the O_3 reactions, these reactions must not necessarily be considered in the future: the total error will be small enough and at least smaller than the experimental one. It should also be noted that V_{55} and V_{60} are similarly dependent on gas pressure ($\propto p$).

Thus, the set of equations (4–7), without any loss in its accuracy, can be reduced to the following, simpler form (for the O^- , O_2^- , O_3^- and O_3 ions, respectively):

$$V_{05} + V_{87} + V_{94} = V_{04} + V_{36} + V_{61} + V_{71}, \quad (9)$$

$$V_{06} + V_{71} + V_{91} + V_{92} = V_{05} + V_{37}, \quad (10)$$

$$V_{61} = V_{06} + V_{76}, \quad (11)$$

$$V_{02} + V_{36} + V_{76} = V_{03} + V_{14} + V_{92}, \quad (12)$$

the set of equations (8–12) holds true at $p < 2$ Torr.

4. Solution of the Kinetic Problem at $p < 0.6$ Torr

In this range of pressures, $[O_3] < 10^{13} \text{ cm}^{-3}$, judging by the absorption of UV radiation by the Hartley continuum [23]. This enables to exclude from (8–12) all processes with the participation of O_3 and O_3^- . Then, we obtain the balance equations for O^- and O_2^- , such as:

$$V_{05} + V_{87} + V_{94} = V_{04} + V_{71}, \quad (13)$$

$$V_{71} = V_{05} + V_{37}. \quad (14)$$

In the set of three equations (8, 13, 14), the concentrations of all reagents (except O^- and O_2^-) are known from the experiments. Quite well-known, depending on the mean energies of the reagents, also are the rates of all of the reactions, except K_{37} , for which theoretical estimation $(0.2 \div 20) \cdot 10^{-10} \text{ cm}^3/\text{s}$ from [25] is used traditionally. For the glow discharge conditions, at $p < 0.6$ Torr, the reaction (R 37) can be critical, since, if $K_{37} \cong 10^{-9} \text{ cm}^3/\text{s}$, then (R 37) is the main process of deattachment and if $K_{37} \cong 10^{-11} \text{ cm}^3/\text{s}$, this reaction can be ignored (see, for comparison, Fig. 7). Therefore, we solve the set of equations (8, 13, 14) with respect to three unknowns K_{37} , $[O^-]$, $[O_2^-]$:

$$K_{37} = \frac{A \cdot ([O_2] \cdot K_{71} + [O] \cdot K_{05}) - [O_2]^2 \cdot K_{04} \cdot K_{05}}{[O_2(a^1\Delta g)] \cdot ([O_2] \cdot K_{71} + [O] \cdot K_{04} - A)}$$

$$[O^-] = \frac{A \cdot (n_e - [e])}{[O] \cdot K_{04} + [O_2(a^1\Delta g)] \cdot K_{37} \cdot B} \quad (15)$$

$$[O_2^-] = n_e - [e] - [O^-]$$

where

$$A = [e] \cdot ([O_2] \cdot K_{87} + [O_2(a^1\Delta g)] \cdot K_{94}) / (n_e - [e])$$

$$B = [O_2] \cdot K_{71} / ([O] \cdot K_{05} + [O_2(a^1\Delta g)] \cdot K_{37})$$

the values of $[O^-]$, $[O_2^-]$ from (15) are presented in Fig. 5 for $i = 100$ mA. The physical pattern of ion conversion is in this case associated with the reactions of the formation of O^- in (R 87) and (R 94), with a subsequent rapid recharge (R 71) against the background of the deattachment processes (R 04, R 05, R 37) (Figs. 6, 7).

The distribution of the O^- and O_2^- ion concentrations, depending on the parameter E/n_e , coincides quite well with the mass-spectrometric investigations of the O_2 plasma at low pressures [33].

Tab. 2 presents the results of determining K_{37} from (15), depending on the values of $E_{0_2^-}$, E/n_e and T in glow discharge. The increase of the K_{37} values, as the mean energy of the O_2^- ion grows, approximately corresponds to the following dependence of the cross-section value of the reaction (R 37): $\sigma_{37} \propto (E_i)^{-0.5}$. Below the analysis will be presented of the dependence of K_{37} on E_i and T in a broader interval of energies. It can be seen

Table 2
Measured values of rate constant of reaction R 37

p , Torr	0.1	0.2	0.3	0.4	0.5	0.6
E/n_e , Td	550	325	220	165	134	110
$E_{O_2^-}$, eV	1.5	0.63	0.38	0.25	0.18	0.14
T , K	330	350	360	370	380	385
K_{37} , $10^{-10} \text{ cm}^3/\text{s}$	1.64	1.26	1.19	0.93	1.07	0.78

from Fig. 7 that (R 37) $O_2^- + O_2(a^1\Delta g) \rightarrow 2O_2 + e$, at gas pressures in the discharge $p = 0.1-0.3$ Torr, is the predominant process of electron deattachment, which exceeds substantially in the efficiency the traditionally considered reactions (R 05) $O_2^- + O \rightarrow O_2 + O^-$ and (R 04) $O^- + O \rightarrow O_2 + e$.

5. Solution of the Kinetic Problem at $p = 0.6 \div 1.4$ Torr

In this interval of pressures, $[O_3] \lesssim 10^{13} \text{ cm}^{-3}$, and ozone complicates considerably the ion conversion. However, the main process of the O_3^- ion formation at $p \leq 1.4$ Torr is the recharge of the O^- and O_2^- ions, and assessment can be made without the solution of the entire set of equations (8 \div 12):

$$\frac{[O_3^-]}{[O^-] + [O_2^-] + [O_3^-]} \gtrsim \frac{[O_3] (K_{61} + K_{73})}{[O] \cdot K_{06} + [O_3] \cdot K_{63} + [O_2] \cdot K_{76} + [O_2^-] \cdot K_{78}} \approx 0.005 \div 0.04 \quad (16)$$

depending on the gas pressure (see Fig. 5).

It follows from (16) that the reactions with the participation of O_3^- do not much influence the conversion of O^- and O_2^- . In the pressure region considered ($p = 0.6 \div 1.4$ Torr), reactions (R 37 and R 71) become inefficient, whose rate constants drop sharply with the decrease of the mean energies of the O^- and O_2^- ions (Tab. 2 and [29]). The maximum error appearing because of the exclusion of these reactions from the set (8–12) at $p = 0.6-0.7$ Torr does not exceed 20–30%.

Taking account of the above-said, the balance equations for O^- , O_2^- and O_3 at $p = 0.6-1.4$ Torr are reduced to:

$$V_{05} + V_{87} + V_{94} = V_{04} + V_{36}, \quad (17)$$

$$V_{91} + V_{92} = V_{05}, \quad (18)$$

$$V_{02} + V_{36} = V_{03} + V_{14} + V_{92}. \quad (19)$$

In (17–19), the least known are the values of K_{92} and K_{36} , the rate constant of the reaction (R 36) being estimated in [25] as $(0.3-30) \cdot 10^{-10} \text{ cm}^3/\text{s}$. The rate constant of the reaction (R 92) increases sharply with the increase of E_e [22], and the contribution of this reaction can be very large at $E_e \cong 3-6$ eV, observed at $p = 0.6-1.4$ Torr. The rate constants of other reactions from (16–18) are known precisely enough (Tab. 1), and the concentrations of all reagents (except O^- and O_2^-) have been measured experimentally. We solve the set of equations (8, 17–19) with respect to four unknowns K_{36} , K_{92} , $[O^-]$, $[O_2^-]$:

$$\begin{aligned} [O^-] &= \frac{K_{02} \cdot [O] \cdot [O_2]^2 + [e] \cdot ([O_2] \cdot K_{87} + [O_2]^2 \cdot K_{91})}{[O]} \\ &\quad + \frac{[O_2(a^1\Delta g)] \cdot K_{94} - [O_3] \cdot ([O] \cdot K_{03} + [O(^1D)] \cdot K_{14})}{\times K_{04}} \\ [O_2^-] &= n_+ - [e] - [O^-] \quad (20) \\ K_{92} &= \frac{[O_2^-] \cdot [O] \cdot K_{05} - [e] \cdot [O_2]^2 \cdot K_{91}}{[O_3] \cdot [e]} \\ K_{36} &= \frac{[O_3] \cdot ([O] \cdot K_{03} + [O(^1D)] \cdot K_{14} + [e] \cdot K_{92}) - [O] \cdot [O_2]^2 \cdot K_{02}}{[O_2(a^1\Delta g)] \cdot [O^-]} \end{aligned}$$

The values of $[O^-]$ and $[O_2^-]$ calculated from the experimental data according to (20) are presented in Fig. 5 for $i = 100$ mA, depending on the gas pressure in discharge. The results of the calculation of $[O^-]$ and $[O_2^-]$ are in fair agreement with the mass-spectrometric investigations of the discharge [33] at the corresponding values of E/n , and also with the data of section 4 of the present paper at lower pressures and of [10] at high gas pressures in the discharge. It can be seen from Figs. 6–9 that the results of a given calculation in the region of relatively low pressures ($p < 2$ Torr) confirm the conclusion about the key role of the reaction (R 92) $O_3 + e \rightarrow O_2^- + O$ in the ion conversion of a glow discharge, which was earlier obtained for a discharge at a higher pressure of $= 2-9$ Torr). The output of the O_2^- ions in (R 92) exceeds by a factor of 2–3 orders (p magnitude the effectiveness of the three-body reaction of electron attachment (R 91) $O_2 + e + O_2 \rightarrow O_2^- + O_2$ in the pressure interval examined. By analogy, rather ineffective also is, at lower pressures, another three-body reaction of ozone formation (R 02) $O + O_2 + O_2 \rightarrow O_3 + O_2$ in comparison with the rapid (R 36) $O^- + O_2(a^1\Delta_g) \rightarrow O_3 + e$ (Fig. 9).

These results of the kinetic analysis agree well with the conclusions of [24] and our investigations in the kinetics of the glow discharge at $p > 2$ Torr [10]. It should be emphasized that a considerable role of the $O(^1D)$ atoms has been found out in the ozone loss in a discharge (reaction R 14) which had somehow been disregarded by other investigators. In the gas pressure interval considered, (R 14) ensures about 1/3 of the total ozone loss rate (Fig. 9).

Tab. 3 presents the results of determining the values of K_{36} and K_{92} from (20), depending on the gas temperature and mean energies of electrons and ions. The calculations used the values of the atomic oxygen concentration $[O(^3P)]$, calculated for our conditions in [40] and close to the experimental data of [12]. The variation of $[O(^3P)]$ by $\pm 50\%$ leads to a similar variation of K_{92} , and the values of K_{37} and K_{36} vary by 15–30% (see (15) and (20)).

Table 3
Measured values of rate constants of reactions R 36 and R 92a

p , Torr	0.6	0.7	0.8	1.0	1.4
E/n , Td	110	96	84	70	45
E_{O^-} , eV	0.66	0.43	0.32	0.22	0.11
E_e , eV	4.9	4.6	4.3	3.9	3.1
T , K	385	390	390	400	415
K_{36} , 10^{-10} cm ³ /s	0.10	0.18	0.75	1.1	3.1
K_{92} , 10^{-8} cm ³ /s	4.9	4.7	1.7	3.6	0.8

At the next stage of the kinetic analysis, the set of equations (4–8) was solved on a computer without simplifying assumptions (sections 4 and 5) using regularization methods for the solution. The obtained “precise” solution practically does not differ from (15) and (20) and is presented in its final form in Tab. 2, 3.

6. Dependences of Reaction Rate Constants

$O^- + O_2(a^1\Delta_g) \rightarrow O_3 + e$, $O_2^- + O_2(a^1\Delta_g) \rightarrow 2O_2 + e$ and $O_3 + e \rightarrow O_2^- + O$ on the Mean Energies of the Reagents From the results of the kinetic analysis of processes in the glow discharge of O_2 , presented in sections 4 and 5 of the present paper, the following conclusion can be drawn: direct measurement of the concentrations of the metastable molecules of $O_2(a^1\Delta_g)$ demands revision of the present notion of their participation in the ion formation, especially in reactions (R 94, R 36, R 37).

Under certain conditions, the $O_2(a^1\Delta_g)$ molecules are more effective in processes of electron deattachment than the atoms of oxygen $O(^3P)$. The contribution of the $O_2(b^1\Sigma_g^+)$ molecules to the conversion of ions is less considerable because the experiment yielded the value for the ratio $[O_2(b^1\Sigma_g^+)]/[O_2(a^1\Delta_g)] \lesssim 0.03-0.05$ over the entire examined interval of gas pressures in a discharge (Fig. 4). All results presented in sections 4, 5 of the present paper and obtained for the values of $p = 0.1-1.4$ Torr are in complete agreement with the results of studying the O_2 glow discharge at $p = 2-9$ Torr published in [10] where one can also find data on measurement of the reaction rate constants (for R 36 and R 37) in the energy range of $T = En/1.5 = 440-605$ K. Figs. 10 and 11 show a complete summary of the K_{36} and K_{37} values measured by us and by the authors of [10]. The results are presented in the form of dependencies on the energy of ions and gas temperature.

Aspects of the dependence of the rate constants of ion-molecular reactions on the ion

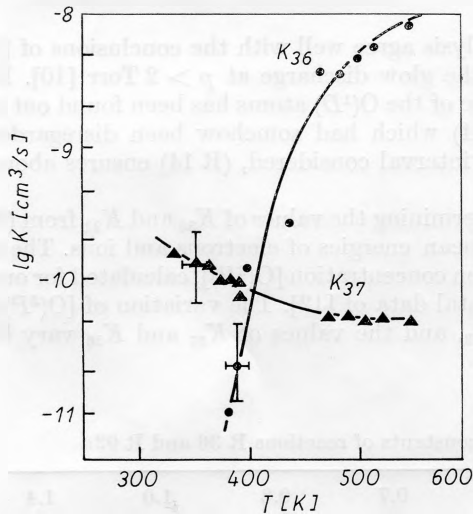


Fig. 10. Results of measurement of rate constant values for reactions R 36 and R 37, as functions of gas temperature. Solid lines designate approximations (21).

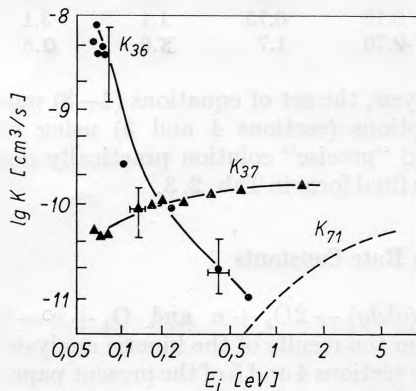


Fig. 11. Results of measurement of rate constant values for reactions R 36 and R 37, as functions of mean energies of ions. Solid lines designate approximations (21). The values of K_{71} have been taken from [22].

energy are analyzed in detail in monograph [22]. In recent works [41, 42] it is pointed out that the rate constants of such reactions must be dependent in a complicated way on the distribution functions of not only ions, but also neutral components. However, it should be noted that there are hardly ever experimental investigations in this field. Practically, there are no investigations of ion-molecular reactions with the participation of electron-excited molecules. Therefore, it is difficult so far to interpret theoretically the values of K_{36} and K_{37} we obtained. By analogy with numerous theoretical analyses of the rate constant of the reaction (R 71) [22, 43], it can be supposed that the reaction (R 36) is accompanied by the formation of an intermediate complex $O^- + O_2(a^1Ag) \rightarrow (O_3^-)^*$, the rate of electron deattachment from which, possibly, depends considerably on the gas temperature and ion energy (Figs. 10 and 11). The weaker dependence of the K_{37} values on E_i and T is in our opinion due to the small binding energy of the complex ion ($O_2-O_2^-$).

To describe the complicated experimental dependences of K_{36} and K_{37} on E_i and T (Figs. 10 and 11) by means of the least square method, we selected the following approximating expressions:

$$\begin{aligned} K_{36} &= (2.5 \pm 0.5) \cdot 10^{-9} \cdot (T/300)^{4 \pm 0.4} \cdot (E_i/0.04)^{-2.6 \pm 0.4}, \\ K_{37} &= (1.0 \pm 0.3) \cdot 10^{-10} \cdot (T/300)^{-2 \pm 0.5} \cdot (E_i/0.04)^{0.23 \pm 0.05} \end{aligned} \quad (21)$$

where K is expressed in cm^3/s , T in $^\circ\text{K}$ and E_i in eV. The approximations (21) hold true at $G = 385-605 \text{ K}$ and $E_{O^-} = 0.10-0.66 \text{ eV}$ for K_{36} , and at $T = 330-605 \text{ K}$ and $E_{O^-} = 0.09-1.5 \text{ eV}$ for K_{37} .

A special role in the glow discharge kinetics for oxygen belongs to the reaction (R 92) $e + O_3 \rightarrow O_2^- + O$, which not only ensures the income of the O_2^- ions, but, due to the fast recharge reaction (R 05) $O_2^- + O \rightarrow O_2 + O^-$, is indirectly the main channel of the formation of the O^- ions in a discharge (Figs. 6, 7). Tab. 4 presents a comparison of the volume rates of basic reactions of electron attachment in an oxygen discharge on the basis of measured values of the reagent concentrations, gas temperature and mean energy of electrons.

Table 4

Volume rates of the formation of negative ions on the discharge axis in reactions R 87, R 91, R 92, R 94, R 95

p , Torr	0.5	1	2	8
V_{87} , $\text{cm}^{-3} \text{ s}^{-1}$	$2 \cdot 10^{15}$	$5 \cdot 10^{15}$	$1.6 \cdot 10^{16}$	$3 \cdot 10^{17}$
V_{91} , $\text{cm}^{-3} \text{ s}^{-1}$	—	—	$1 \cdot 10^{14}$	$2 \cdot 10^{16}$
V_{92} , $\text{cm}^{-3} \text{ s}^{-1}$	$7.3 \cdot 10^{14}$	$1.2 \cdot 10^{16}$	$5 \cdot 10^{17}$	$3 \cdot 10^{18}$
V_{94} , $\text{cm}^{-3} \text{ s}^{-1}$	$4 \cdot 10^{15}$	$9 \cdot 10^{15}$	$3 \cdot 10^{16}$	$6 \cdot 10^{16}$
V_{95} , $\text{cm}^{-3} \text{ s}^{-1}$	$5 \cdot 10^{15}$	$1.5 \cdot 10^{16}$	$4 \cdot 10^{16}$	$1 \cdot 10^{17}$

Fig. 12 shows a summary of the results of measurements of K_{92} obtained in this paper and also in [10, 22]. It can be seen that the values of K_{92} we obtained do not contradict the experimental data of [22] and, on the whole, within the experimental error, they coincide with the continuous curve, depending on the mean energy of electrons. The form of the dependence is typical for the endothermic electron attachment reactions (for instance, (R 87) $e + O_2 \rightarrow O + O^-$) and is likely to be related to the resonance form of the cross-section of reaction (R 92). The relative error of the K_{92} values reaches $\pm 50\%$ and is chiefly due to the fact that the $[O(^3P)]$ values are not so well known (see section 5 of this paper).

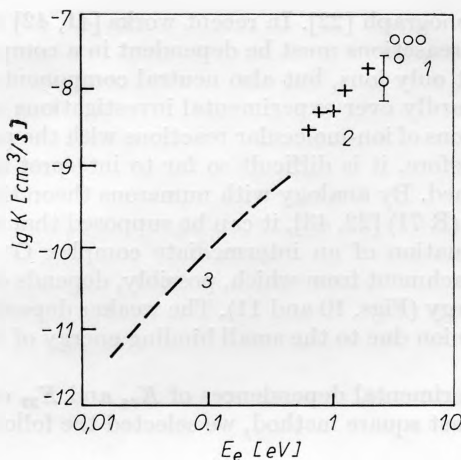


Fig. 12. Experimental values of rate constants of reactions R 92a. Designations: 1 — the present paper, 2 — [10], 3 — [22].

7. Discussion of Results

As already been stated in the introduction, the role of metastable molecules of $O_2(a^1\Delta_g)$ in the processes of ozone formation and conversion of negative ions has been proved experimentally. However, direct measurements of the concentrations of metastable atoms and molecules of oxygen we performed show that for an adequate description of the kinetics in an oxygen discharge, successive accounting for reactions with the participation of $O(^1D)$ and $O_2(b^1\Sigma_g^+)$ is also necessary. In spite of the fact that their relative concentrations in gas do not exceed $1 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$, respectively, due to their high reactive capacity, these excited components influence considerably the processes of ozone formation in a discharge. The role of the $O(^1D)$ atoms in an oxygen discharge is demonstrated in the most spectacular way in the circumstance that the reaction $O(^1D) + O_2 \rightarrow O + O_2(b^1\Sigma_g^+)$ is predominant over all the remaining processes of population of the level $b^1\Sigma_g^+$ in the pressure interval from 0.1 to 9 Torr, as has been shown in [10]. Such a mechanism of populating the second metastable level of the O_2 molecule is absolutely different from the mechanism of populating the lower metastable level of O_2 : the reaction $e + O_2 \rightarrow O_2(a^1\Delta_g) + e$, which is predominant at $p = 2-8$ Torr [10]. The predominant reactions of deactivation of the singlet levels of the oxygen molecule, $O_2(a^1\Delta_g) + O^- \rightarrow O_3 + e$ and $O_2(b^1\Sigma_g^+) + O_3 \rightarrow O_2^* + O_3^*$, respectively, are also different. Thus, taking account of the experimental data, it can be concluded that all excited and ionized components in a discharge are in close dynamical interdependence, and disregard of individual excited components may lead to inadequate theoretical description of the kinetics of chemical processes in a positive column of the glow discharge. This statement appears to be experimentally proved for at least the lower excited metastable levels of the atoms and molecules of oxygen. At the same time, one must be careful that there is no high content of impurities in the discharge, especially of water, because their reactions with some metastable components may have gas-kinetic rates. Even a low concentration of impurities can result in a radical change of the entire reaction kinetics of the discharge. The high degree of reproducibility of the results in our investigations is, in our opinion, due to systematic control of the content of impurities where $\gamma < 10^{-3}\%$ may be considered admissible.

Satisfactory agreement between the theoretical model of the chemical kinetics of the processes in the discharge and the experimental data made it possible to estimate, over a broad interval of energies, the rate constants of three reactions (R 36, R 37, R 92) less studied so far. All of these reactions play an important part in the mechanism of ion conversion of the *D*-region in the atmosphere, the (R 36) reaction being the main channel of loss of the O⁻ ions at heights 60–85 km in the Earth's ionosphere. Aeronomical applications of the results obtained in this paper are considered in detail in [20, 21, 26, 47].

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Received July 17, 1989;

final revised manuscript received January 25, 1990