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EQUILIBRIA AND PROCESSES IN DISSOCIATED AIR

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Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, 125412, Russia
e-mail: bmsmirnov@gmail.com

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Abstract. For atmospheric air as a mixture of molecular gases in thermodynamic equilibrium, an algorithm is presented for calculating the density of atoms and molecules in the case of separation of dissociative transition regions for each component. The result is compared with an approximation where the partial pressures of nitrogen and oxygen are temperature-independent. Ionization equilibrium at temperatures below 7000 K occurs through the formation of molecular ion NO^+, and at higher temperatures, the formation of atomic ions of oxygen and nitrogen dominates. It is shown that at pressures around atmospheric, with accuracy higher than 10%, electron-excited states of atoms can be neglected in the analysis of ionization equilibrium up to complete ionization of air. For the analysis of air plasma in the lightning conducting channel, the use of results and experimental data shows that the passage of the main electric current during the return stroke phase is temporally separated from the subsequent expansion of the heated channel. It is shown that the plasma temperature of the conducting channel between adjacent flashes, as well as before the passage of the main electric current, is approximately 4 kK. This temperature is maintained by small external electric fields.

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1. INTRODUCTION

Interest in the properties of dissociated and ionized air at atmospheric and near-atmospheric pressure has arisen repeatedly over the last century in connection with atmospheric processes, the use of air in chemical production and material processing by air jets flowing from flowthrough plasma torches, electrical and laser excitation of air, as well as in the analysis of spacecraft and space objects passing through the atmosphere. We will further focus on one of these phenomena – the passage of electric current through the conducting channel of lightning.

When atmospheric air is excited to its dissociation and ionization, partial or complete, under certain conditions, thermodynamic equilibrium is established with respect to its components, although this equilibrium may relate to a limited region of space (local thermodynamic equilibrium) and be maintained for a limited time. The nature of this equilibrium can change during the evolution of excited air depending on external conditions and processes that determine the development of excited air. Nevertheless, when analyzing the state of excited air, its parameters at a given moment can be expressed through temperature and pressure.

Under these conditions, in the first approximation, the degree of dissociation and ionization of excited air is determined by the Saha formula [1, 2] in accordance with the parameters of molecules, atoms, and ions of nitrogen and oxygen. In this case, due to the large statistical weight of continuous spectrum states, noticeable gas dissociation begins at temperatures which, when expressed in energy units, are an order of magnitude lower than the dissociation energies of air molecules. The same applies to the ionization of atomic gas. Based on this, we find that the dissociation of air molecules becomes noticeable at temperatures of several thousand degrees, and the ionization of atoms begins at tens of thousands of degrees. However, in dissociated air, a new ionization channel emerges, associated with the formation of a molecular ion NO^+ from nitrogen and oxygen atoms [3, 4] due to the high dissociation energy of this molecular ion. Therefore, the initial ionization of air during temperature increase accompanies the dissociation of nitrogen molecules.

The nature of thermodynamic equilibrium in air determines a simple algorithm for calculating thermodynamic parameters of hot air, but before the advent of personal computers, such calculations were a cumbersome computational task. Therefore, the parameters of equilibrium excited air were usually presented in the form of tables or approximated functions [5-8]. Now such calculations are accessible for modern personal computers, and this article will analyze algorithms for analyzing dissociative and ionization equilibria in equilibrium excited air.

The topic of this article is the analysis of processes occurring in air plasma. At a high degree of ionization, plasma created by an external electric field is unstable due to current-convective instability. This instability has the same nature as in the case of using a magnetic field for plasma stabilization [9, 10]. Specifically, temperature perturbation, leading to perturbation in plasma expansion velocity, creates vortices that destroy the plasma. Accordingly, the development time of current-convective instability slightly exceeds the characteristic time of plasma movement, in our case, the expansion time of the lightning conductive channel. To establish thermodynamic equilibrium in such plasma, elastic collisions between atoms and electrons must lead to thermodynamic equilibrium within atomic and electronic subsystems during this time. The equilibrium between atomic and electronic subsystems results from inelastic collisions of electrons with nitrogen and oxygen atoms, corresponding to transitions between fine structure states of atoms and ions.

Analysis of plasma formed during electric current passage through gas is simplified in the case of thermodynamic equilibrium in it. In this article, this is used to analyze the passage of lightning electric current through the atmosphere.

Lightning is a complex physical phenomenon, various aspects of which have been studied in detail over the last century. Due to its complexity, understanding of the main elements of this phenomenon comes from experimental studies, and then, based on these and general physical principles, evaluations are made and models are created that allow a deeper understanding of the physical nature of individual aspects of this phenomenon.

In this article, the results obtained from the analysis of equilibrium hot air are used to study two stages of lightning electric current flow through the conductive lightning channel. This relates to the return stroke stage, when maximum electric current flows through the conductive channel, while the channel itself expands and breaks down. Another stage is associated with the time interval between adjacent lightning flashes. This time is determined by charge movement at the lower edge of the cloud. Specifically, charge separation in the cloud creates an atmospheric electric field and causes subsequent lightning discharge. By connecting different parameters of the processes under consideration, it is possible to estimate plasma parameters during the time interval between adjacent lightning flashes, as well as the strength of the external electric field that should maintain the plasma of the lightning conductive channel until the next flash.

2. DISSOCIATIVE EQUILIBRIUM IN HEATED AIR

Considering dissociative equilibrium in air at near-atmospheric pressure and at high temperatures up to 30 kK, the maximum temperature in the lightning conductive channel, let us first present the calculation algorithm in the general case, which can be used for other gas mixtures as well. We will assume that atoms and molecules are in their ground electronic states, and in the case of air, we will use their parameter values presented in the table.

$$\begin{gathered} \mathrm{O}_2(^3\Sigma_g^-) \leftrightarrows 2\mathrm{O}(^3P), \\ \mathrm{N}_2(^3\Sigma_g^+) \leftrightarrows 2\mathrm{N}(^4S), \\ \mathrm{NO}(X\,^2\Pi) \leftrightarrows \mathrm{N}(^4S) + \mathrm{O}(^3P) \end{gathered} \tag{1}$$

The dissociative equilibrium in air is described by equations of molecules and atoms according to the Saha formula [1, 2]

$$f(T) \equiv \frac{[\mathrm{X}]^2}{[\mathrm{X}_2]} = \frac{1}{2}\frac{g_a^2}{g(\mathrm{X}_2)}\frac{g_c(\mathrm{X}-\mathrm{X})}{g_m}\exp\left(-\frac{D}{T}\right), \tag{2}$$

$$g_c(\mathrm{X}-\mathrm{X}) = \left(\frac{\mu T}{2\pi\hbar^2}\right)^{3/2},$$

$$g_m = \frac{T}{B}\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right]^{-1}.$$

Here [X] – density of atoms X, g_a and $g(\mathrm{X}_2)$ – statistical weights of electronic states of atom X and molecule X_2 respectively, $g_c(\mathrm{X}-\mathrm{X})$ – statistical weight for the continuous spectrum of two X atoms, g_m – statistical weight of rotational and vibrational states of the molecule X_2. The coefficient 1/2 accounts for the symmetry of the molecule X_2, μ – reduced mass of atoms, equal to half the atom mass,

Table. Parameters of molecular particles relevant to equilibrium in hot air [11]

Parameter	$N_2(X^1\Sigma_g^+)$	$O_2(X^2\Sigma_g^-)$	$NO(X^2\Pi_{1/2})$	$NO^+(X^2\Sigma^+)$
B, cm^{-1}	1.998	1.445	1.672	1.43
$\hbar\omega$, cm^{-1}	2359	1580	1904	2377
D, eV	9.58	5.12	6.50	10.85
J_m, eV	15.58	12.07	9.26	–
J_a, eV	14.53	13.62	–	–

B – rotational constant, $\hbar\omega$ – vibrational excitation energy of the molecule, D – dissociation energy of the molecule X_2. The values of the last three parameters, as well as the potentials of atoms J_a and molecules J_m are given in the table.

For simplicity, we will consider that air consists of two components – nitrogen and oxygen, with nitrogen nuclei concentrations c_N and oxygen c_O equal to $c_N = 0.79$ and $c_O = 0.21$ respectively in each macroscopic element of air. According to the equation of state of air as a gas for the total density N of atomic particles we have

$$N(T) \equiv [N_2] + [N] + [O_2] + [O] = \frac{p}{T} \tag{3}$$

In addition, since during dissociation the relative number of nuclei for each component is preserved in each element of air, we have the following relationship:

$$\frac{2[N_2] + [N]}{2[O_2] + [O]} = \frac{c_N}{c_O}. \tag{4}$$

Expanding equation (2) separately for dissociative equilibrium in nitrogen and oxygen, we obtain the following equations:

$$\begin{aligned} f_N(T) &\equiv \frac{[N]^2}{[N_2]} = \\ &= \xi_N \sqrt{T} B_N [1 - \exp(-\hbar\omega_N/T)] \exp(-D_N/T), \\ f_O(T) &\equiv \frac{[O]^2}{[O_2]} = \\ &= \xi_O \sqrt{T} B_O [1 - \exp(-\hbar\omega_O/T)] \exp(-D_O/T), \end{aligned} \tag{5}$$

where

$$\xi_N = g(N)^2/g(N_2) = 16,$$
$$\xi_O = g(O_2)^2/g(O) = 27,$$

$g(X)$ – statistical weight of particle X, corresponding to its electronic state, and the indices indicate the molecules to which the considered quantities relate. Combining formulas (3), (4), and (5), we will further determine the densities of nitrogen and oxygen atoms and molecules in the transition temperature range where the transition to dissociated air occurs.

Four equations – (3), (4), and (5) – allow determining four atomic particle densities, namely, [N], [N_2], [P], [O_2]. The analysis of this system of equations is simplified since the temperature ranges for the dissociative transition of oxygen and nitrogen are separated. Indeed, the transition of oxygen to a dissociated state occurs at temperatures at which nitrogen atoms are practically absent in thermodynamically equilibrium air, while nitrogen dissociation occurs at temperatures at which oxygen molecules are practically absent in equilibrium air. This allows excluding the second equation (5) when analyzing the dissociative equilibrium of nitrogen, as well as the first equation (5) when analyzing the dissociative equilibrium of oxygen. As a result, we have

$$\begin{aligned} c_N N &= (1 + c_O)[N_2] + [N], \quad [O_2] \ll [O], \\ c_O N &= [O_2] + (1 + c_O)[O]/2, \quad [N] \ll [N_2]. \end{aligned} \tag{6}$$

Solving the system of equations (5) and (6) separately for nitrogen and oxygen in the areas of dissociative transition for each of these components, for atom densities in these areas we obtain

$$\begin{aligned} [N] &= \sqrt{\frac{f_N^2}{4(1+c_O)^2} + \frac{f_N c_N N}{1+c_O}} - \frac{f_N}{2(1+c_O)}, \\ [N_2] &= \frac{c_N N}{1+c_O} - \frac{[N]}{1+c_O}, \quad [N] \ll [N_2], \\ [O] &= \sqrt{\frac{(1+c_O)^2 f_O^2}{4} + f_O c_O N} - \frac{(1+c_O) f_O}{2}, \\ [O_2] &= c_O N - (1+c_O)[O]/2, \quad [O] \gg [O_2]. \end{aligned} \tag{7}$$

Fig. 1 shows the dependence of oxygen and nitrogen atom density on temperature in equilibrium hot air

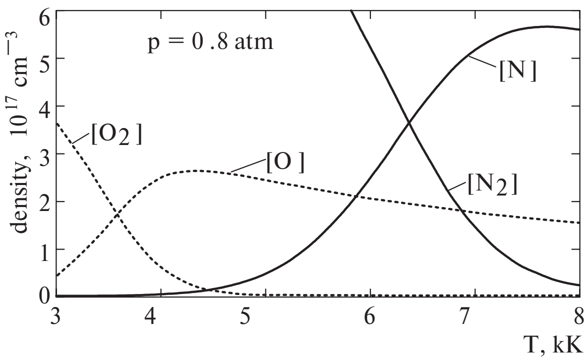

Fig. 1. Temperature dependencies of the density of nitrogen and oxygen atoms and molecules in equilibrium hot air at pressure $p = 0.8$ atm according to formulas (7)

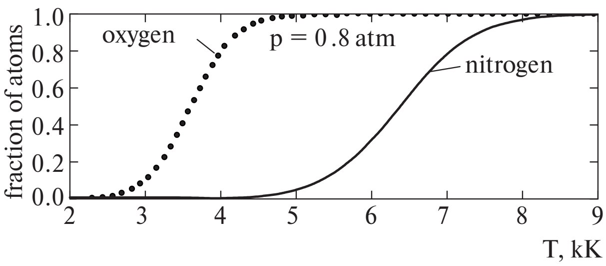

Fig. 2. Temperature dependencies of the fractions of nitrogen atoms $C_N(T)$ and oxygen $C_O(T)$, determined by formulas (8), in equilibrium hot air at pressure $p = 0.8$ atm

at pressure $p = 0.8$ atm in the area of dissociative transition for the corresponding component. This pressure for the standard atmosphere, i.e., for the atmosphere with time-averaged parameters across the globe, is realized at an altitude of $h = 2$ km. By relating the results of specific calculations to this pressure, we thereby focus on hot equilibrium air formed at the specified height during the passage of electric current through the atmosphere in the linear lightning channel. Subsequent specific calculations relate to this pressure.

Let's introduce the fractions of atoms C_N and C_O for corresponding components as the relative number of atoms of a given type in accordance with expressions

$$C_N(T) = \frac{[N]}{[N]+[N_2]}, \quad C_O(T) = \frac{[O]}{[O]+[O_2]}, \quad (8)$$

where expressions for atom and ion densities are given by formulas (7). Fig. 2 shows the temperature dependencies of the degree of dissociation of nitrogen and oxygen in hot air.

Note that the presented algorithm for determining the degree of molecular dissociation in a gas mixture is valid in cases where the dissociative transition for each of its components occurs in different temperature regions. In this case, atoms and molecules are in their ground electronic states, which is valid for the dissociative transition temperatures of nitrogen and oxygen. Furthermore, the obtained results confirm general principles regarding the nature of the transition of equilibrium molecular gas to a dissociated state, according to which this transition occurs at temperatures expressed in energy units that, at atmospheric pressure, are an order of magnitude lower than the molecular dissociation energy. This is due to the large statistical weight of the continuous spectrum states of molecular gas.

The exact solutions presented above for the density of nitrogen and oxygen atoms and molecules are valid in a limited temperature range. It is convenient to use an approximate method when there is no interaction between components, i.e., each component's contribution to the total gas pressure is independent of temperature. This approximation corresponds to replacing the exact relation (4) with the following:

$$c_N N = [N] + [N_2],$$
$$c_O N = [O] + [O_2].$$

This gives the following for atomic densities instead of (6)

$$[N] = \sqrt{f_N^2/4 + f_N c_N N} - f_N/2,$$
$$[O] = \sqrt{f_O^2/4 + f_O c_O N} - f_O/2. \quad (9)$$

As can be seen, the interaction between components during the dissociative transition occurs due to changes in pressure contribution from different components during the dissociation of each of them. In the case of air, the oxygen contribution to pressure changes from 21% for molecular oxygen to 35% for dissociated oxygen and molecular nitrogen. The approximate method for determining the degree of dissociation, which neglects the interaction between components through their contribution to pressure, gives values close to the exact values of atom densities in equilibrium atmospheric air.

Let's evaluate the accuracy of the approximate method by comparing the partial pressure of nitrogen at temperatures where the densities of oxygen or nitrogen atoms are equal. In the first case, the partial pressure of nitrogen for the approximate solution of equations (9) at the temperature where oxygen is half-dissociated is $(1 + c_O/3)$ lower than the exact value, and at the temperature where nitrogen is half-dissociated, it is $(1 + c_O/2)$ higher than the exact solution gives. Hence, the accuracy of the approximate method is estimated at 10%.

3. IONIZATION EQUILIBRIUM IN AIR WITH PARTICIPATION OF MOLECULAR IONS

The ionization transition in equilibrium air is expected at higher temperatures than the dissociative transition, since the ionization potentials of atoms significantly exceed the dissociation energies of molecules. However, in air as a multicomponent system, there is an additional ionization channel associated with the formation of the nitrogen oxide molecular ion [3, 4]. This ionization channel occurs at lower temperatures than in the case of pure nitrogen or oxygen. This channel corresponds to the process

$$N(^4S) + O(^3P) \rightleftarrows NO^+(X^1\Sigma^+) + e + \Delta\varepsilon. \quad (10)$$

The transition energy $\Delta\varepsilon$ for the considered process in the case of the ground state of the participating particles can be found in two ways:

$$\Delta\varepsilon = J(NO) - D(NO) = \\ = J(O) - D(NO^+) = 2.77 \text{ eV}, \quad (11)$$

where $J(NO) = 9.264$ eV is the ionization potential of the molecule NO, $D(NO) = 6.497$ eV is the dissociation energy of the molecule NO, $J(O) = 13.62$ eV is the ionization potential of the oxygen atom, $D(NO^+) = 10.85$ eV is the ionization potential of the oxygen atom, NO^+ [11]. As can be seen, the energy (11) is noticeably lower than the dissociation energies and ionization potentials of atomic particles formed in air. Therefore, ionization based on channel (10) occurs at temperatures that lead to the dissociation of air molecules. Moreover, only the Σ-state of the molecular ion NO^+ can participate in this process, which corresponds to the ground electronic state of the nitrogen atom and oxygen ion forming it.

Based on the equilibrium of process (10) in hot air and the Boltzmann distribution for the densities of atomic particles participating in it, and assuming that the formation of the molecular ion NO^+ does not affect the density of atoms, for equilibrium in process (10) we have

$$\frac{[NO^+]N_e}{[N][O]} = \frac{g_m g_c(e{-}NO^+)}{g g_c(N{-}O)} \exp\left(-\frac{\Delta\varepsilon}{T}\right). \quad (12)$$

Here $[N]$, $[O]$, $[NO^+]$ are the current densities of the specified atomic particles, N_e is the electron density, g is a combination of statistical weights for electronic states of atomic particles participating in process (10), g_m is the statistical weight of rotational and vibrational states of the nitrogen oxide molecular ion, expressed through its parameters according to formula (2) g_c is the statistical weight of continuous spectrum states for atomic particles indicated in parentheses.

The statistical weight of the rotational and vibrational states of the molecular ion NO^+ is determined by the formula

$$g_m = \frac{T}{B}\frac{1}{1 - \exp(-\hbar\omega/T)}, \quad (13)$$

where the rotational constant B and energy $\hbar\omega$ of vibrational excitation in the molecule are given above in the table. For the statistical weight of continuous spectrum states, we have the following expressions according to the Saha formula:

$$g_c(e{-}NO^+) = \xi T^{3/2}, \\ g_c(N{-}O) = \left(\frac{\mu}{m_e}\right)^{3/2} \xi T^{3/2}, \quad (14) \\ \xi = \left(\frac{m_e}{2\pi\hbar^2}\right)^{3/2},$$

where m_e is the electron mass. The combination of statistical weights for the electronic states of the nitrogen atom $N(^4S)$, oxygen ion $O^+(^4S)$ and electron $g_e = 2$, which participate in the equilibrium under consideration, is

$$g = \frac{g(N)g(O)}{g(NO^+)g_e} = 18,$$

where the particles to which the statistical weight of electronic states relates are indicated in parentheses.

Taking into account the quasi-neutrality of air plasma ($[NO^+] = N_e$), based on formula (12) for electron density in equilibrium hot air in the temperature range under consideration according to scheme (10), including the case when ion NO^+ is an intermediate product of this process, we obtain

$$N_e = \sqrt{\frac{g_m}{18}\left(\frac{m_e}{\mu}\right)^{3/2}[N][O]} \exp\left(-\frac{\Delta\varepsilon}{2T}\right). \quad (15)$$

Here $\mu = 7.5$ at.units is the reduced mass of nitrogen and oxygen atoms. Formula (15) gives the electron density at relatively low temperature when air is partially dissociated and ionization corresponds to scheme (10).

Obviously, at higher temperatures, molecular ions NO^+ decompose forming atomic oxygen ions, which occurs according to the scheme

$$NO^+(X^1\Sigma^+) \rightleftarrows N(^4S) + O^+(^4S). \qquad (16)$$

In this case, the dissociation of the nitrogen oxide molecular ion occurs at relatively high temperature in equilibrium air due to the large dissociation energy of the molecular ion, and the dissociative equilibrium between atomic and molecular ions in hot equilibrium air is determined by formula (2)

$$\frac{[O^+][N]}{[NO^+]} = \frac{g' g_c(N\text{–}O^+)}{g_m}\exp\left(-\frac{D}{T}\right),$$
$$g_c(N\text{–}O^+) = \left(\frac{\mu}{m_e}\right)^{3/2}\xi T^{3/2}, \qquad (17)$$

where the statistical weight g_m of the molecular ion is given by formula (13). The parameters of the molecular ion NO^+, taken from the table, are $B = 1.43$ cm^{-1} – rotational constant, $\hbar\omega = 2377$ cm^{-1} – vibrational excitation energy, $D = 10.85$ eV – dissociation energy of the molecular ion, $g' = 16$ – combination of statistical weights of atomic particles relating to their electronic state, $\mu = 7.5$at.units – reduced mass of nitrogen and oxygen atoms.

As a consequence of processes (10) and (16), the maximum density of molecular ions NO^+ corresponds to a temperature of 6750 K at hot air pressure $p = 0.8$ atm and equals $5 \cdot 10^{14}$ cm^{-3}. In this case, the equality of molecular ion densities NO^+ and atomic ion densities O^+ is achieved at a temperature of 7200 K.

At high temperatures, atomic ions are the main type of ions in air plasma. The corresponding ionization equilibrium processes follow the schemes

$$N(^4S) \leftrightarrow e + N^+(^3P),$$
$$O(^3P) \leftrightarrow e + O^+(^4S). \qquad (18)$$

Then the Saha formula [1, 2] leads to the following relationship between the densities of electrons, ions, and oxygen atoms, assuming that atoms and ions are in their ground electronic states:

$$\frac{N_e[O^+]}{[O]} = F_O(T),$$
$$F_O(T) = \frac{g_e g(O^+)}{g(O)}\xi\exp\left(-\frac{J_O}{T}\right). \qquad (19)$$

Here [O] and $[O^+]$ are the densities of oxygen atoms and ions respectively, the statistical weights of these atomic particles are

$$g(O) = 9, \quad g(O^+) = 4, \quad g_e = 2.$$

Furthermore, $J_O = 13.62$ eV is the ionization potential of the oxygen atom according to the table data. Note that the ionization equilibrium (17) can be obtained as the product of distributions (12) and (15). This means that the ionization equilibrium (10) with increasing temperature transitions into the equilibrium described by the second equation of formula (18). Similar to equation (19) for oxygen, for nitrogen we have

$$\frac{N_e[N^+]}{[N]} = F_N(T),$$
$$F_N(T) = \frac{g_e g(N^+)}{g(N)}\xi\exp\left(-\frac{J_N}{T}\right). \qquad (20)$$

This equation includes the same parameters as equation (19), but they relate to nitrogen.

Along with this, we have the plasma quasi-neutrality condition, which is described by the equation

$$N_e = [N^+] + [O^+] + [NO^+]. \qquad (21)$$

To this we should add the equation for the total pressure of excited air, as well as the equation for conservation of the relative mass of nitrogen and oxygen in any macroscopic volume, which are analogous to formulas (3) and (4) for dissociative equilibrium and have the form

$$N(T) = [N] + [N^+] + [O] + [O^+] + N_e,$$
$$\frac{[N] + [N^+]}{[O] + [O^+]} = \frac{c_N}{c_O}. \qquad (22)$$

As a result, we get five equations (19)–(22), which determine five particle densities [N], $[N^+]$, [O], $[O^+]$, $[N_e]$. Thus, based on these equations, we can determine the densities of atomic particles in equilibrium partially ionized air.

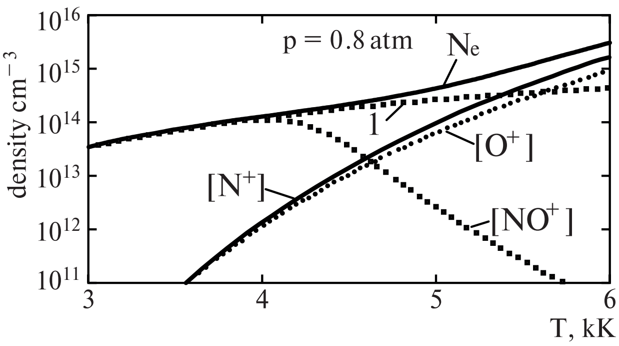

Fig. 3. Temperature dependencies of charged atomic particle density in equilibrium hot air, corresponding to the low-temperature part of ionization equilibrium. Number 1 marks the density of electrons resulting from the formation of ions $[NO^+]$

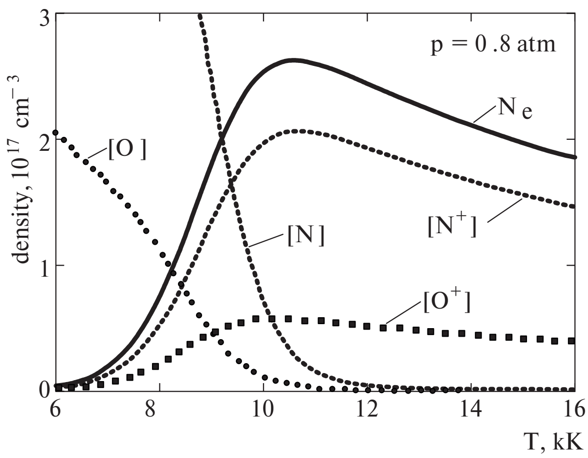

Fig. 4. Temperature dependencies of nitrogen and oxygen atom and ion densities, as well as electron density in equilibrium ionized air, calculated using formulas (20), (21), (22), and (23) at air pressure $p = 0.8$ atm

Fig. 3 shows electron and ion densities at relatively low temperatures, where nitrogen molecule dissociation is incomplete and the main or significant contribution to ionization occurs through the formation of molecular ions $[NO^+]$. The electron density through this channel, as well as the molecular ion density $[NO^+]$, is several orders of magnitude lower than the electron density at high temperatures due to the small parameter m_e/μ in formula (15).

Fig. 4 shows the temperature dependencies of electron, ion, and atom densities in the case of ionization equilibrium (18). using the assumption where interactions between components are neglected. Then the total density of nitrogen ions and atoms equals $c_N N$, and the total density of oxygen ions and atoms equals $c_O N$, so that the second equation of formula (22) is automatically satisfied. This allows decoupling the system of five equations, dividing it into two independent systems of two equations, separately for nitrogen and oxygen. Accordingly, the densities of nitrogen and oxygen ions equal

$$[N^+] = c_N \sqrt{F_N^2 + NF_N} - c_N F_N, \quad [O^+] = c_O \sqrt{F_O^2 + NF_O} - c_O F_O. \tag{23}$$

Note that the considered method is based on the assumption that atoms and ions in the ground state participate in ionization equilibrium. Taking into account excited electronic states of atoms and ions leads to replacing the statistical weights of atoms and ions in ground states with statistical sums in the corresponding formulas, and the role of excited states in ionization equilibrium increases with temperature rise. However, at temperatures where ionization transition occurs, accounting for the role of excited electronic states of atoms and ions leads to an increase in their statistical weights by several percent, which does not exceed the accuracy of the provided calculations.

As follows from Figs. 3 and 4, the first stage of ionization equilibrium occurs at temperatures of dissociative transition through the formation of molecular ion NO^+. Accordingly, the density of ions and electrons at these temperatures is low. In particular, the maximum density of molecular ions NO^+ is approximately 10^{14} cm^{-3}. At higher temperatures, when ionization equilibrium is determined by atomic ionization, the densities of electrons and ions increase by three orders of magnitude.

Note that when considering ionization equilibrium in air, we focus on the plasma of the lightning conducting channel, whose maximum temperature can reach 30 kK. In the high-temperature region, this plasma becomes fully ionized. Moreover, starting from approximately 28 kK, doubly charged ions dominate in this plasma.

4. PLASMA OF THE LIGHTNING CONDUCTING CHANNEL

In conducting this analysis, we assumed that thermodynamic equilibrium is maintained in the air plasma. However, with a significant degree of plasma ionization, current-convective instability develops [9, 10] if the plasma is created by electric current. This instability occurs at a low degree

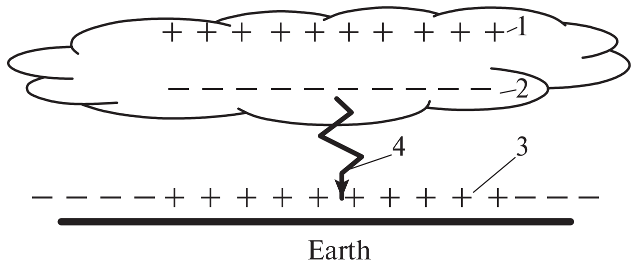

Fig. 5. Atmospheric conditions leading to lightning formation: 1, 2 – areas containing water microdroplets of the specified charge sign; 3 – induced electric charge on Earth's surface under the influence of the cloud's lower edge charge; 4 – charge transfer from the cloud's lower edge to Earth's surface

of ionization when interactions between charged particles dominate. Practically, ionized air is stable at an ionization degree less than 1% [12]. At higher ionization degrees, plasma stabilization is possible in a jet flowing from a plasmatron [13, 14]. In other cases, we deal with pulse plasma that exists for a limited time, but with sufficient plasma density, thermodynamic equilibrium is established in a shorter time.

In the case of air plasma, inelastic collisions involving ions and atoms play an important role in establishing equilibrium, resulting in changes to their electronic state while maintaining the structure of the electron shell. In the case of atom and ion collisions in air at atmospheric and near-atmospheric pressure, the characteristic time for establishing this equilibrium is estimated to be about 1 μs. Therefore, if the characteristic time of plasma parameter changes exceeds this value, thermodynamic equilibrium is maintained during plasma evolution.

Indeed, in air plasma at a temperature of several thousand degrees, inelastic transitions during collisions of atoms and ions occur as a result of the intersection of corresponding electronic terms of colliding particles [15, 16]. The cross-section of the inelastic transition σ is of the order of atomic magnitude, $\sigma \sim 10^{-16}$ cm^2, so that the characteristic time for establishing equal gas and electron temperatures is $\tau \sim (Nv\sigma)^{-1} \sim 10^{-6}$ s, where $N \sim 10^{17}$ cm^{-3} is the characteristic density of colliding atomic particles (atoms and ions) at atmospheric pressure and considered temperatures, $v \sim 10^5$ cm/s is the characteristic velocity of these particles.

Considering the evolution of air plasma at atmospheric and comparable pressure, if a significant change in its state occurs over times exceeding microseconds, we can assume that at each moment in time it maintains thermodynamic equilibrium, where gas and electron temperatures are equal. Then the nature of air plasma evolution is described by changes in temperature T of the plasma, its pressure and composition. In this case, we focus on the plasma of the lightning conducting channel.

We use the results of examining equilibrium atmospheric air at high temperatures to analyze the plasma of the lightning conducting channel. Lightning, as one of the stages of atmospheric electricity, is a complex phenomenon [17–24] and begins with the formation of an electric field in a cumulus cloud due to the drift of charged water microdroplets [25] towards Earth's surface under its gravitational field. This leads to charge separation in the cumulus cloud, so that more often a negative charge forms on the lower edge of the cumulus cloud, which, due to the high conductivity of Earth's surface, induces a positive charge on it, as shown in Fig. 5. This pattern of electric charge transfer from the cloud's lower edge to Earth's surface is possible during warm seasons when charged droplets at the cloud's lower edge lose their charge due to molecular ion evaporation. Then the charge of the cloud's lower edge is determined by molecular ions, more often negatively charged, so that charge drift to Earth's surface under its gravitational field stops [26].

Considering charge transfer from clouds to Earth's surface as a global process, we will assume that, according to measurements [27], the electrical potential U of pre-storm clouds is U = 20–100 MB. The typical electric field strength in pre-storm weather is $E_0 = 300$ V/cm [28–30], and as can be seen, this field strength can be maintained at a distance of several kilometers between clouds and Earth's surface. Furthermore, this electric field strength corresponds to the charge density at the cloud's lower edge and induced on Earth's surface, which is about $10^8 e/\mathrm{cm}^{-2}$. Since the typical charge carried by an average lightning bolt is estimated as $Q = 20$ C [17], we find that the characteristic cloud size providing charge transfer for an average lightning bolt is about 10 km.

The first stage of lightning electric current passage between a cloud and the Earth's surface is the leader – an ionization wave that creates a conducting channel between them. In the next stage, during the return stroke, the main part of the charge is transferred within a short time, about 1 μs, and hot equilibrium air plasma is created inside the lightning conducting channel. The relaxation of this plasma is accompanied by cooling and plasma dispersion, which is described by corresponding models [31–33] using the assumption that the effect of external fields at this stage of lightning development is insignificant. Due to the geometry of electric charge distribution (see Fig. 5), only part of the charge is transferred as a result of the current pulse, and the electric current is blocked when sufficient positive charge in the form of positive ions accumulates at the throat of the conducting channel.

However, this charge is small compared to the charge of the cloud's lower edge, and therefore, when it disperses in space, a new lightning flash may occur, which differs from the first flash in that instead of a stepped leader, the conducting channel is created by a dart leader in weakly conducting air. Obviously, in the absence of an external field, the conducting channel decays in less than a millisecond, and subsequent charge transfer from clouds to the Earth's surface could occur through a new conducting channel. Thus, between adjacent flashes, the plasma of the conducting channel is maintained by the external field. Our task is to estimate the plasma parameters of the conducting channel during the time interval between adjacent lightning flashes.

Due to the complexity of lightning as a physical phenomenon, experimental results are the foundation for understanding this phenomenon, and therefore Fig. 6 presents data on plasma relaxation in the lightning conducting channel, which is useful for this purpose. The temperature is derived from the ratio of spectral line intensities belonging to a multiplet located in the optical spectrum region and including spectral transitions for doubly charged ions. Since the density of doubly charged ions sharply decreases with distance from the center of the conducting channel, the presented temperature refers to the center of the conducting channel. Air pressure is recovered from the spectral line width.

According to the data in Fig. 6, the relaxation time of the plasma temperature in the lightning conducting channel equals $\tau_T \approx 54$ μs in the first stage of plasma evolution, while the pressure relaxation time equals $\tau_p \approx 9$ μs. This indicates that the first stage of plasma relaxation in the lightning return stroke is determined by plasma expansion, whereas temperature relaxation occurs much more slowly. The characteristic time for

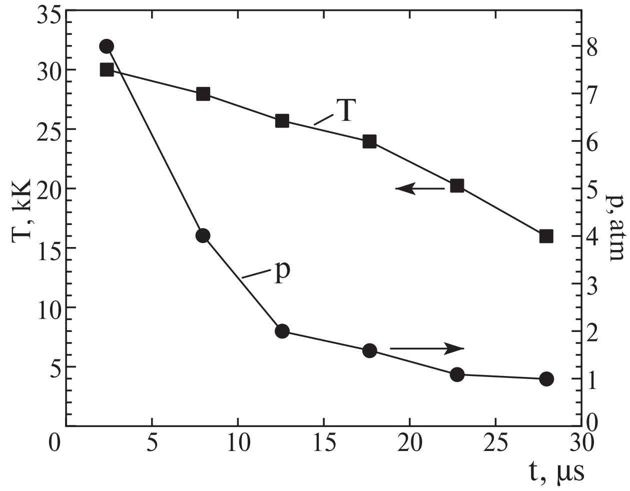

Fig. 6. The nature of plasma temperature changes in the lightning conducting channel and pressure changes during its relaxation at the return stroke stage [34]

establishing ionization equilibrium can be estimated for quasi-neutral plasma at high temperatures as the characteristic time of threeparticle recombination, which is on the order of magnitude [35, 36]

$$\frac{1}{\tau_{ion}} = N_e^2 K_{ion}, \quad K_{ion} = \frac{e^{10}}{m_e^{1/2} T^{9/2}}. \tag{24}$$

Note that according to the nature of the three-particle process for plasma containing multiply charged ions with charge Z, the triple recombination rate constant $K_{ion} \sim Z^3$. The ionization degree

$$\zeta = \frac{N_e}{[\mathrm{N}] + [\mathrm{O}]}$$

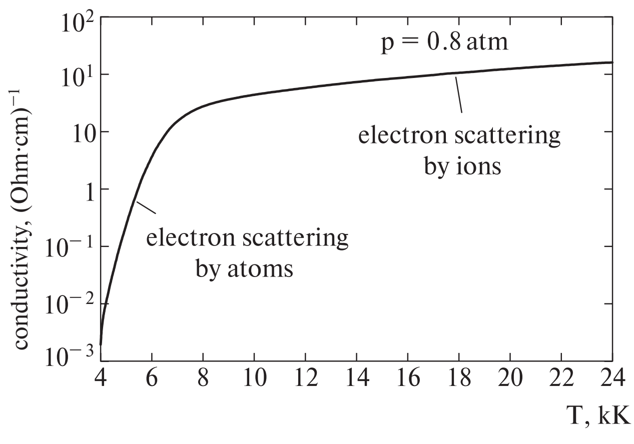

Fig. 7. Temperature dependence of equilibrium plasma conductivity of plasma

equals 0.02 at a temperature of 10 kK and $\zeta \approx 1$ at a temperature of 15 kK. At the considered pressure of $p = 0.8$ atm, the characteristic time for establishing ionization equilibrium is $\tau_{ion} \sim 10^{-5}$ s at a temperature of 10 kK and $\tau_{ion} \sim 5 \cdot 10^{-5}$ s at a temperature of 15 kK. These times are comparable to the time relaxation in the conducting channel formed during the passage of electric current at the return stroke stage.

Let us describe the evolution of plasma in the lightning conducting channel during the return stroke and continuous current stages, i.e., between adjacent flashes, when thermodynamic equilibrium is maintained in the plasma. At these stages, we have the following equation for temperature evolution:

$$Nc_p \frac{dT}{dt} = iE - \frac{Nc_p \Delta T}{\tau_T}, \tag{25}$$

where $c_p = 5/2$ is the heat capacity per atomic particle, N is the total density of electrons, ions, and atoms, i is the electric current density, E is the electric field strength, ΔT is the temperature change at the given moment of time, τT is the temperature relaxation time. To this, we should add Ohm's law in the form

$$i = \Sigma E, \tag{26}$$

where E is the electric field strength that maintains the plasma, Σ is its conductivity.

Since the plasma is in equilibrium, we can construct the dependence of its conductivity on temperature, $\Sigma(T)$, based on the standard procedure [37], expressing plasma conductivity through the frequency of electron collisions with nucleons. Then at high temperatures, the conductivity is given by Spitzer's formula [38], which only accounts for electron scattering on ions. At low temperatures, plasma conductivity is determined by electron scattering on atoms, with the measured diffusion cross-section of electron collision with nitrogen atom being $\sigma_{ea} \approx 2 \cdot 10^{-16}$ cm^2 [39, 40] and weakly depending on electron energy at electron energies around 1 eV. Based on this, we construct shown in Fig. 7 dependence of equilibrium plasma conductivity on temperature for the specified pressure.

We use some experimental data related to the return stroke plasma within a model where the equilibrium plasma is uniform inside a cylinder of radius R, and outside this column there is cold air at the considered pressure of $p = 0.8$ atm. We assume that at the initial stage of the return stroke, the plasma is affected by the average electric field observed in stormy weather, with a field strength of $E \approx 300$ V/cm [28–30]. At high temperatures, the conductivity of atmospheric pressure air plasma, as follows from the data in Fig. 7, is $\Sigma \sim 100\ \Omega^{-1} \cdot \mathrm{cm}^{1}$. Hence, for the current density, we have $i \simeq 2 \cdot 10^4$ A/cm^2. For a medium-intensity lightning, the peak electric current at the return stroke stage is 10–20 кA [17, 18]. Accordingly, the plasma column radius at the first stage of the return stroke is about 1 cm. This size is formed as a result of plasma expansion, which occurs at the speed of sound $c_s \sim 10^5$ cm/s and takes place over time $\tau \sim R/c_s \sim 10$ μs. This time corresponds to the plasma pressure relaxation time.

Let us also consider the continuous current stage between adjacent lightning flashes, which time is between 0.01 and 0.1 s, and the electric current strength at this stage for mediumintensity lightning is 10–100 A. Therefore, to maintain the plasma until the next flash, it is necessary to sustain the plasma with an external electric field. Since the conducting channel radius after the return stroke completion according to lightning return stroke models [31–33] is approximately $R \sim 10$ cm, formula (26) gives $\Sigma \sim 10^{-3} - 10^{-2}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, which corresponds to a plasma temperature of approximately 4–5 кK.

Obviously, the electric field strength acting on the lightning conducting channel plasma during the continuous current stage is less than its average value in stormy weather but exceeds this value (~1 V/cm) for calm atmosphere. Meanwhile, the conducting channel radius is significantly larger than during the return stroke stage, and due to convective transfer in the air, tongues and jets break away from it. However, the electric current under the external electric field stabilizes the conducting channel and maintains suitable conductivity and high temperature compared to the surrounding air temperature. It should be noted that the electron density in the conducting channel at this stage exceeds the corresponding value for the glow discharge.

Based on the data in Fig. 6, it is also possible to estimate the plasma temperature of the lightning conducting channel before the main electric current pulse. The duration of this pulse is relatively short, and during the pulse, the nuclei of atoms and ions do not have time to shift significantly. The density of air atoms does not change. For plasma with characteristics shown in Fig. 6, the energy deposited into the plasma leads to an increase in pressure and temperature by approximately 8 times. Accordingly, the plasma temperature before the electric pulse energy is deposited into it, i.e., after the leader passes, is approximately 4 kK. Thus, using experimental data for the analysis of equilibrium atmospheric air allows us to reconstruct the numerical parameters of the lightning conducting channel plasma.

5. CONCLUSIONS

The development of computer technology creates new conditions for solving physical problems, which leads to shifting the main load from the computation itself to the algorithm and calculation accuracy. This paper presents an algorithm for analyzing dissociative and ionization equilibria in air as a two-component molecular system at near-atmospheric pressure. In this case, with accuracy better than 10% it can be assumed that the atomic particles participating in the equilibrium are in the ground electronic state.

When thermodynamic equilibrium exists in a gas or plasma system, its parameters can be expressed through pressure and temperature. This paper examines the behavior of the lightning conducting channel plasma as a plasma cord through which electric current flows. During evolution, thermodynamic equilibrium is more or less maintained in this plasma, except for the initial stages of creating the conducting channel as a result of stepped leader propagation.

Analysis of experimental data from the perspective of equilibrium excited air allows understanding certain aspects of lightning as a complex physical phenomenon. It was found that after the passage of a stepped leader, the plasma of the lightning conducting channel remaining behind it must be maintained by an external electric field. Furthermore, the relaxation of the lightning conducting channel plasma at the first stage of the return stroke after the passage of the main lightning electric current occurs due to plasma expansion, which corresponds to pressure relaxation. Then the plasma temperature relaxation develops through heat transfer and radiation.

Lightning is a complex physical phenomenon whose properties at each stage of its development depend on different factors. One of the features of lightning is the repetition of lightning flashes with the passage of an electric current pulse through the same conducting channel. As follows from Fig. 5, this is possible due to charge redistribution at the lower edge of the cloud with a large cloud size. This requires the absence of complete plasma relaxation of the conducting channel after the return stroke, so that in the time interval between adjacent flashes, the conducting channel is maintained by a weak electric current under the action of an external electric field.

Note that the analysis of lightning properties using experimental data is conducted based on a simple model, in which the lightning conducting channel is represented as a cord with more or less uniform plasma inside it, while cold air is outside the cord. The cord radius and plasma parameters inside it change during lightning development. Theoretical models describing individual stages of lightning development use a different approach. These models are based on conditions that more or less correspond to real ones, and within these conditions, plasma properties are investigated in detail, including their radial distribution during plasma evolution. As can be seen, these approaches for analyzing the plasma of the lightning conducting channel complement each other. We should add that the numerical plasma parameters of the conducting channel presented above refer to lightning of medium intensity in accordance with [17, 41].

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