43. INVESTIGATION OF THE FAST AIR HEATING MECHANISMS IN GAS DISCHARGES

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Abstract. Fast heating of nitrogen-oxygen mixtures excited by gas discharges is investigated numerically with taking into account for the following main processes: reactions of predissociation of highly excited electronic states of oxygen molecules (which are populated via electron impact or via quenching of the excited states of \( N_2 \) molecules), reactions of quenching of the excited atoms \( O(1D) \) by nitrogen molecules, VT relaxation reactions, etc. The calculated results adequately describe all experimental data on the dynamics of air heating in gas-discharge plasmas. It is shown that, over a broad range values of the reduced electric field \( E/N \), gas heating is maintained by a fixed fraction of the discharge power that is expended on the excitation of the electronic degrees of freedom of molecules (for discharges in air, \( \eta_e \approx 28\% \)). The lower is oxygen content in the mixture, the smaller is the quantity \( \eta_e \). The problem of fast heating in nitrogen with a small admixture of oxygen is discussed.

Introduction

The processes responsible for gas heating principally govern the stable stage of self-sustained volume discharges [1] and are recognized as a basic mechanism for the propagation of microwave discharges in pre-breakdown fields [2,3]. Gas heating is one of the main issues in the theory of breakdown because, as gas temperature increases, additional ionization processes make the current-voltage characteristic decreasing [4].

In this paper, gas heating will be regarded as being fast if it occurs on time scales much shorter than the vibrational relaxation time. There are some experiments with reduced electric fields \( E/N > 80-100Td \) (see, e.g., [5-10]), in which the rate of gas heating in the initial discharge stage was observed to be anomalously high (in comparison with the VT relaxation rate). Based on the experimental observations of the gas dynamics expansion, Baranov et al. [5] determined the evolution of molecular nitrogen temperature under the action of a self-sustained pulsed discharge \( (P=100Torr, \tau_{pu}=30\mu s) \), the deposited energy being about 0.5J/(cm²atm)). They revealed that nitrogen was heated in two stages: a short stage with a duration of about 30\mu s, during which nearly 10% of the deposited energy was released, and a longer stage with a duration of about 500\mu s, during which the energy release amounted to about 38%. Based on the results of theoretical investigations, Baiadze et al. [6] explained the longer stage of gas heating by the model of VV exchange in a system of anharmonic oscillators. At the same time, they failed to explain the experimental data on fast heating in terms of the relaxation of rotational energy of gas particles and the elastic collisions between the electrons and gas particles. However, they noted that the fast gas heating might be a consequence of the energy release during quenching of electronically excited states of nitrogen molecules. Analogous results were obtained in [7] for broader ranges of the released energy.

A large series of investigations [8,9] was devoted to determining the temperature of molecular gases in pulsed microwave discharges. Most of the measurements were carried out in nitrogen and air in the pressure range \( P=10-40Torr \) for an effective reduced electric field \( E/N \) ranging from 80 to 250Td (here, \( E_e = \frac{E \cdot \nu}{\sqrt{2(\nu^2 + \omega^2)}} \), where \( \nu \) is the effective electron collision frequency, \( E \) and \( \omega \) - are the amplitude and frequency of the microwave field). Gas temperature in the discharge volume was determined from the relative intensity of the rotational spectrum of the second positive nitrogen system. Also, the experiments of [8,9] were aimed at measuring the electron density and some other parameters of the discharge plasma.

The results obtained in the cited experiments with microwave discharges confirmed the earlier conclusions that there exists a mechanism of the fast molecular gas heating at a strong reduced electric field \( E/N \). Aleksandrov et al. [9] also showed that the heating rate increases with gas pressure and substantially increases with \( E/N \). Based on analysis of the available experimental data, most researchers attribute fast gas heating during the discharge to the energy relaxation in the quenching processes of electronically excited nitrogen molecules. The quenching processes may serve to explain rapid heating at a strong reduced electric field \( E/N \), when the fraction of the deposited energy that is expended on the excitation of the electronic states of molecules is large.

In [8,9], it was supposed that the mechanism for rapid gas heating is associated with...
the self-quenching of the excited molecules $N_2(A^3\Sigma^+_u)$:

$$
N_2(A^3\Sigma^+_u) + N_2(A^3\Sigma^+_u) \rightarrow N_2(X^1\Sigma^+_g) + N_2(B^3\Pi_u, C^3\Pi_g) + \varepsilon_R
$$

However, the mechanism proposed in [8,9] fails to explain the full set of experimental data. Thus, Bogatov et al. [10], who measured not only the gas temperature but also the concentration of $N_2(A^3\Sigma^+_u)$ molecules, emphasized that the experimental data on the dynamics of the gas temperature cannot be explained in terms of this mechanism. It is also well known that the concentrations of $N_2(A^3\Sigma^+_u)$ molecules in air and nitrogen differ by several times because, in air $N_2(A^3\Sigma^+_u)$ are efficiently quenched by oxygen. Consequently, gas-heating rate should be lower in mixtures with higher oxygen contents. However, this conclusion contradicts the available experimental data [8-10].

This paper is devoted to the investigation of the processes that occur in nitrogen-oxygen mixtures excited by gas discharge. Gas heating is described with the aid of the processes of electron-impact dissociation of $N_2$ and $O_2$ molecules, quenching of electronically excited nitrogen molecules by oxygen molecules, and quenching of the metastable atoms $O(\text{I}D)$ by $N_2$ molecules. The results of calculations are compared with the available experimental data.

**Model description**

The proposed kinetic model is aimed to describing the dynamics of the main components of a nitrogen-oxygen mixture excited by discharge with a relatively strong reduced electric field (when a significant fraction of the discharge energy is expended on the excitation of the electronic states of molecules). The dependencies of the rates of the corresponding processes on the reduced electric field $E/N$ and the degree of vibrational excitation of molecules are taken from [11-12]. The main reactions involving neutral particles and related rate constants are presented in [13-15].

The dynamics of gas heating during the discharge was described with allowance for the following processes.

### 1. Recombination of molecular ions with electrons:

$$
e + O_2^+ \rightarrow O(\text{I}D) + e + \varepsilon_R,
$$

$$
e + NO^+ \rightarrow O(\text{I}D) + N(\text{I}D) + \varepsilon_R,
$$

$$
e + N_2^+ \rightarrow N(\text{I}S) + N(\text{I}D) + \varepsilon_R.
$$

The energy released in these reactions is distributed between the electronic and translational degrees of freedom of the produced atoms. Thus, in the electron-ion dissociative recombination reactions involving $O_2^+$ and $N_2^+$ ions, the quantity $\varepsilon_R$ should be about 5eV and 3.5eV, respectively. However, for $E/N \leq 300$Td, these reactions do not play a governing role in gas heating because the energy expended on the ionization of molecules is relatively low.

### 2. Dissociation of nitrogen and oxygen molecules by electron impact:

$$
e + N_2 \rightarrow O(\text{I}D) + N(\text{I}D) + \varepsilon_R,
$$

$$
e + O_2 \rightarrow O(\text{I}D) + O(\text{I}D) + \varepsilon_R.
$$

The $N_2$ and $O_2$ molecules are dissociated by predissociation of the electronic states of these molecules [13], which are excited from the ground state by electron impact. The kinetic energy of the products of predissociation reactions may be significant (this is evidenced by the behavior of the vibrational and electronic terms of the $N_2$ and $O_2$ molecules [16,17]).

### 3. Quenching of the electronically excited states of nitrogen molecules by oxygen molecules

These quenching processes are also accompanied by the population of the excited states $O_2(B^3\Sigma^+_u,v)$, $O_2(A^3\Sigma^+_u,v)$, $O_2(c^1\Sigma^+_u,v)$ etc. of oxygen molecules. A predissociation of these states leads to the dissociation of $O_2$ molecules and the transfer of the excess energy into the translational degrees of freedom of the produced oxygen atoms. The main reactions of quenching of electronically excited states of $N_2$ molecules in nitrogen-oxygen mixtures are listed in the table.

The reactions of the dissociation of $O_2$ molecules can also involve the electronically excited triplet states $N_2(B^3\Pi_u, B^3\Sigma_u^-, W^1\Delta_u)$, which are efficiently produced from the ground state by electron impact. Incorporating the resonant nature of the energy exchange between the levels of these states [13] into the model makes it possible to describe the processes of oxygen dissociation by introducing the effective state $N_3(\text{B})$, population...
rate of which is determined by the total concentration of molecules in these electronically excited states and quenching rate is determined from the corresponding data on the molecular state \( N_2(B^3I_u) \).

Analogous considerations are also valid for the excited singlet states \( N_2(a^1I_u,a^3I_u,w^1\Delta_u) \) [18], which can be described in terms of the effective state \( N_2(a) \). The quenching rate of the \( N_2(a) \) state is set equal to that of the \( N_2(a^1\Sigma_u^-) \) state. An analysis of the scheme of electronic terms of the singlet states of nitrogen molecules (Fig.1) makes it possible to suggest that \( O_2 \) molecules that quench these excited states will be dissociated primarily through the \( B^3\Sigma_u^- \) state.

The energy \( \varepsilon_R \) that is transferred into the translational degrees of freedom in each reaction (R1,R7,R9) is determined from Frank-Condon model [19]. It’s assumed, that each rate coefficient \( k_v \) is proportional to a function of the reaction energy defect \( \Delta E \):

\[
k_v \propto q_1 q_2 \cdot \exp \left( -\frac{\Delta E}{k_b T} \right),
\]

where \( q_1 \) and \( q_2 \) - are the Frank-Condon factors coupling initial and final states in energy-transfer processes (R1,R7,R9). Based on expression (1), the energy \( \varepsilon_R \) is described by the equation:

\[
\varepsilon_R = \varepsilon^* - \varepsilon_{\text{diss}} - \sum \varphi_v \varepsilon_v, \quad \varepsilon_v = \frac{k_v}{\sum k_v},
\]

where \( \varepsilon^* \) - is excitation energy of considered electronic states \( N_2(A^3\Sigma_u^+,B^3I_u,a^3\Sigma_u^-) \), \( \varepsilon_{\text{diss}} \) - is the dissociation limit of the corresponding oxygen states, \( \varepsilon_v \) - is vibrational energy of the product \( N_2(A^3\Sigma_u^+,v) \) molecules.

For a high degree of dissociation of \( O_2 \) molecules, it is necessary to take into account the quenching of the electronically excited nitrogen molecules by oxygen atoms. For nitrogen molecules in the state \( N_2(A^3\Sigma_u^+) \), this quenching

<table>
<thead>
<tr>
<th>No.</th>
<th>REACTION</th>
<th>Rate constant, cm³/s</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2(v) + 2 \cdot O(3P) + \varepsilon_1 )</td>
<td>( 1.7 \times 10^{-12} )</td>
<td>[14]</td>
</tr>
<tr>
<td>R2</td>
<td>( N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2(v) + O_2(b^3\Sigma_g^+,v) )</td>
<td>( 7.5 \times 10^{-13} )</td>
<td>[14]</td>
</tr>
<tr>
<td>R3</td>
<td>( N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(v) + N_2(B^3I_u) )</td>
<td>( 7.7 \times 10^{-11} )</td>
<td>[13]</td>
</tr>
<tr>
<td>R4</td>
<td>( N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(v) + N_2(C^3I_u) )</td>
<td>( 1.6 \times 10^{-10} )</td>
<td>[13]</td>
</tr>
<tr>
<td>R5</td>
<td>( N_2(A^3\Sigma_u^+) + N_2(v&gt;4) \rightarrow N_2(v) + N_2(B^3I_u) )</td>
<td>( 10^{-16} \times \exp(-1500/T) )</td>
<td>[13]</td>
</tr>
<tr>
<td>R6</td>
<td>( N_2(A^3\Sigma_u^+) + O(3P) \rightarrow N_2(v) + O(1S) )</td>
<td>( 3.0 \times 10^{-11} )</td>
<td>[15]</td>
</tr>
<tr>
<td>R7</td>
<td>( N_2(B^3I_u) + O_2 \rightarrow N_2(v) + 2 \cdot O(3P) + \varepsilon_7 )</td>
<td>( 3.0 \times 10^{-10} )</td>
<td>[13]</td>
</tr>
<tr>
<td>R8</td>
<td>( N_2(B^3I_u,v=0) + N_2 \rightarrow N_2(A^3\Sigma_u^+) + N_2(v) )</td>
<td>( 1.0 \times 10^{-11} )</td>
<td>[13]</td>
</tr>
<tr>
<td>R9</td>
<td>( N_2(a^3\Sigma_u^-) + O_2 \rightarrow N_2(v) + O(3P) + O(1D) + \varepsilon_9 )</td>
<td>( 2.8 \times 10^{-11} )</td>
<td>[14]</td>
</tr>
<tr>
<td>R10</td>
<td>( N_2(a^3\Sigma_u^-) + N_2 \rightarrow N_2(v) + N_2(v) )</td>
<td>( 2.0 \times 10^{-13} )</td>
<td>[14]</td>
</tr>
</tbody>
</table>

Table.

Fig.1. Scheme of the electronic terms of \( N_2 \) and \( O_2 \) molecules [16,17].
The excited oxygen atoms $O^1(D)$ are produced in a significant number of reactions in which the $O_2$ molecules are dissociated. The excited atoms $O^1(D)$ are quenched primarily by $O_2$ and $N_2$ molecules:

$$O^1(D) + N_2 \rightarrow O^3(P) + N_2(v) + \varepsilon_R,$$
$$O^1(D) + O_2 \rightarrow O^3(P) + O_2(b^1\Sigma_g^+, \nu = 2).$$

The quenching of the excited atoms $O^1(D)$ by nitrogen molecules was studied in a number of papers, in which it was shown that the quenching reaction proceeds through the formation of an intermediate complex. The measurements [21] confirmed theoretical predictions that (30±10%) of the energy released in this exoergic reaction is expended on the vibrational excitation of $N_2$ molecules. In accordance with the results of those papers, the model is supplemented with the assumption that about 70% of the excitation energy of the metastable states $O^1(D)$ is expended on gas heating.

5. Reactions of the VT relaxation of the vibrational levels $N_2(\nu)$

The most important among these processes is the reaction of VT relaxation by the excited oxygen atoms $O^3(P)$:

$$N_2(\nu) + O^3(P) \rightarrow N_2(\nu-1) + O^3(P) + \varepsilon_R$$

These reactions make a significant contribution to the total rate of gas heating when the degree of dissociation of $O_2$ molecules is sufficiently high. For calculations, the rate constants of the VT relaxation reactions were taken from [22].

Calculation results

The gas heating dynamics was simulated for conditions corresponding to the experiments of [23,24], which were aimed at investigating the heating of nitrogen-oxygen mixtures by high-current pulsed discharges initiated in a tube with the radius $R=0.5cm$ at pressures $P=0.4-1$ Torr. The discharge current density was $j=0.5-10$ A/cm$^2$, the pulse duration being $t_s=0.1-100\mu s$. The gas temperature was determined from the relative emission intensities of the $2^+$ (0→2) nitrogen system transition.

In the model proposed here, the evolution of the discharge parameters and the $N_2$ : $O_2$ mixture composition is described by solving a set of balance equations for neutral and charged particles together with the equation for the electric field. For a given discharge current $I$, the electric field at each instant is determined from the equation:

$$E = \frac{I}{2\pi e} \int \left[ N_e(r) \mu_e(r) r dr \right]_0$$

where $N_e(r)$ and $\mu_e(r)$ are the radial profiles of the electron density and electron mobility.

The electron density is calculated from the equation:

$$\frac{\partial N_e}{\partial t} = \frac{1}{e} \frac{\partial}{\partial r} (r D_e \frac{\partial N_e}{\partial r}) + N_e (V_{\text{ion}} - V_{\text{att}}) - Q_{\text{rec}} + Q_{\text{det}}$$

where $D_e$ is the ambipolar diffusion coefficient, $V_{\text{ion}}$ and $V_{\text{att}}$ are the ionization and electron attachment frequencies, $Q_{\text{rec}}$ is the electron-ion recombination rate, and the rate constant $Q_{\text{det}}$ accounts for all the processes of electron detachment from negative ions by $O^1(D)$ atoms, $O_2(a^1\Delta_g)$ molecules, etc. [14]. The model includes analogous balance equations for the charged particles of all species, specifically, the following ten species of positive and negative ions: $O_2^+, O_2^-, O_2^+, N_2^+, N_2^-, NO^+, O^-, O_2^+, O_3^+$. The dynamics of gas temperature is described by the equation:

$$C_v N \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ (r \lambda(T)) \frac{\partial T}{\partial r} \right] + \frac{\varepsilon_u - \varepsilon_v(T)}{\tau_{\text{vib}}} + W_R$$

Here, $C_v$ is the specific heat capacity of the gas at constant volume, $\lambda(T)$ is the thermal conductivity, $\varepsilon_u$ is the mean vibrational energy per $N_2$ molecule,
\( \tau_{VT} \) - is the characteristic time of the VT relaxation of \( N_2(v) \), and \( W_R \) - is the gas heating rate in chemical reactions. Equation (4) describes isochoric gas heating corresponding, in particular, to the experimental conditions of [23,24], under which the discharges were initiated over almost the entire volume of the system.

The boundary conditions for Eqs. (3) and (4) were chosen to conform the assumptions that the discharge region is axisymmetric, the charged particles at the wall of the discharge tube are absent, and the gas temperature at the wall is equal to the wall temperature \( T_w \):

\[
\left. \frac{\partial N_e}{\partial r} \right|_{r=0} = 0, \quad \left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \\
N_e \mid_{r=R} = 0, \quad T \mid_{r=R} = T_w.
\]

Under the above conditions for \( P=0.5 \text{Torr}, \ R=0.5 \text{cm}, \) and \( T=800 \text{K} \ (\lambda=5.7\times10^{-8} \text{W/(cm-K)}) \), the characteristic time during which the gas is cooled due to the heat conduction is about \( \tau_{\text{c}} \approx 18 \mu\text{s} \), which is appreciably shorter than the pulse duration [23]. For this reason, the equation for gas temperature is supplemented with the heat conduction term.

The relative concentrations of oxygen atoms that were measured by Kalinin et al. [24] as functions of time are shown Fig.2 for \( P=0.4 \text{Torr} \) and \( j=1 \text{A/cm}^2 \) and for different contents oxygen in the mixture \( \delta \). For comparison with the calculated results (which are illustrated in Fig.2 by solid curves), the corresponding relative concentrations are multiplied by \( 6 \times 10^{14} \text{cm}^{-3} \). One can see that, the calculated results correlate reasonably well with the experimentally recorded dynamics of the oxygen atom concentrations.

Figure 3 illustrates the results of modeling the dynamics of the main excited components at the axis of a discharge in air for the experimental conditions of [23,24] and for \( P=0.5 \text{Torr} \) and \( j=2 \text{A/cm}^2 \). A decrease in the concentration of nitrogen molecules excited state \( N_2(a^3\Sigma_u^+) \) at \( t \approx 30 \mu\text{s} \) is associated with the production of atomic oxygen and an increase in the rate of quenching of this state in reaction 6. On time scales \( t \approx 7-10 \mu\text{s} \), the concentrations of the excited particles \( \{ N_2(a^3\Sigma_u^+) \}, \{ N_2(a^1\Sigma_u^-) \} \) and \( \{ O(\Delta) \} \) that take part in gas heating change insignificantly. Consequently, on these time scales, the gas heating rate should be expected to be approximately constant, \( \partial W_R / \partial t \equiv \text{const} \).

Figure 4 displays radial profiles of the air temperature calculated under the experimental conditions of [23,24] and for \( P=0.5 \text{Torr} \) and \( j=2 \text{A/cm}^2 \).
direction changes only slightly. Presumably, the experimentally measured temperatures correspond to those in the central discharge region.

Figure 5 compares the experimental data of [23] and the results of numerical calculations of air heating dynamics near the discharge axis for $P=0.5\text{Torr}$. Curves 1-3 were calculated for the discharge current densities $j=4$, 2, and 1 A/cm$^2$, respectively. The dashed curve was calculated for $j=4$ A/cm$^2$ without allowance for gas cooling via heat conduction. The effect of heat conduction becomes important for gas temperatures $T\approx700$-800 K.

Fig. 5. Dynamics of the gas heating at the discharge axis for $R=0.5\text{cm}$, $P=0.5\text{Torr}$ and different discharge current densities: $j=4$ A/cm$^2$ (1), 2 A/cm$^2$ (2), and 1 A/cm$^2$ (3). The points refer to the experimental data of [23], and the results calculated with and without allowance for heat conduction are shown by the solid curves and the dashed curve, respectively.

Here, $\eta_R$ and $\eta_E$ - are the fractions of the discharge power that are expended on gas heating and the electronic excitation of molecules, respectively, and $\eta_E$ - is the fraction of the energy of the electronic degrees of freedom of molecules that is expended on gas heating. Figure 6 presents the parameters $\eta_R$ and $\eta_E$ calculated as functions of the reduced electric field in the discharge. We can see that the parameter $\eta_E$ changes with $E/N$ (as well as with the electron density and gas pressure) only slightly. That is why this parameter can be used for a simplified description of gas heating in discharges.

Fig. 6. Parameters $\eta_R$ and $\eta_E$ as functions of $E/N$ in an $N_2:O_2=4:1$ mixture.

In the proposed model of gas heating, an important role is played by reactions involving oxygen molecules. For this reason, the parameter $\eta_E$ and the gas heating rate are expected to change with the oxygen content $\delta$ of the mixture. Figure 7 illustrates the experimental data of [24] and the calculation results of the gas heating rate as a function of the content oxygen in an $N_2:O_2$ mixture for $P=0.4\text{Torr}$ and $j=1$ A/cm$^2$. The calculations based on the presented model agree satisfactorily with experiments for mixtures with oxygen content $\delta\lesssim4\%$. However, for low oxygen content $\delta$, disagreement between the numerical results and the experimental data is far greater. This disagreement indicates that, in pure nitrogen with no $O_2$ admixtures, there may be an additional mechanism for gas heating. The dashed curve in Fig. 7 illustrates the calculations of the gas heating rate in reaction $R3$ with $e\lesssim4\text{eV}$. Recall that this reaction is one of the processes underlying the model of rapid gas heating that was developed in [9,23,24] for nitrogen-oxygen mixtures. Reaction $R3$ makes it possible to explain the data of experiments with discharges in nitrogen with small

For a simplified description of heat release in the discharge, it is worthwhile to analyze the behavior of the plasma parameters:

$$\eta_R = \frac{W_R}{jE\cdot N}, \quad \eta_E = \frac{\eta_R}{\mu_E},$$
$O_2$ admixtures. However, for mixtures with higher oxygen content, the discrepancy with the experimental data becomes very significant, because, in reaction R3, the excited molecules $N_2(A^2Σ_g^+)$ are efficiently quenched by oxygen molecules.

**Conclusion**

In this paper, a model of fast heating of nitrogen-oxygen mixtures excited by gas discharges has been developed. According to this model, the gas is heated mainly in the reactions of predissociation of highly excited electronic states of oxygen molecules that are produced either by electron impact or during the quenching of the excited states of $N_2$ molecules. The results of model calculations are found to adequately describe available experimental data on the dynamics of air heating in gas-discharge plasmas.

It is shown that over a broad range of the reduced electric field $E/N$, the fraction of the discharge power that goes into the gas heating is fixed. Specifically, it is the fraction that is expended on the excitation of the electronic degrees of freedom of molecules (for discharges in air, $\eta_E$=28%). This circumstance can be used to simplify a description of heat sources in gas discharges. However, it should be noted that the condition $\eta_E=const$ may fail to hold for high degrees of dissociation of oxygen molecules (i.e., for high-energy depositions), when the electronically excited nitrogen molecules are quenched primarily by $O(3P)$ atoms. In this case, the reactions of VT relaxation on oxygen atoms may also play an important role in gas heating.

According to the proposed model, the lower is the oxygen content in the mixture, the smaller is the parameter $\eta_E$. For mixtures with an oxygen content $\delta$=4%, the results of the related model calculations agree with the experimental data. The question of the rapid heating of pure nitrogen and nitrogen with small oxygen admixtures remains open and requires further investigation.

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**References**