Screening of a dust particle charge in a humid air plasma created by an electron beam

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Abstract. A kinetic model has been developed for charged particle reactions in a humid air plasma produced by a fast electron beam. The model includes over 550 reactions with electrons, 33 positive ion species and 14 negative ion species. The model has been tested by solving 48 non-steady state equations for number densities of charged particles in humid air electron beam plasma, and by comparing with the available experimental data. The system of 48 steady state equations has been solved by iterative method in order to define the main ion species of the humid air plasma. A reduced kinetic model has been developed to describe the processes with the main ions and electrons. Screening constants have been calculated on the basis of the reduced system by means of Leverrier–Fadeev method. The dependencies of screening constants on gas ionization rates have been found for the rates from 10 to $10^{18}$ cm$^{-3}$s$^{-1}$ and the fraction of water molecules from 0 to 2%. The analysis of the constants has revealed that one of them is close to the inverse Debye length, and the other constants are defined by the inverse diffusion lengths passed by ions in the characteristic times of the attachment, recombination, and ion conversion. Pure imaginary screening constants appear at low rates of gas ionization.

1. Introduction

Low temperature air plasmas containing H$_2$O molecules are of high importance for atmospheric phenomena, climate control, biomedical applications, surface processing, and purification of air and water. A humid air plasma created by an external ionization source is a good model of the troposphere where ions are produced by the galactic cosmic rays and decay products of air and soil radioactive elements such as Rn$^{222}$. Study of microparticle charge screening in a dry air plasma generated by an external ionization source was performed in [1, 2]. In the present paper we consider effects of water admixture on the ionic composition and on the screening in the ionized humid air at atmospheric pressure and room temperature. The ionization rate is varied in the range of $10^1$–$10^{18}$ cm$^{-3}$s$^{-1}$. The humid air with $\leq 1.5\%$ water admixture that corresponds to the relative humidity of $\leq 67\%$ at the air temperature equal to 20°C is considered.
Table 1. Energies per electron–ion pair production for all possible ionization channels [3] and partial ionization rates by an electron beam in the humid air with 1.5% water admixture that corresponds to the relative humidity of 67% at the air temperature equal to 20°C (\(e_b\) is a fast beam electron).

| \(\ell\) | Process | \(\varepsilon_{\ell,0}\) (eV) | \(Q_{\text{ion},\ell}/Q_{\text{ion}}\) |
|-----|----------|----------------|------------------|
| 1   | \(\text{O}_2 + e_b \rightarrow \text{O}_2^+ + e + e_b\) | 154.4 | 0.2154 |
| 2   | \(\text{O}_2 + e_b \rightarrow \text{O}^+ + \text{O} + e + e_b\) | 527.5 | 0.0630 |
| 3   | \(\text{N}_2 + e_b \rightarrow \text{N}_2^+ + e + e_b\) | 58.5 | 0.5685 |
| 4   | \(\text{N}_2 + e_b \rightarrow \text{N}^+ + \text{N} + e + e_b\) | 236.5 | 0.1406 |
| 5   | \(\text{H}_2\text{O} + e_b \rightarrow \text{H}_2\text{O}^+ + e + e_b\) | 4098 | 0.0081 |
| 6   | \(\text{H}_2\text{O} + e_b \rightarrow \text{H}^+ + \text{OH} + e + e_b\) | \(1.92 \times 10^4\) | 0.0017 |
| 7   | \(\text{H}_2\text{O} + e_b \rightarrow \text{OH}^+ + \text{H} + e + e_b\) | \(1.48 \times 10^4\) | 0.0023 |
| 8   | \(\text{H}_2\text{O} + e_b \rightarrow \text{O}^+ + \text{H}_2 + e + e_b\) | \(1.07 \times 10^5\) | 0.0003 |
| 9   | \(\text{H}_2\text{O} + e_b \rightarrow \text{H}_2^+ + \text{O} + e + e_b\) | \(8.69 \times 10^6\) | \(3.8 \times 10^{-6}\) |

2. Electron beam ionization

Energies per electron–ion pair production, \(\varepsilon_{\ell,0}\), for all possible ionization channels calculated by the Monte-Carlo method in [3] for humid air of the following composition

\([\text{N}_2]_0 = 1.97 \times 10^{10} \text{ cm}^{-3}, \quad [\text{O}_2]_0 = 4.925 \times 10^{18} \text{ cm}^{-3}, \quad [\text{H}_2\text{O}]_0 = 3.75 \times 10^{17} \text{ cm}^{-3}\)

are presented in table 1. For other air compositions with the number densities \([N_k]\), \([O_2]\) and \([H_2O]\) the values of the energy of electron–ion pair production in the \(\ell\)-channel (see table 1) are recalculated using the following relations: \(\varepsilon_\ell = \varepsilon_{\ell,0}[\text{N}_2]_0/[\text{N}_2]\) for \(\ell = 1, 2\); \(\varepsilon_\ell = \varepsilon_{\ell,0}[\text{O}_2]_0/[\text{O}_2]\) for \(\ell = 3, 4\) and \(\varepsilon_\ell = \varepsilon_{\ell,0}[\text{H}_2\text{O}]_0/[\text{H}_2\text{O}]\) for \(\ell = 5–9\). Partial ionization rates are calculated as in the following way:

\[
Q_{\text{ion},\ell} = \frac{\varepsilon_\Sigma}{\varepsilon_\ell} Q_{\text{ion}}, \quad \frac{1}{\varepsilon_\Sigma} = \frac{1}{\varepsilon_1} + \cdots + \frac{1}{\varepsilon_\ell} + \cdots + \frac{1}{\varepsilon_9}.
\]

3. Ion–molecule processes

We consider the following ion species: \(e, \text{O}_2^+, \text{O}^+, \text{N}_2^+, \text{N}^+, \text{O}_4^+, \text{N}_4^+, \text{O}_2^+ (\text{N}_2), \text{NO}^+, \text{NO}_2^+, \text{NO}_3^+ (\text{O}_2), \text{H}_2\text{O}^+, \text{OH}^+, \text{H}^+, \text{H}_2^+, \text{H}_3\text{O}^+, \text{H}_3\text{O}^+ (\text{OH}), \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{n=1-6}, \text{O}_2^+ (\text{H}_2\text{O}), \text{H}_2\text{O}^+ (\text{N}_2), \text{NO}^+ (\text{H}_2\text{O})_{n=1-4}, \text{H}_2\text{NO}^+, \text{H}_2\text{NO}^+ (\text{H}_2\text{O}), \text{N}_2\text{H}^+, \text{O}_2^-, \text{O}_4^-, \text{O}_5^+ (\text{H}_2\text{O})_{n=1-12}\).

Electron–recombination coefficients are mainly taken from [4] and [5]. The main processes of electron loss in the humid air are three body attachment to oxygen molecules. The rate constants of these processes are presented in table 2.

The forward rate constants of third-order reactions are calculated according to [6]

\[
k_i[M] = \frac{k_{i,L}[M]k_{i,H}^+}{(k_{i,L}[M] + k_{i,H})} F,
\]

where \(k_{i,H}\) is the high pressure limit and \(k_{i,L}\) is the low pressure limit of the rate constant, \([M]\) is the number density of third body particles, \(F\) is the general broadening factor (see [9, 10]):

\[
\log F = \frac{\log F_c}{1 + [\log (k_{i,L}[M]/k_{i,H})]^2}, \quad F_c = 0.6.
\]

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Figure 1. Number densities of the main ions vs time obtained in numerical simulations (a) using set of reaction constants from [6] and (b) using corrected set: the reverse rate constant of \( \text{O}_2^+ + \text{N}_2 + \text{M} \leftrightarrow \text{O}_2^+ (\text{N}_2) \) is reduced by a factor of 10, the reverse rate constant of \( \text{H}_3\text{O}^+ (\text{H}_2\text{O}) + \text{H}_2\text{O} + \text{M} \leftrightarrow \text{H}_3\text{O}^+ (\text{H}_2\text{O})_2 + \text{M} \) is increased 2-fold, the low-pressure limit of the rate constant of \( \text{NO}^+ (\text{H}_2\text{O}) + \text{H}_2\text{O} + \text{M} \leftrightarrow \text{NO}^+ (\text{H}_2\text{O})_2 + \text{M} \) is reduced by a factor of 10\(^2\). Curve 1 is the number density of electrons, 2—ions \( \text{O}_2^+ \), 3—\( \text{O}_2^+ \), 4—\( \text{NO}^+ \), 5—\( \text{H}_3\text{O}^+ \), 6—\( \text{H}_3\text{O}^+ (\text{OH}) \), 7—\( \text{H}_3\text{O}^+ (\text{H}_2\text{O})_2 \), 8—\( \text{H}_3\text{O}^+ (\text{H}_2\text{O})_3 \), 9—\( \text{NO}^+ (\text{H}_2\text{O}) \), 10—\( \text{NO}^+ (\text{H}_2\text{O})_2 \), symbols △—\( \text{O}_2^+ \), ◦—\( \text{N}_2^+ \), ⋄—\( \text{N}_2^+ \).

Table 2. Rate constants of electron attachment processes in the humid air \( (t_e = 300/T_e, t_g = 300/T) \). 

| Process | Rate constant \( (\text{cm}^6/\text{s}) \) | Reference |
|---------|---------------------------------|-----------|
| \( e + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}_2 \) | \( 1.4 \times 10^{-29} t_e e^{-2t_e} e^{(t_e-t_0)/3} \) | [7] |
| \( e + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \) | \( 1.07 \times 10^{-31} t_e^2 e^{-70/T} e^{5(t_e-t_0)} \) | [7] |
| \( e + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2^+ + \text{H}_2\text{O} \) | \( 1.4 \times 10^{-29} \) | [8] |

The high pressure limit of the rate constant is calculated according to [11]:

\[
k_{i,H} = k_L \times \begin{cases} [1 + t_3 (t_1 - 1)], & x \geq 2; \\ [1 + t_3 (t_2 - 1)], & x \leq 2; \end{cases}
\]

(2)

where \( t_1 = \{1 + 2\mu_D^2/\{3\alpha(A_{\text{rot}} + C_{\text{rot}})\}\}^{1/2} \), \( k_L = 2\pi e^2 \alpha/\sqrt{\mu} \), \( \mu = m_1 m_2/(m_1 + m_2) \), \( \alpha = 11.87 \) is the polarizability of the water molecule in atomic units, \( m_1 \) is the \( \text{H}_2\text{O} \) mass, \( m_2 \) is the mass of an initial ion, \( x = \mu_D/\sqrt{2\alpha T} \); \( A_{\text{rot}} = 27.3hc \), \( B_{\text{rot}} = 14.65hc \) and \( C_{\text{rot}} = 9.536hc \) are the rotational constants of \( \text{H}_2\text{O} \), \( h \) is Planck’s constant, \( c \) is the speed of light, \( \mu_D = 1.857 \) D is the
Table 3. Low-pressure limits of the rate constants (cm³/s) of third-order reactions with positive ions (tₖ = 300/Τ, u = T/300 – 1).

| No. | Process | Rate constant | Reference |
|-----|---------|---------------|-----------|
| 1   | N₂⁺ + N₂ + M ⇄ N₂⁺ + M | 6.2 × 10⁻²⁹tₖ¹.⁷ | [6] |
| 2   | O₂⁺ + O₂ + M ⇄ O₂⁺ + M | 4.0 × 10⁻³⁰tₖ¹.⁹ | [6] |
| 3   | O₂⁺ + N₂ + M ⇄ O₂⁺ (N₂) + M | 8.0 × 10⁻³¹tₖ⁵ | [6] |
| 4   | NO⁺ + N₂ + M ⇄ NO⁺(N₂) + M | 2.4 × 10⁻³¹tₖ⁵ | [6] |
| 5   | NO⁺ + O₂ + M ⇄ NO⁺(O₂) + M | 3.0 × 10⁻³¹tₖ⁵ | [6] |
| 6   | N⁺ + N₂ + M ⇄ N⁺ + M | 4.0 × 10⁻²⁹tₖ⁵ | [6] |
| 7   | O⁺ + N₂ + M ⇄ NO⁺ + N + M | 6.0 × 10⁻²⁹tₖ³ | [7] |
| 8   | O₂⁺ + H₂O + M ⇄ O₂⁺(H₂O) + M | 2.6 × 10⁻²⁸tₖ³ | [6] |
| 9   | H₂O⁺ + N₂ + M ⇄ H₂O⁺(N₂) + M | 9.0 × 10⁻³⁰tₖ⁵ | [6] |
| 10  | H₃O⁺ + H₂O + M ⇄ H₃O⁺(H₂O) + M | 3.2 × 10⁻²⁷tₖ³ | [6] |
| 11  | H₃O⁺(H₂O) + H₂O + M ⇄ H₃O⁺(H₂O)₂ + M | 7.4 × 10⁻²⁷tₖ³ | [6] |
| 12  | H₃O⁺(H₂O)₂ + H₂O + M ⇄ H₃O⁺(H₂O)₃ + M | 2.5 × 10⁻²⁷tₖ³ | [6] |
| 13  | H₃O⁺(H₂O)₃ + H₂O + M ⇄ H₃O⁺(H₂O)₄ + M | 3.3 × 10⁻²⁸tₖ³ | [6] |
| 14  | H₃O⁺(H₂O)₄ + H₂O + M ⇄ H₃O⁺(H₂O)₅ + M | 4.0 × 10⁻₂⁹tₖ⁵ | [6] |
| 15  | H₃O⁺(H₂O)₅ + H₂O + M ⇄ H₃O⁺(H₂O)₆ + M | 4.5 × 10⁻³⁰tₖ₆ | [6] |
| 16  | NO⁺ + H₂O + M ⇄ NO⁺(H₂O) + M | 2.0 × 10⁻²⁸tₖ⁴ | [6] |
| 17  | NO⁺(H₂O) + H₂O + M ⇄ NO⁺(H₂O)₂ + M | 1.13 × 10⁻²⁷e⁻¹⁰.⁵⁶u | This paper |
| 18  | NO⁺(H₂O)₂ + H₂O + M ⇄ NO⁺(H₂O)₃ + M | 4.84 × 10⁻²⁸e⁻¹⁴.⁰₄u | This paper |
| 19  | NO⁺(H₂O)₃ + H₂O + M ⇄ NO⁺(H₂O)₄ + M | 1.11 × 10⁻²⁸e⁻¹⁷.₃₃u | This paper |

a Obtained by an analysis and approximations of rate constants presented in [12,18,19].

H₂O dipole moment, y = (t₁ – 1)/(t₂ – 1),

\[
t_₂ = \begin{cases} 
  0.4767x + 0.62, & x \geq 2; \\
  (x + 0.509)^2 / 10.526 + 0.9754, & x \leq 2;
\end{cases}
\]

(3)

\[
t_₃ = \begin{cases} 
  1 - 0.065y^{1.3} - 0.069y^{3.8}, & y \leq 1; \\
  1 - 0.134y^{-4.2}, & y \geq 1.
\end{cases}
\]

(4)

The rate constant of the reverse reactions is defined by \((n_{st} \approx 2.5 \times 10^{19} \text{ cm}^{-3})\)

\[
k_{i,r} = k_in_{st} \exp \left( \frac{\Delta H_i}{T} - \frac{\Delta S_i}{R} \right).
\]

(5)

The rate constants and thermodynamic characteristics of ion conversion and charge transfer in the humid air obtained by analysis of [4–7,12–17] are presented in tables 3, 4, 5 and 6. The ion–ion recombination coefficients are shown in table 7.

4. Ionic composition in a humid air plasma

To test the kinetic model of ion-molecular processes the system of 48 non-steady state number balance equations was solved using the fourth order Runge–Kutta method for the experimental conditions in [26]. In that paper the experimental time-resolved ion profiles were measured for the ionized H₂O : O₂ : N₂ = 0.00174 : 0.0292 : 0.969 mixture at 420 Pa and 380 K by pulsed electron beam with duration \(τ₁ = 1.3\) ms. Figure 1(a) shows the time dependencies of the
Table 4. Thermodynamic data of third-order reactions in the humid air ($R$ is the gas constant).

| No. | Reaction | $\Delta H_i$ (K) | $\Delta S_i/R$ | Reference |
|-----|-----------|-------------------|-----------------|-----------|
| 1   | $N_2^+ + N_2 + M \leftrightarrow N_2^+ + M$ | -11871 | -9.81 | [6] |
| 2   | $O_2^+ + O_2 + M \leftrightarrow O_4^+$ | -4775 | -9.96 | [6] |
| 3   | $N_2 + N_2 + M \leftrightarrow N_2^+ (N_2) + M$ | -2718 | -8.76 | [6] |
| 4   | $NO^+ + N_2 + M \leftrightarrow NO^+ (N_2) + M$ | -2562 | -9.51 | [6] |
| 5   | $NO^+ + O_2 + M \leftrightarrow NO^+ (O_2) + M$ | -1708 | -8.20 | [6] |
| 6   | $N^+ + N_2 + M \leftrightarrow N_2^+ + M$ | -36539 | -13.59 | [6] |
| 7   | $O_2^+ + O_2 + M \leftrightarrow O_4^+$ | -8046 | -9.01 | [6] |
| 8   | $H_2O + N_2 + M \leftrightarrow H_2O^+ (N_2) + M$ | -2670 | -9.06 | [6] |
| 9   | $H_2O^+ + N_2 + M \leftrightarrow H_2O^+ (N_2) + M$ | -16164 | -13.29 | [20] |
| 10  | $H_2O^+ (H_2O) + H_2O + M \leftrightarrow H_2O^+ (H_2O) + M$ | -10273 | -10.73 | [20] |
| 11  | $H_2O^+ (H_2O) + H_2O + M \leftrightarrow H_2O^+ (H_2O) + M$ | -8661 | -14.00 | [20] |
| 12  | $H_2O^+ (H_2O) + H_2O + M \leftrightarrow H_2O^+ (H_2O) + M$ | -6143 | -12.09 | [20] |
| 13  | $H_2O^+ (H_2O) + H_2O + M \leftrightarrow H_2O^+ (H_2O) + M$ | -5841 | -12.34 | [20] |
| 14  | $H_2O^+ (H_2O) + H_2O + M \leftrightarrow H_2O^+ (H_2O) + M$ | -5640 | -14.00 | [20] |
| 15  | $NO^+ + H_2O + M \leftrightarrow NO^+ (H_2O) + M$ | -9309 | -11.57 | [6] |
| 16  | $NO^+ (H_2O) + H_2O + M \leftrightarrow NO^+ (H_2O) + M$ | -7818 | -10.22 | [18] |
| 17  | $NO^+ (H_2O) + H_2O + M \leftrightarrow NO^+ (H_2O) + M$ | -7697 | -14.43 | [18] |
| 18  | $NO^+ (H_2O) + H_2O + M \leftrightarrow NO^+ (H_2O) + M$ | -5412 | -9.62 | [18] |
| 19  | $O_2 + H_2O + M \leftrightarrow O_2 (H_2O) + O_2$ | -9265 | -10.12 | [21] |
| 20  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -8661 | -12.64 | [21] |
| 21  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -7755 | -14.20 | [21] |
| 22  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -7192 | -15.61 | [22] |
| 23  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -7072 | -15.85 | [22] |
| 24  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -6391 | -20.39 | [22] |
| 25  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -5299 | -15.00 | [22] |
| 26  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -8168 | -17.63 | [22] |
| 27  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -6538 | -18.02 | [22] |
| 28  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -5634 | -16.60 | [22] |
| 29  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -5679 | -16.91 | [22] |
| 30  | $O_2 (H_2O) + H_2O + O_2 \leftrightarrow O_2 (H_2O) + O_2$ | -5735 | -13.83 | [22] |

The corrected values of $\Delta S_i/R$ to get the reverse rate constants presented in table 5 are $a$—14.90, $b$—16.13, $c$—16.38, and $d$—17.99.

The number densities of the main ions obtained by a kinetic model of the ion-molecular processes from [6]. A comparison of these dependencies with the experimental ion profiles [26] shows that

- the reduced number density of $O_2^+$ drops below 1% at 2 ms in the experiment and only at 5 ms in figure 1(a);
- the reduced number density of $N_2^+$ decreases more slowly in the experiment than it does in figure 1(a) (up to 1% at 2 ms);
- the reduced number density of $H_3O^+$ runs in the experiment as in figure 1(a);
- the reduced number density of $H_3O^+$ runs in the experiment as in figure 1(a);
- the reduced number density of NO runs nonmonotonously during the first 2 ms in the experiment and then goes close to the corresponding curve in figure 1(a);
Table 5. Rate constants (cm$^3$/s or cm$^6$/s) of processes with negative ions ($\theta_g = \sqrt{T}/300$, $t_g = 300/T$, $k_f$ is the forward and $k_r$ is the reverse rate constants).

| No. | Process | Rate constant | Reference |
|-----|---------|---------------|-----------|
| 1   | $O_2^- + N_2 \rightarrow O_2 + N_2 + e$ | $1.9 \times 10^{-12} \theta_g e^{-4990/T}$ | [7] |
| 2   | $O_2^- + O_2 \rightarrow O_2 + O_2 + e$ | $2.7 \times 10^{-10} \theta_g e^{-5590/T}$ | [7] |
| 3   | $O_2^- + O_2 + M \rightarrow O_2^+ + M, M = N_2, O_2$ | $3.5 \times 10^{-31} f_g$ | [7] |
| 4   | $O_3^- + M \rightarrow O_2^- + O_2 + M, M = N_2, O_2$ | $10^{-10} e^{-1044/T}$ | [7] |
| 5   | $O_4^- + O_2 \rightarrow O_2^- + 2O_2$ | $1.6 \times 10^{-14}$ | [13] |
| 6   | $O_2^- + H_2O + O_2 \rightarrow O_2^- (H_2O) + O_2$ | $1.6 \times 10^{-28}$ | [13] |
| 7   | $O_4^- + H_2O \rightarrow O_2^- (H_2O) + O_2$ | $1.5 \times 10^{-09}$ | [13] |
| 8   | $O_2^- (H_2O) + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_2 + O_2$ | $k_f = 5.4 \times 10^{-28}$ | [13] |
|     |                                   | $k_r = 1.1 \times 10^{-14}$ | [13] |
| 9   | $O_2^- (H_2O)_2 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_3 + O_2$ | $k_f = 2.1 \times 10^{-28}$ | [8, 13] |
|     |                                   | $k_r = 3 \times 10^{-13}$ | [8, 13] |
| 10  | $O_2^- (H_2O)_3 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_4 + O_2$ | $k_f = 1.0 \times 10^{-28}$ | [8] |
|     |                                   | $k_r = 1.2 \times 10^{-12}$ | [8] |
| 11  | $O_2^- (H_2O)_4 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_5 + O_2$ | $k_f = 5.0 \times 10^{-29}$ | [8] |
|     |                                   | $k_r = 4.5 \times 10^{-12}$ | [8] |
| 12  | $O_2^- (H_2O)_5 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_6 + O_2$ | $4.8 \times 10^{-29}$ | This paper |
| 13  | $O_2^- (H_2O)_6 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_7 + O_2$ | $3.7 \times 10^{-29}$ | This paper |
| 14  | $O_2^- (H_2O)_7 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_8 + O_2$ | $2.9 \times 10^{-29}$ | This paper |
| 15  | $O_2^- (H_2O)_8 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_9 + O_2$ | $2.4 \times 10^{-29}$ | This paper |
| 16  | $O_2^- (H_2O)_9 + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_{10} + O_2$ | $2.0 \times 10^{-29}$ | This paper |
| 17  | $O_2^- (H_2O)_{10} + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_{11} + O_2$ | $1.7 \times 10^{-29}$ | This paper |
| 18  | $O_2^- (H_2O)_{11} + H_2O + O_2 \leftrightarrow O_2^- (H_2O)_{12} + O_2$ | $1.5 \times 10^{-29}$ | This paper |

- the reduced number density of NO$^+(H_2O)$ is equal to 5% at 5 ms in the experiment and to 0% in figure 1(a);
- the reduced number density of H$_3$O$^+(H_2O)$ is equal to 12% at 5 ms in the experiment and to 6% in figure 1(a);
- the reduced number density of H$_3$O$^+(H_2O)_2$ is equal to 70% at 5 ms in the experiment and to 88% in figure 1(a);
- the reduced number density of H$_3$O$^+(H_2O)_3$ is equal to 4% at 5 ms in the experiment and to 6% in figure 1(a).

Figure 1(b) shows the time dependencies of the number densities of the main ions obtained by the corrected kinetic model of ion-molecular processes presented in our paper. A comparison of the obtained data with the experiment [26] shows a good agreement. Thus, hereafter the kinetic model with the constants and parameters presented in tables 1–7 will be used.

5. Ionic composition of electron beam created plasma in the humid air

We study the steady state ionic composition of electron beam created plasma in the humid air at the atmospheric pressure and the room temperature for the ionization rates $10^{-10}$–$10^{16}$ cm$^{-3}$s$^{-1}$ and the humidity 0.015%, 0.15% and 1.5%. The system of 48 balance equations is solved by the iteration method. Using the steady state number densities we define the main ion species.
Table 6. Rate constants of bimolecular reactions in the humid air ($t_g = 300/T$).

| No. | Process                                                                 | Rate constant ($\text{cm}^3\text{s}^{-1}$) | Reference |
|-----|-------------------------------------------------------------------------|-------------------------------------------|-----------|
| 1   | $\text{N}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}$          | $2.8 \times 10^{-10}$                     | [7]       |
| 2   | $\rightarrow \text{O}^+ + \text{NO}^+$                               | $2.5 \times 10^{-10}$                     | [7]       |
| 3   | $\rightarrow \text{O}^+ + \text{NO}$                                  | $2.8 \times 10^{-11}$                     | [7]       |
| 4   | $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$         | $3 \times 10^{-12} e^{-0.00311 T}$       | [7]       |
| 5   | $\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$        | $3.3 \times 10^{-11} e^{-0.00169 T}$     | [7]       |
| 6   | $\text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2$   | $6 \times 10^{-11} I_{g}^{0.5}$          | [7]       |
| 7   | $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$      | $10^{-17}$                                | [7]       |
| 8   | $\text{N}_3^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O} + \text{N}_2$ | $5.8 \times 10^{-11} t_g \delta_{\text{NO}^+}^a$ | [23]      |
| 9   | $\rightarrow \text{NO}^+ + \text{N}_2$                               | $5.8 \times 10^{-11} t_g (1 - \delta_{\text{NO}^+}^a)$ | [23]      |
| 10  | $\text{N}_4^+ + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{N}_2$   | $2.5 \times 10^{-10}$                     | [7]       |
| 11  | $\text{O}_4^+ + \text{N}_2 \rightarrow \text{O}_2^+ \text{N}_2 + \text{O}_2$ | $4.61 \times 10^{-12} t_g^{-2.5} e^{-2650/T}$ | [7]       |
| 12  | $\text{O}_2^+ \text{N}_2 + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2$ | $6.4 \times 10^{-10}$                    | [6]       |
| 13  | $\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{N}_2$ | $1.8 \times 10^{-9}$                     | [6]       |
| 14  | $\rightarrow \text{N}_2\text{H}^+ + \text{OH}$                     | $5.3 \times 10^{-10}$                    | [6]       |
| 15  | $\text{N}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}$ | $2.9 \times 10^{-9} t_g^{0.52}$          | [6]       |
| 16  | $\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{O}$ | $2.6 \times 10^{-9}$                     | [6]       |
| 17  | $\text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O}$ | $4.1 \times 10^{-10}$                    | [6]       |
| 18  | $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$ | $1.7 \times 10^{-9}$                     | [6]       |
| 19  | $\text{OH}^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{O}$ | $2.9 \times 10^{-10}$                    | [6]       |
| 20  | $\text{OH}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{OH}$      | $5.9 \times 10^{-10}$                    | [6]       |
| 21  | $\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}$ | $2.8 \times 10^{-9}$                     | [6]       |
| 22  | $\text{N}_4^+ + \text{H}_2\text{O} \rightarrow \text{H}_4\text{O}^+ + 2\text{N}_2$ | $2.4 \times 10^{-9}$                     | [6]       |
| 23  | $\text{N}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{NO}^+ + \text{N}_2$ | $2.8 \times 10^{-9} f(T, P)^b$           | [24]      |
| 24  | $\text{O}_4^+ + \text{H}_2\text{O} \rightarrow \text{O}_2^+ \text{H}_2\text{O} + \text{O}_2$ | $1.7 \times 10^{-9}$                     | [6]       |
| 25  | $\text{O}_3^+ \text{N}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2^+ \text{H}_2\text{O} + \text{N}_2$ | $2.2 \times 10^{-9}$                     | [6]       |
| 26  | $\text{H}_2\text{O}^+ \text{(N}_2\text{)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{N}_2 + \text{OH}$ | $2.6 \times 10^{-9} (1 - 0.6 t_g^7)$     | [6]       |
| 27  | $\rightarrow \text{H}_3\text{O}^+ \text{(OH)} + \text{N}_2$          | $2.6 \times 10^{-9} 0.6 t_g^{7}$          | [6]       |
| 28  | $\text{O}_2^+ \text{(H}_2\text{O)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} + \text{O}_2$ | $1.3 \times 10^{-9}$                     | [6]       |
| 29  | $\text{N}_2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{N}_2$ | $2.6 \times 10^{-9}$                     | [6]       |
| 30  | $\text{NO}^+ \text{(N}_2\text{)} + \text{H}_2\text{O} \rightarrow \text{NO}^+ \text{(H}_2\text{O)} + \text{N}_2$ | $2.2 \times 10^{-9}$                     | [6]       |
| 31  | $\text{NO}^+ \text{(O}_2\text{)} + \text{H}_2\text{O} \rightarrow \text{NO}^+ \text{(H}_2\text{O)} + \text{O}_2$ | $2.2 \times 10^{-9}$                     | [6]       |
| 32  | $\text{H}_2\text{NO}^+ + \text{H}_3\text{O} \rightarrow \text{products}^c$ | $2.3 \times 10^{-9}$                     | [6]       |
| 33  | $\text{H}_2\text{NO}^+ \text{(H}_2\text{O)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{products}$ | $2.3 \times 10^{-9}$                     | [6]       |
| 34  | $\text{NO}^+ \text{(H}_2\text{O)}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \text{(H}_2\text{O)}_2 + \text{HNO}_2$ | $7.5 \times 10^{-11}$                    | [6]       |
| 35  | $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}$ | $6.9 \times 10^{-9} t_g^{1/2}$           | [25]      |
| 36  | $\text{H}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2$ | $3.9 \times 10^{-9} t_g^{1/2}$           | [25]      |

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- $\delta_{\text{NO}^+} = 0.099 e^{-337/300}$ for $T = 64-520$ K and $\delta_{\text{NO}^+} = 1$ for $T > 520$ K.
- $f(T, P) = (0.41 + 0.66 (T/2600 + P_{\text{bar}}))^{-1}[24].$
- Ion $\text{H}_3\text{O}^+$ was absent in products of process (32), so it is supposed in our paper that the process results in production of $\text{H}_2\text{NO}^+\text{(H}_2\text{O)}.$
Table 7. Ion–ion recombination coefficients in the humid air.

| Process                                      | Coefficient (cm³/s or cm⁶/s) | Reference |
|----------------------------------------------|------------------------------|-----------|
| $\text{O}_2^- + \text{B}^+ \rightarrow \text{O}_2 + \text{B}$ | $k_I \simeq 2 \times 10^{-7} \rho^{0.5}$ | [7]       |
| $\text{B}^+= \text{N}_2^+, \text{O}_2^+, \text{O}^+, \text{NO}^+, \text{NO}_2^+, \text{H}_2\text{O}^+$ | $k_{II} \simeq 10^{-7}$ | [14, 15] |
| For other pair of negative and positive ions | $2 \times 10^{-25} \rho^{2.5}$ | [7]       |
| $\text{A}^- + \text{B}^+ + \text{M} \rightarrow \text{products} + \text{M}$ | | |

Figure 2. The summary number densities of positive and negative ions (a) and steady-state number densities (b) as a function of the gas ionization rate. Subfigure (a): curve 1 is calculated using the full model of ion-molecular processes, 2 using the reduced model at $[\text{H}_2\text{O}]=1.5\%$, 3 is the full model total number density at $[\text{H}_2\text{O}]=0.15\%$ and 4 at $[\text{H}_2\text{O}]=0.015\%$. Subfigure (b): solid lines were calculated using the full system of kinetic equations, the symbols were calculated using the reduced system, $[\text{H}_2\text{O}]=0.15\%$: 1 is the electron number density, 2 is the number density of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$ ions, 3 $\text{H}_3\text{O}^+(\text{H}_2\text{O})_5$, 4 $\text{O}_2^-(\text{H}_2\text{O})_4$, 5 $\text{O}_2^- (\text{H}_2\text{O})_5$, 6 is the sum of the number densities of positive or negative ions.

whose number densities exceed 5% of the summary positive or negative ion number density. The analysis of numerical results reveals that the system of kinetic equations can be reduced to five equations describing the number densities of electrons and the main ions: $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, NO$^+(\text{O}_2)$, NO$^+_2$, O$_2^-$ (H$_2$O) (see figure 2). Comparison between steady-state ion number densities calculated at $Q_{\text{ion}}=10^{-12}$ cm$^{-3}$s$^{-1}$ using the full system and the reduced one are shown in figure 3. We see that the reduced system of the balance equation well describes the humid air electron beam plasma. The relative changes of number densities at the reduction of the full system of the number balance equations are shown in figure 3. One can see that relative changes do not exceed 10% and are due to the number densities of minor ion species.

The number densities of $\text{O}_2^- (\text{H}_2\text{O})_n$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ions in dependence of the number of water molecules at different plasma parameters are presented in figures 4, 5 and 6. These figures show that the main ion species are virtually unchanged when the plasma parameters are changed and that it is insufficiently to take into account positive ion clusters only up to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$. We see that number densities of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$ ions is high enough so we should take into account the conversion of this ion to ions with higher number of water molecules.
Figure 3. The relative changes of number densities of electrons and main ion species at the reduction of the full system of the number balance equations for $[\text{H}_2\text{O}] = 1.5\%$ ($y_k$ are the number densities of the full system and $z_k$ are the ones of the reduced system).

Figure 4. Reduced to the summary number density of negative ions the number densities of $\text{O}^-_{n}\text{(H}_2\text{O)}$ as a function of the number of water molecules $n$ at $[\text{H}_2\text{O}] = 1.5\%$ for the ionization rates $Q_{\text{ion}} = 10, 10^{6}, 10^{11}$ and $10^{16}\text{ cm}^{-3}\text{s}^{-1}$.

Figure 5. The number densities of $\text{O}^-_{n}\text{(H}_2\text{O)}$ negative ions as a function of the number of water molecules at the ionization rate $Q_{\text{ion}} = 10^{16}\text{ cm}^{-3}\text{s}^{-1}$ for $[\text{H}_2\text{O}] = 1.5\%, 0.15\%$ and $0.015\%$.

Figure 6. The number densities of $\text{H}_3\text{O}^+_{n}\text{(H}_2\text{O)}$ positive ions as a function of the number of water molecules at the ionization rate $Q_{\text{ion}} = 10^{16}\text{ cm}^{-3}\text{s}^{-1}$ for $[\text{H}_2\text{O}] = 1.5\%, 0.15\%$ and $0.015\%$.

6. The microparticle screening in a humid air plasma
The charging of a microparticle placed in the origin $r = 0$ of the spherical coordinate system is described by the reduced system of the number balance equations of main ion species and the
Figure 7. The real part (a) and imaginary part (b) of screening constants versus $Q_{\text{ion}}$ at [H$_2$O] = 0.15% and $n_{\text{short}} = 5$. Subfigure (a): symbols 1–5 are the numerical calculations, 6–10 are the approximations of screening constants: 6 is $k_D$ (11), 7 is $k_e$ (12), 8 is $k_s$ (13), 9 is $k_{c1}$ (14), 10 is $k_{c2}$ (15). Subfigure (b): the imaginary part of the 3rd (1), 4th (2) and 5th screening constants.

Poisson equation:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \mathbf{j}_e = Q_{\text{ion}} - \sum_{\sigma=1}^{N_{\text{pos}}} \beta_{e\sigma} n_e n_{p,\sigma} - \sum_{\tau=1}^{N_{\text{neg}}} \alpha_{\tau} n_e - S_{e\delta}(\mathbf{r}),$$  \hspace{1cm} (6)

$$\frac{\partial n_{p,\sigma}}{\partial t} + \nabla \cdot \mathbf{j}_{p,\sigma} = Q_{\text{ion},\sigma} + \sum_{\lambda=1, \lambda \neq \sigma}^{N_{\text{pos}}} \nu_{\sigma\lambda} n_{p,\lambda} - \sum_{\lambda=1, \lambda \neq \sigma}^{N_{\text{pos}}} \nu_{\lambda\sigma} n_{p,\sigma} - \beta_{e\sigma} n_e n_{p,\sigma}$$

$$- \sum_{\tau=1}^{N_{\text{neg}}} \beta_{\tau\sigma} n_{p,\sigma} n_{n,\tau} - S_{\sigma\delta}(\mathbf{r}), \hspace{1cm} \sigma = 1, 2, \ldots, N_{\text{pos}},$$  \hspace{1cm} (7)

$$\frac{\partial n_{n,\tau}}{\partial t} + \nabla \cdot \mathbf{j}_{n,\tau} = \alpha_{\tau} n_e + \sum_{\lambda=1, \lambda \neq \tau}^{N_{\text{neg}}} \nu_{\tau\lambda} n_{n,\lambda} - \sum_{\lambda=1, \lambda \neq \tau}^{N_{\text{neg}}} \nu_{\lambda\tau} n_{n,\tau}$$

$$- \sum_{\sigma=1}^{N_{\text{pos}}} \beta_{\tau\sigma} n_{n,\sigma} n_{n,\tau} - S_{\tau\delta}(\mathbf{r}), \hspace{1cm} \tau = 1, 2, \ldots, N_{\text{neg}},$$  \hspace{1cm} (8)

$$\Delta \phi = -4\pi e \left( \sum_{\sigma=1}^{N_{\text{pos}}} n_{p,\sigma} - n_e - \sum_{\tau=1}^{N_{\text{neg}}} n_{n,\tau} \right) - 4\pi eq\delta(\mathbf{r}),$$  \hspace{1cm} (9)

where $n_e$ is the number densities of electrons, $n_{p,\sigma}$ are the number densities of main positive ions: $\sigma = 1, \ldots, N_{\text{pos}}$, $n_{n,\tau}$ are the number densities of main negative ions: $\tau = 1, \ldots, N_{\text{neg}}$; $\mathbf{j}_{\sigma} = -D_{\sigma}(\nabla n_{\sigma} + \frac{e_{\sigma}}{m_{\sigma}} n_{\sigma} \nabla \phi)$, $\sigma$ denotes plasma species, $e_{\pi e} = -e$, $e$ is the proton charge, $e_{\sigma} = e$, $\sigma = 1, \ldots, N_{\text{pos}}$, $e_{\tau} = e_{\tau} = -e$, $\tau = 1, \ldots, N_{\text{neg}}$; $D_{\sigma}$ is the diffusion coefficient of $\sigma$-ions; $S_{\sigma}$ is the sink of $\sigma$-ions to the microparticle with the charge $q$; $Q_{\text{ion},\sigma}$ is the effective production rate of the $\sigma$-th positive ions which is defined by the ion conversion rate constants of this ion.
with minor ion species, \( \alpha_r \) is the effective attachment frequency of electrons with the production of the \( \tau \)-th negative ion, \( \beta_{\sigma,\tau} \) is the coefficient of electron–ion recombination, \( \beta_{\nu,\sigma} \) is the ion–ion recombination coefficient, \( \nu_{\lambda\sigma} \) and \( \nu_{\lambda\tau} \) are the rate frequencies of ion–molecular conversion processes with the main ion species.

The system of equations (6)–(9) was solved by means of linearization and 3D Fourier transform. The screening in this plasma is defined by \( n_{\text{short}} = (N_{\text{pos}} + N_{\text{neg}} + 1) \) screening constants \( k_{\text{sh},i} \), \( i = 1, 2, \ldots, n_{\text{short}} \) and in case of the real screening constants the potential is the sum of \( n_{\text{short}} \) Debye exponentials:

\[
\phi (r) = \sum_{i=1}^{n_{\text{short}}} \frac{eq}{r} A_i \exp \left( -k_{\text{sh},i} r \right). \tag{10}
\]

Screening constants are calculated on the basis of the reduced system by means of the Leverrier–Fadeev method. The dependencies of the screening constants on \( Q_{\text{ion}} \) are shown in figure 7.

The screening constants are approximated by the following expressions:

\[
k_D^2 = 4\pi e^2 \sum_{\sigma=1}^{n_{\text{short}}} \frac{n_{\sigma,0}}{D_\sigma}, \tag{11}
\]

\[
k_e^2 = \sum_{\tau=1}^{N_{\text{neg}}} \frac{\alpha_\tau}{D_e} + \sum_{\sigma=1}^{N_{\text{pos}}} \left( \frac{\beta_{\sigma,\tau} n_{\sigma,0}}{D_\sigma} + \frac{\beta_{\nu,\sigma} n_{\sigma,0} n_{\xi,0}}{D_\xi n_{\Sigma,\text{neg}}} \right), \tag{12}
\]

\[
k_\Sigma^2 = \sum_{\sigma=1}^{N_{\text{pos}}} \sum_{\tau=1}^{N_{\text{neg}}} \beta_{\nu,\sigma} n_{\sigma,0} n_{\tau,0} \left( \frac{1}{D_\sigma} + \frac{1}{D_\tau} \right), \tag{13}
\]

\[
k_{e1}^2 = \frac{\nu_{\lambda_1} \lambda_2}{D_{\lambda_1}} + \frac{\nu_{\lambda_2} \lambda_1}{D_{\lambda_2}}, \tag{14}
\]

\[
k_{e2}^2 = \frac{\nu_{\lambda_3} \lambda_4}{D_{\lambda_3}} + \frac{\nu_{\lambda_4} \lambda_3}{D_{\lambda_4}}, \tag{15}
\]

where \( n_{\sigma,0} \) is the number density of the \( \sigma \) main ions in the unperturbed plasma, \( \xi \) is the head ion of the main negative hydrated ions, \( n_{\Sigma,\text{neg}} = \sum_{\tau=1}^{N_{\text{neg}}} n_{\tau,0} \) (\( n_{\Sigma,\text{neg}} \approx n_{\Sigma,\text{pos}} \approx \sum_{\sigma=1}^{N_{\text{neg}}} n_{\sigma,0} \)), \( \lambda_1 \), \( \lambda_2 \) and \( \lambda_3 \), \( \lambda_4 \) are ions which convert to each other, the effective production rates of the main positive ions are given by expressions: \( Q_{\text{ion},\sigma} = Q_{\text{ion}} \) for \( \sigma = \xi \) ion and otherwise \( Q_{\text{ion},\sigma} = 0 \) for \( \sigma \neq \xi \).

One can see that the first constant is properly approximated by the inverse Debye length, the others are described by the characteristic spatial scales of recombination and attachment processes. Calculations also reveals the regions where the screening constants are complex and pure imaginary. For the pure imaginary screening constant, \( ik_{\text{sh},e} \), the potential distribution get the form

\[
\phi (r) = \sum_{i=1}^{N} \frac{eq}{r} A_i \exp \left( -k_{\text{sh},i} r \right) + \frac{eq}{r} A_c \cos \left( k_{\text{sh},c} r \right). \tag{16}
\]

7. Conclusion

In the present paper a kinetic model has been developed for charged particle reactions in a humid air plasma produced by a fast electron beam. The model includes over 550 reactions with electrons, 33 positive ion species and 14 negative ion species. The model has been tested by solving 48 non-steady state equations for number densities of charged particles in the humid air electron beam plasma, and comparing with available experimental data. The system of 48 steady state equations has been solved by iterative method in order to define the main ion species of the humid air plasma. A reduced kinetic model has been developed to describe
the processes with the main ions and electrons. Screening constants have been calculated on the basis of the reduced system by means of Leverrier–Fadeev method. The analysis of the constants has revealed that one of them is close to the inverse Debye length, and the other constants are defined by the inverse diffusion lengths passed by ions in the characteristic times of the attachment, recombination, and ion conversion. In this paper $H_3O^+(H_2O)_n$ positive ions up to $n = 6$ were taken into account. In paper [27] the positive ion clusters up to $H_3O^+(H_2O)_9$ are supposed to take into account, so we should develop our model to include processes with these ions.

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