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Kinetics and dynamics of nanosecond streamer discharge in atmosphericpressure gas bubble suspended in distilled water under saturated vapor pressure conditions

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Abstract

We perform computational studies of nanosecond streamer discharges generated in helium bubbles immersed in distilled water under atmospheric pressure conditions. The model takes into account the presence of water vapor in the gas bubble for an accurate description of the discharge kinetics. We find that the dynamic characteristics of the streamer discharge are different at low and high positive trigger voltages with the axial streamer evolution dominant for low voltages and a surface hugging mode favored for high voltages. We also find a substantial difference in initiation, transition and evolution stages of discharge for positive and negative trigger voltages with the volumetric distribution of species in the streamer channel much more uniform for negative trigger voltages on account of the presence of multiple streamers. We observe that the presence of water vapor does not affect the breakdown voltage even for oversaturated conditions but significantly influences the composition of dominant species in the trail of the streamer as well as the flux of the dominant species on the bubble surface.

Keywords: streamer in bubbles, plasma reforming, fluid model, water plasma

(Some figures may appear in colour only in the online journal)

1. Introduction

Plasmas generated by electrical discharges in liquids or in the immediate vicinity of liquids have attracted attention due to numerous applications in areas related but not limited to dielectric insulation [1], pollution remediation [2–5], clean energy based liquid fuel reforming [6–13], nanomaterials and nanoparticle synthesis [14, 15], water sterilization [16] and plasma medicine [18]. Non-equilibrium plasma discharges are particularly effective in the production of highly reactive chemical species that drive chemical reaction in the liquids for a number of applications [17]. The work of Lu *et al* [18] provides an in-depth review of reactive species generation through non-equilibrium atmospheric-pressure plasma jets and their interaction with tissue cells. In particular, non-equilibrium nanosecond plasma discharges have the advantage of coupling most of the input electrical energy to the electrons with negligible gas heating. These discharges also make it possible to achieve efficient and non-uniform spatial production of active chemical species if one can exercise some measure of control on the direction of streamer propagation.

Plasma discharges generated directly in liquid medium require much higher breakdown electric fields due to very high liquid densities compared to densities in a gas [19, 20]. For example, breakdown electric fields for distilled water under atmospheric pressure conditions is of the order of 0.1–0.4 MV cm⁻¹ while the breakdown fields in argon is around 0.3 kV cm^{-1} [21, 22].

One approach to realizing the benefits of a plasma for liquid processing is to bubble gas into the liquid and generate the plasma in the gas bubbles [22]. Sommers et al [24] showed that oscillations of deformed gas bubbles could result in significant electric field enhancement at the bubble surface which can be used as a tool to facilitate plasma breakdown in gas bubbles immersed in liquids. The method of injection of bubbles into liquids and generation of plasma within these gas bubbles has been studied extensively both experimentally [23-27] and computationally [28-34] this past decade. Several groups have also conducted experiments to study the fundamentals of discharge in a single bubble immersed in liquid dielectric [23–26]. Discharges at atmospheric-pressure conditions and high voltages are seen to evolve through streamers where the liquid dielectric constant, liquid conductivity and overvoltage can be chosen in such a way so as to control the direction of the streamer propagation [28] and make it move along the bubble axis or along its surface. This results in selective and non-uniform generation of the active chemically reactive species in the trail of the streamer. For liquids with a reasonably high vapor pressures, the gas bubble can be saturated with the liquid vapor which in turn has a strong influence on the bubble plasma kinetics.

With this in mind and motivated by the experimental work of Hamdan and Cha [26], we present a computational model to study the kinetic and dynamic characteristics of plasmas generated in a single bubble immersed in distilled water taking into account the saturated vapor pressure of the water at atmospheric-pressure conditions. We investigate the effect of water vapor on the breakdown voltage and study the evolution of streamers for a range of positive and negative trigger voltages. We also discuss the spatial and temporal distribution of dominant species and compare the distribution of these species for positive and negative trigger voltages.

2. Description of the numerical model

The present model is based on the self-consistent, multispecies and continuum description of plasma [35]. The model solves fluid equations for the species continuity, the electron temperature equation coupled with the Poisson's equation for the electrostatic potential. Here we provide an overview of the model for completeness. Species continuity equations are solved to compute the species number densities in the plasma and are formulated as

$$\frac{\partial n_k}{\partial t} + \nabla \cdot \overrightarrow{\Gamma}_k = \dot{G}_k. \tag{1}$$

The species continuity equation (1) is solved for all the species except the dominant background species (i.e. He and H_2O) and ideal gas law

$$p = n_{\rm b} k_{\rm b} T_{\rm b} \tag{2}$$

is used to update the number densities of the dominant background species, with the assumption that the total pressure and the bulk temperature remain constant during the time scales (~few nanoseconds) of the discharge. The source term in the continuity equation is computed using the rate coefficients associated with the production and/or consumption of the appropriate species. These rate coefficients are computed as a function of the mean electron energy by solving the 0D electron Boltzmann equation solver BOLSIG⁺ [36].

The species flux terms for both charged and neutral species are estimated using drift-diffusion formulation

$$\overrightarrow{\Gamma_k} = n_k \, \overrightarrow{u_k} = -\mu_k n_k \, \vec{\nabla} \, \varphi - D_k \, \vec{\nabla} \, n_k, \tag{3}$$

which is a simplification of the species momentum equation for a collisional plasma [37]. In equation (3), μ_k and D_k are the mobility and diffusion coefficient of *k*th species and u_k is the flux velocity of *k*th species. Electron transport properties are computed as a function of electron temperature T_e using the Boltzmann equation solver [36] while the ion transport properties are referred using experimental data [44]. The electrostatic potential in the plasma is obtained by solving the self-consistent Poisson's equation

$$\nabla^2 \varphi = -\frac{q_{\rm e}}{\varepsilon_r \varepsilon_0} \sum_k Z_k n_k. \tag{4}$$

Here q_e is the elementary charge, Z_k is the charge of *k*th species, ε_r is the dielectric constant (1 for plasma and 80 for liquid), and ε_0 is the permittivity of free space. The mean electron energy e_e is defined in terms of the electron temperature as

$$e_{\rm e} = \frac{3}{2} n_{\rm e} k_{\rm B} T_{\rm e}.$$
 (5)

where $k_{\rm B}$ is the Boltzmann constant, and $e_{\rm e}$ is defined by the electron energy conservation equation

$$\frac{\partial e_{\rm e}}{\partial t} + \nabla \cdot \overrightarrow{\Gamma_{\varepsilon}} = S_{\varepsilon} \tag{6}$$

Here, $\overrightarrow{\Gamma_{\varepsilon}}$ is the flux of electron energy and S_{ε} is the source term. They are defined as

$$\overrightarrow{\Gamma_{\varepsilon}} = (e_{\rm e} + p_{\rm e}) \overrightarrow{u_{\rm e}} - \kappa_{\rm e} \vec{\nabla} T_{\rm e}$$
(7)

$$S_{\varepsilon} = -q_{\rm e} \overrightarrow{\Gamma_{\rm e}} \vec{E} - q_{\rm e} \sum_{i} \Delta E_{i}^{\rm e} r_{i} - \frac{3}{2} k_{\rm B} n_{\rm e} \frac{2m_{\rm e}}{m_{k_{\rm b}}} (T_{\rm e} - T_{\rm g}) \nu_{\rm e,k_{\rm b}}.$$
(8)

In equation (7), κ_e is the electron thermal conductivity, u_e is the electron flux velocity, and p_e is the electron pressure defined by the ideal gas law (2). In equation (8), *E* is the electric field,

	Table 1. Species present in the finite-rate reaction chemistry model.
Charged Species	$e, \text{ He}^+, \text{ He}_2^+, \text{ HeH}^+, \text{ H}^+, \text{ H}^-, \text{ H}_2^+, \text{O}^+, \text{ O}^-, \text{ O}_2^+, \text{ OH}^+, \text{ OH}^-, \text{ H}_2\text{O}^+, \text{ H}_3\text{O}^+, \text{ H}_4\text{O}_2^+, \text{ H}_5\text{O}_2^-, \text{ H}_7\text{O}_3^-, \text{ H}_7\text{O}_4^-, \text{ H}_{10}\text{O}_5^+, \text{ H}_{13}\text{O}_6^+, \text{ H}_2\text{O}_2^-, \text{ H}_3\text{O}_2^-, \text{ H}_5\text{O}_3^-$
Neutrals	H, He*, He [*] ₂ , H, O, O(¹ D), H ₂ , O ₂ , O ₂ (<i>a</i>), O ₂ (<i>b</i>), O ₃ , OH, OH(A), HO ₂ , H ₂ O ₂
Background	He, H ₂ O



Figure 1. Geometry of the gas bubble-liquid problem and the computational domain.



Figure 2. (a) Electron number density (in m⁻³), (b) electron temperature (in eV) and (c) reduced electric field (in Td) distribution at the breakdown voltage for positive trigger i.e. 1.5 kV at t = 3 ns.

 $\Delta E_i^{\rm e}$ is the energy lost per electron (in eV) due to inelastic collisions in the *i*th reaction, $\nu_{{\rm e},k_{\rm b}}$ is the electron momentum transfer collision frequency, $m_{\rm e}$ is the mass of electron, $m_{k_{\rm b}}$ is the mass of *k*th species, and r_i is the rate of *i*th reaction. The first term in equation (8) describes the electron Joule heating, the second term describes the contribution of the inelastic collisions, and the last term describes the contribution of elastic collisions. The heavy species (ions and neutral) are assumed

to have a common temperature T_g same as the bulk gas temperature T_g . Photoionization is neglected since photons emitted by de-excitation of the oxygen excimers are not energetic enough to ionize the background gas species.

Kinetic Maxwellian flux condition combined with secondary electron emission flux is used to specify the boundary flux of the electrons at the wall surfaces (electrode wall and the bubble dielectric interface):



Figure 3. Transient evolution of the reduced electric field distribution (in Td) for 2 kV at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns.



Figure 4. Transient evolution of the reduced electric field distribution (in Td) for 8 kV at (a) t = 0.2 ns, (b) t = 0.25 ns, (c) t = 0.3 ns, (d) t = 0.35 ns.

$$\overrightarrow{\Gamma_{\varepsilon}} \cdot \widehat{n} = \frac{1}{4} n_{\rm e} \sqrt{\frac{8k_{\rm B}T_{\rm e}}{\pi m_{\rm e}}} - \gamma_{\rm eff} \overrightarrow{\Gamma_{\rm ion}} \cdot \widehat{n}$$
(9)

where \hat{n} is the unit normal vector pointing toward the wall. The first term in (9) indicates the Maxwellian flux of the electrons to the surface and the second term is the secondary electron emission flux of the electrons from the wall surface. The effective secondary electron emission coefficient is approximated as a function of the reduced electric field normal to the cathode surface $(E/N)_c$ as described by Phelps and Donko [45, 46]

$$\gamma_{\rm eff} = 0.01 \cdot \left(\frac{E}{N}\right)_{\rm c}^{0.6}.$$
 (10)

Here the reduced electric field is expressed in kilo-Townsend (kTd) and the approximation is valid in the range 3 kTd $< (E/N)_c < 20$ kTd (1 Td $= 10^{-21}$ V \cdot m²). The secondary electron emission coefficient from the dielectric surface is set

to a constant value of 0.01 (He), 0.03 (H, H_2O species) and 0.05 (O species). Mobility limited flux condition is imposed at the walls for ions using

$$\vec{\Gamma}_{i} \cdot \hat{n} = \frac{1}{4} n_{i} \sqrt{\frac{8k_{\rm B}T_{\rm g}}{\pi m_{i}}} + n_{i} \cdot \max\left(0, -\mu_{i} \hat{n}_{\rm s} \cdot \vec{\nabla} \varphi\right) \tag{11}$$

and Maxwellian flux condition is specified at the walls for the neutral species using equation

$$\overrightarrow{\Gamma}_{n} \cdot \widehat{n} = \frac{1}{4} n_{n} \sqrt{\frac{8k_{\rm B}T_{\rm g}}{\pi m_{n}}}.$$
(12)

For the electron energy equation, the energy flux incident at the walls is given by

$$Q_{\rm e}^{\rm w} = \frac{5}{2} k_{\rm B} T_{\rm e} \Gamma_{\rm e}^{\rm w}.$$
 (13)

Here, Γ_e^w is the electron number flux at the walls. The electrostatic potential on the dielectric surface is determined using

Electron Number Density (n_e)



Electron Temperature (T_e)



Figure 5. Transient evolution of the electron number density (#/m³) in top half and electron temperature, bottom half (eV) for 2kV at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns.

the total surface charge density accumulated on the surface. The equation for the evolution of the net surface charge density is given by [47]:

$$\frac{\partial \rho_{\rm s}}{\partial t} = \sum_{k=1}^{K_{\rm g}} q_{\rm g} Z_k \overrightarrow{\Gamma}_k \cdot \widehat{n}, \qquad (14)$$

where ρ_s is the surface charge density.

In the present model, we do not consider the species dissolution in water (see, for instance, discussion in [33]). In general, this process can affect the plasma component content because species such as OH, HO_2 and H_2O_2 have high Henry's constants and easily dissolve in water. However, on the time scale of the streamer propagation through the bubble (see discussion below) fluxes of heavy species to the bubble wall are small and solution of species does not play significant role on the active species production/consumption and on the streamer dynamics.

The governing equations are cast as transient convectiondiffusion-source conservation equations and discretized using a cell-centered finite volume approach. Spatial discretization of fluxes is performed using Scharfetter–Gummel exponential scheme [48] while backward Euler approach is used for temporal discretization. The equations are cast in a semi-implicit form and solved using a sparse linear solver. A time-splitting approach is used to solve different governing equations which requires solving each governing equation individually in a segregated fashion with characteristic time steps defined by accuracy and stability criterion for that equation.

The gas bubble is filled with the helium and water vapor mixture (He/H₂O) at a constant pressure of one atmosphere and a constant bulk temperature of 300 K, with water vapor included to Electron Number Density (n_e)



Electron Temperature (T_e)



Figure 6. Transient evolution of electron number density, top half (in m⁻³) and electron temperature, bottom half (in eV) for 8 kV at (a) t = 0.2 ns, (b) t = 0.25 ns, (c) t = 0.3 ns, (d) t = 0.35 ns.

allow for a more accurate description of the gas phase discharge. The finite-rate reaction chemistry mechanism is based on work of Bruggeman *et al* [38] and consists of 40 species and 143 reactions (tables 1 and A1). In the present model, the reactions are assumed to occur only in the gas-phase within the bubble and we neglect the diffusion of species into the liquid phase.

Here let us note that the computational domain shown in figure 1 is different from the ones used in studies of Babaeva and Kushner. In their studies, the geometry was either pinto-plane [28–30, 34] or symmetrical electrode configuration [31, 32]. The computational domain (figure 1) in the present work consists of a spherical bubble with diameter of 1 mm surrounded by distilled water acting as the dielectric with a relative permittivity of 80.4. Here, we employ a pin-to-hollow tube geometry. The trigger electrode is pin shaped with flat tip of 1 μ m and a base length of 0.6 mm, while the ground electrode is a hollow tube with a flat base and the inner and outer diameter of 0.3 mm and 0.6 mm, respectively. Both the electrodes are completely immersed in the dielectric, with the flat pin electrode off from the surface of the gas bubble by 0.01 mm and the tube electrode off from the surface of the gas bubble by 0.12 mm. The choice of these parameters is similar to the experiments reported in [26].

The numerical grid comprises an unstructured mesh with appropriately refined regions near the electrodes and the bubble surface to capture the sheath and time evolution of discharge in the gas bubble. The mesh consists of approximately 60000 cell elements of which 36000 cells are located inside the gas bubble.

3. Results and discussion

We have performed simulations for direct-current trigger voltage of both positive and negative polarity of the pin electrode. For the majority of the investigations, the molar concentration of water vapor in the helium bubble is 3% (saturated

Number density of He+



Number density of H₂O+



Figure 7. Transient number densities of He⁺, H₂O⁺, OH⁺ and H⁺ ions (in m⁻³) at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns.

He/H₂O) computed using the saturated vapor pressure of water at atmospheric-pressure conditions [39]. The bubble was initially seeded with a plasma (electrons and He⁺ ions) of density 10¹² m⁻³. The density of other species (ions and radicals) is 10^9 m^{-3} . We also have studied the influence of the non-homogeneous distribution of the initial plasma density and observe no influence on the simulation results if the initial plasma density is below 10^{12} m⁻³. The dielectric used in the present studies is distilled water similar to previous numerical studies [28-34]. The dielectric constant of water is high which allows breakdown at lower trigger voltages. The influence of liquid dielectric constant and bubble radius has been investigated before in [28] and [32], respectively. In the present work, we keep the liquid dielectric constant and the bubble radius constant as our primary focus is to study the effect of water vapor on the breakdown voltage and the transients of streamers for a range of positive and negative trigger voltages.

3.1. Breakdown voltage

The breakdown voltage in the He/H₂O mixture is found to be ~1.5 kV for the positive trigger voltage and is ~ -1.5 kV for the negative trigger voltage (i.e. $|E_{app}| \sim 1.5$ MV m⁻¹). Figure 2 shows the dynamic characteristics of the discharge at the breakdown voltage (1.5 kV) for positive trigger studies. We find that the breakdown voltage also remains constant for the water vapor density in the range 0–10%, i.e. from pure helium case (0%) to highly oversaturated He/H₂O mixture (10%). This indicates that the breakdown voltage is unaffected by the low density of water vapor present in the bubble at atmospheric-pressure conditions and is primarily defined

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Number Density of OH+



Number Density of H+



Figure 7. (Continued)

by the dominant He species. The breakdown voltage can be estimated as [40]

$$V_{\rm b} = \frac{Bpd}{\ln(Apd) - \ln\left[\ln\left[1 + \frac{1}{\gamma_{\rm sc}}\right]\right]}.$$
 (15)

where, V_b is the breakdown voltage in Volts, p is the pressure in Torr, d is the distance between electrodes in cm, γ_{se} is the secondary electron emission coefficient due to ion impact, and A and B are experimentally determined coefficients; for helium these values are roughly constant for electric fields in the range 30–250 Td [40]. For p = 760 Torr, d = 1.1 cm and $\gamma_{se} = 0.01$ used in our study, equation (15) gives $V_b = 1.52$ kV which agrees with the breakdown voltage obtained in the present work. The trigger voltage is slightly lower for the breakdown in the bubble compared to the parallel plate configuration due to the large local electric field at the tip of the pin electrode and electric field enhancement at the surface of the bubble.

Depending on the electrode polarity, the streamer stage of discharge is preceded by the avalanche growth at the pin electrode or in the cathode–anode gap [41]. This is confirmed in figure 2(a) where we observe electron number density $\sim 10^{20} \, m^{-3}$ near the pin electrode at $V_{br} = 1.5 \, kV$ for positive polarity. Peak electron temperatures of $\sim 10 \, eV$ are observed at the head of the corona while the electron temperature in the body drops to $\sim 3.2 \, eV$ (figure 2(b)). Quantitatively, the avalanche-to-streamer transition is described by the Meek's criterion [41] which for parallel plate configuration is given as

$$\alpha(E_{\rm app})x \sim 18. \tag{16}$$

Here E_{app} is the applied electric in V cm⁻¹, x is the distance from the cathode in cm and α is the Townsend ionization coefficient of the helium in cm⁻¹. Assuming x is the bubble diameter, we get the value of α to be in the range of 180–210 cm⁻¹.

Number Density of O



Number Density of OH



Figure 8. Transient number densities of OH and O radicals (in m⁻³) at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns.

Using the relation between Townsend ionization coefficient and applied electric field for He determined experimentally by two different sources, Chanin *et al* [42] and Davis *et al* [43], we get $E_{app} = 1.6-2.1$ MV m⁻¹. Though Meek's criterion (16) was derived for parallel plate configuration, the value of electric field for avalanche-to-streamer transition agrees quite well with the conditions for the present configuration.

3.2. Positive trigger voltage of the pin electrode

For the positive trigger voltage, the simulation results have shown that in the beginning the electron/ion avalanche (also called corona) [41] grows near the pin electrode as seen in figure 2(a). The electric field enhancement is observed at the streamer head as seen in figure 2(c) with the peak value of E/N reaching ~150 Td. We identify this as the breakdown reduced electric field $(E/N)_{br}$ necessary for the streamer formation in the atmospheric pressure He gas bubble of 1 mm diameter immersed in water. Later, when the Meek's criterion (16) is satisfied this corona transforms to the cathode-directed streamer (i.e. negative streamer). The streamer propagates toward the cathode due to the acceleration of background electrons present in front of the streamer head.

We also carried out the simulations for the positive trigger voltage in the range 1.5-15 kV. We find that the discharge evolves through two completely different modes depending on the applied voltage. For the positive trigger voltage in the range 1.5-3 kV, the discharge is initiated through a corona phase at the bubble-anode interface. Once the Meek's criterion (16) is satisfied, corona transforms to the streamer (figure 3(a)). The streamer moves primarily along the axis of the bubble till it reaches the center of the bubble (figure



Figure 9. Transient number densities of molecular oxygen at (a) t = 2.5 ns, (b) t = 3 ns and (c) t = 3.5 ns.



Figure 10. Time evolution of the integrated flux of the dominant species to the surface of the bubble at $2 \, \text{kV}$.

3(b)). This is due to the fact that as the applied voltage is close to the breakdown voltage the inclined electric field lines from the pin anode have magnitude lower than the breakdown voltage, i.e. the electric field exceeds $(E/N)_{br}$ only near the bubble axis. This prevents the streamer deviation from the axis. We also see from figures 3(a) and (b) that the electric field at the head of the streamer decreases during its axial motion. This is because of the decreasing influence of the bubble wall on the electric field at the streamer head when it approaches the bubble center. Equation(17) shows that this results in a decrease in the net electric field at the streamer head. The radius of the streamer remains almost constant during this axial propagation phase of the discharge and is very close to the thickness of the base of the pin electrode. This indicates axial mode dominance during the initial stages of the discharge and agrees with the experimental results of Hamdan and Cha [26].

Figure 3(c) shows that as the streamer head crosses the center of the bubble its radius increases. One can conclude that the electric field at the head of the streamer increases as well. The radius increases due to the influence of refracted

electric field lines from the cathode. The magnitude of electric field is higher than $(E/N)_{br}$ and thus sufficient to change the direction of the streamer propagation. The net electric field at the head is the sum of both the applied external electric field and the induced space charge field defined by

$$E_{\text{head}} = E_{\text{app}} + E_{\text{ind}}.$$
 (17)

The streamer head has a convex shape with radius of curvature R. Therefore, the electric field of the space charge at the streamer head can be defined by

$$E_{\rm ind} = \frac{eN_{\rm e}}{R^2}$$
, where $N_{\rm e} = \exp(\alpha x)$. (18)

Hence, we conclude that while the increase in the radius decreases the space charge field (18), the applied external electric field increases much more at the head due to its proximity to the cathode. This more than compensates the space charge field reduction and results in the substantial increase of the electric field at the streamer head once it crosses the center of the bubble as seen in figures 3(c) and (d).

The simulation results have shown that for higher voltages (8kV) the streamer, once again, evolves through a corona formed at the bubble-anode interface. In this case, however, the streamer moves both along the surface and the axis of the bubble during the initial stage of the discharge (see figure 4(a)). This is due to the fact that the electric field lines originating from the pin anode are inclined at an angle to the axis owing to the shape of the anode. Thus, the region where electric field exceeds $(E/N)_{\rm br}$ expands for increasing trigger voltage and is enough to incline the streamer from the bubble axis. Figure 4(b) shows that the streamer hugs the surface of the bubble during the initial stage of the discharge. Once the streamer head moves further away from the anode the axial component of electric field becomes dominant. Thus, the streamer moves along the bubble axis as seen in figure 4(c). As the streamer approaches the cathode the refracted electric field lines cause the expansion of the streamer head similar to the low voltage case (compare figures 3(d) and 4(d)).



Figure 11. Transient evolution of the reduced electric field distribution (in Td) for -2 kV at (a) t = 2 ns, (b) t = 2.2 ns, (c) t = 2.7 ns, (d) t = 3 ns from left to right.



Figure 12. Transient evolution of the reduced electric field distribution (in Td) for -8 kV at (a) t = 0.2 ns, (b) t = 0.22 ns, (c) t = 0.25 ns, (d) t = 0.3 ns.

Figure 5 shows the transient evolution of the electron number density (n_e) and electron temperature (T_e) for low voltage (2 kV). We see that the region of high electron density is mainly concentrated near the bubble axis and consists primarily of low-energy electrons with temperature (~4 eV) much lower than the temperature at the streamer head (~15 eV). The electron temperature at the head decreases slightly during the initial stage of the discharge (figures 5(a) and (b)) due to decrease in the net electric field at the streamer head (figure 3) and increases after the streamer head crosses the bubble center due to the increased proximity of the streamer head to the cathode.

At a higher voltage (8kV) we see from figure 6 that the axial region consisting of high electron density is longer and wider than this region for 2kV (figure 5). The high electron temperature in the spherical ionization wave front is

concentrated near the bubble surface as seen in figure 6(b), which is opposite to the case shown in figure 5. This clearly demonstrates the surface propagation mode during the initial stages of the discharge for higher voltage. However, a closer observation of the results indicate that the streamer does not necessarily propagate along the bubble surface, as was obtained for instance in [28], but in close vicinity to the surface. This can be explained by faster streamer propagation under the conditions in our study so that the dielectric has no time to be charged and to attract the streamer.

We obtain that for 2kV the dominant positive ions are He^+ , H_2O^+ , OH^+ and H^+ (figure 7) with the density of He^+ being an order of magnitude higher than the densities of other positive ions. The production of helium ions is high both at the streamer head and in the axial region in its tail. The latter is, in spite of the low electron temperature near the

Electron Number density n_e (#/m3)



Electron Temperature $T_e(eV)$



Figure 13. Transient evolution of the electron number density (in m⁻³), and electron temperature (in eV) for -2 kV at (a) t = 2 ns, (b) t = 2.2 ns, (c) t = 2.5 ns, (d) t = 3 ns from left to right.

streamer axis, due to the high electron density in this region. This results in a net high electron energy ($\propto n_e T_e$) near the axis as compared to the streamer head. Since the dominant production reaction of these ions is the electron impact ionization $e + \text{He} \rightarrow \text{He}^+ + 2e$, we conclude that the high net electron energy near the axis results in the high ion density near the discharge axis and not at the streamer head.

Our simulation results have shown that at the considered conditions, the dominant active neutral species are O, H and OH (see figure 8). The densities of both H and OH are comparable since the dominant reaction for production of these species is the electron impact dissociation of water

$$e + H_2 O \rightarrow H + OH + e. \tag{19}$$

The densities of H and OH radicals are two orders of magnitude higher than the density of O radicals, because the primary reactions for the production of O is the dissociation reaction $e + OH \rightarrow O + H + e$. The density of OH radicals is much smaller than the density of H₂O. As a consequence, the rate of OH generation is much larger than that of O.

The spatial profile of the O_2 density is shown in figure 9. It is interesting to note that its density in the discharge body is negligible while the majority of O_2 is concentrated at the bubble surface near the anode. This indicates that the main contribution to the production of molecular oxygen is through surface quenching reactions such as destruction of ions and neutrals at the bubble surface rather than the volumetric production in chemical reactions. The dominant surface reactions

Electron Number density $n_e(\#/m3)$



Electron Temperature $T_e(eV)$



Figure 14. Transient evolution of the electron number density, (in m⁻³), and electron temperature (in eV) for -8 kV at (a) t = 0.2 ns, (b) t = 0.22 ns, (c) t = 0.25 ns, (d) t = 0.3 ns. Here 'AC' refers to anode corona. 'PS' refers to positive streamer and 'NS' refers to negative streamer.

for the production of O_2 include destruction of heavier water complex cations such as $H_{11}O_5^+$ and $H_9O_4^+$, H_2O^+ ions and OH radicals with the contributions dependent on the transient distribution of the flux of these species at the bubble surface.

Figure 10 shows the flux of the dominant species to the bubble wall for 2 kV. The largest flux is obtained for He⁺ (not shown). Also, the flux of H⁺ is one order of magnitude smaller than that of H₂O⁺. This is explained by much smaller density of H⁺ than the density of H₂O⁺ (figure 7). The flux of H radicals is comparable with that of OH and therefore not shown here. Flux of O radicals is ~ 2 orders of magnitude lower than the flux of OH radicals and thus not significant for positive trigger voltages.

The dominant water complex species for conditions of our study are $H_{11}O_5^+$, $H_9O_4^+$ and $H_{13}O_6^+$ with the peak number density of these species reaching the values ~ 10^{19} m⁻³ after

3.5 ns. It is interesting to note that the dominant negative ion found in the current work is the heavier water complex anion $H_5O_3^-$ with the density an order of magnitude higher than the density of other major negative ion OH⁻. This is due to the fact that hydroxyl anions undergo rapid attachment to form $H_5O_3^-$ through the two step three-body recombination reactions:

$$OH^- + H_2 O + M \to H_3 O_2^- + M,$$
 (20)

$$H_3O_2^- + H_2O + M \to H_5O_3^- + M.$$
 (21)

Here M = He. The rate coefficients of both reactions are of the order of 10^{-28} cm⁶ s⁻¹ (table A1). Substituting the densities of He and H₂O we estimate the rates of both reactions as ~ 10^{21} - 10^{22} cm⁻³ s⁻¹. For comparison, the rates of ion-ion recombination reactions (e.g. He⁺ and OH⁻) are ~ 10^{18} - 10^{19} cm⁻³ s⁻¹ Number density of He⁺



Number Density of H₂O⁺



Figure 15. Transient evolution of He⁺, H₂O⁺, OH⁺, H⁺ (in m⁻³) for -2 kV at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns from left to right.

which is much smaller than the rate of ion conversion reactions shown above.

3.3. Negative trigger voltage of the pin electrode

Next, we apply the negative trigger voltage in the range from -1.5 kV to -15 kV to the pin electrode. We find that the discharge evolves through completely different modes as compared to the positive trigger voltage discussed above.

For the low voltage studies, we see the formation of the electron/ion avalanche on the axis of the bubble at a finite distance from the pin cathode (see figures 11(a) and 13(a)). This avalanche moves toward the anode along the bubble axis. The avalanche is not transformed into a streamer owing

to the low plasma densities. As a consequence, there is no self-consistent mechanism for the propagation of the avalanche to the anode and the avalanche propagates due to the plasma generation by the electrons which are being accelerated in the high electric field present between the avalanche and the anode. The plasma density in the avalanche is enough to marginally screen the applied electric field but not enough to cause the local enhancement of electric field. One can see from figure 11(a) the high-voltage sheath between the cathode and the avalanche because the electrons need to travel some distance to gain the energy and form a rather dense plasma to screen the applied electric field.

Figure 12 shows the electric field profile obtained for -8 kV. We conclude from figure 12(a) that dense avalanche is formed

Number density of OH⁺



Number density of H⁺



Figure 15. (Continued)

on the axis of the bubble and closer to the cathode which is explained by shorter distance necessary for seeded electrons to generate dense plasma. Figure 14(a) shows that this avalanche transforms into an anode-directed streamer (positive streamer). This implies that the Meek's criterion (16) is satisfied for this avalanche.

One observes from figures 11-14 the formation of the cathode-directed streamer for both trigger voltages. The mechanism of this streamer formation is analogous to that described in section 3.2. The anode-directed streamer (positive streamer) moves much faster as compared to its counterpart cathode-directed one, i.e. negative streamer (figures 14(c) and (d)). The anode-directed streamer propagates primarily along the axis of the bubble due to the shape of the anode with

the radius of the anode-directed streamer comparable to the anode radius, while the cathode-directed streamer spreads as it moves towards the anode due to the influence of the inclined electric field lines originating from the pin shaped cathode (figure 14(c)).

Figure 13 shows the transient evolution of the electron density and the electron temperature for the trigger voltage -2 kV. The comparison between figures 13(a) and (d) allows us to conclude that the most efficient plasma generation occurs during the propagation of the cathode-directed streamer. This is explained by the electric field distortion caused by the streamer (see figure 11 and 13). Namely, one can see from figure 11 that during the stage shown in figures 13(a) and (b) the largest electric field is obtained in the vicinity

Number Density of OH



Number Density of monoatomic oxygen (O)



Figure 16. Transient evolution of OH and O radicals (in m⁻³) for -2 kV at (a) t = 2 ns, (b) t = 2.5 ns, (c) t = 3 ns, (d) t = 3.5 ns from left to right.

of the cathode (figures 11(a) and (b)) where electron density is small. The electric field in the bubble does not exceed 80 Td. Figures 11(c) and (d) show high electric field at the head of the cathode-directed streamer (~200 Td) which explains higher rate of plasma generation during the streamer stage of discharge. Figures 13(c) and (d) show that the region of high electron density is mainly concentrated near the bubble axis and consists primarily of low-energy electrons with the energy ~3–4 eV which is much lower than the energy at the streamer head (~12–15 eV) (see discussion in section 3.2).

Our simulation results also showed that the avalanche propagating toward the anode promotes the formation of the cathode-directed streamer for low trigger voltages. Namely, the avalanche pre-ionizes the bubble increasing the electron number density before the head of the cathode-directed streamer. Also, the electric field between the avalanche and the anode corona increases when the distance between them decreases. This means that the Meek's criterion (16) is satisfied earlier. Moreover, we conclude from figure 13(b) that the cathode-directed streamer does not start until the avalanche reaches the anode.

The increase in the trigger voltage results in the increase of the electric field in the bubble. As a consequence, the streamer dynamics and plasma parameters change (figure 14). Figure 14(a) shows faster growth of the anode corona which transforms to the streamer earlier than in the case of -2kV(figure 13). On one hand, this is caused by the larger applied electric field. On the other hand, the formation and propagation of the anode-directed streamer changes the electric field in the bubble drastically. Namely, anode-directed streamer can be considered as the moving pin. Then, the electric field between the anode corona and this streamer increases with time which means the earlier satisfaction of Meek's criterion (16). Figures 14(a) and (b) allow us to conclude that



Figure 17. Transient number densities of oxygen molecules (in m^{-3}) for -2kV at (a) t = 2.5 ns, (b) t = 3 ns and (c) t = 3.5 ns from left to right.



Figure 18. Transient integrated flux of the dominant species to the surface of the bubble at -2 kV.

the anode-directed streamer promotes the cathode-directed streamer formation only through the electric field distortion. Since the cathode-directed streamer is formed when the anode-directed one is still far from the anode (figures 12(a) and 14(a)), we conclude that there is no promotion of the cathode-directed streamer formation through pre-ionization by the anode directed streamer.

The anode directed streamer (positive streamer) merges with the corona originating at the anode as seen in figure 14(c). When the streamer and corona merge, we do not obtain any streamer in the bubble. However, the merging of streamers leads to the fast redistribution of the electric field in the bubble (figure 12(c)) and, as a consequence, leads to the penetration of high electric field in the bodies of both streamer and corona. This electric field heats electrons and leads to the fast generation of plasma whose density is ~10²¹ m⁻³. This plasma screens the applied electric field leading to its concentration only in the sheath around the bubble. One can conclude from figure 14(c) that the peak electron density is obtained in the position where the streamer and the corona merged. In this location we obtained the largest electric field and, as a consequence, the largest T_e and n_e .

It is also important to note that, for all negative trigger voltage (-1.5 kV to -15 kV), we did not observe any surface hugging mode of the streamers (see figures 13(a) and 14(a)), whereas, for larger positive trigger voltages (8 kV-15 kV), we spotted the cathode directed streamer hugging the bubble wall during the initial stage of the discharge (figure 4(a)).

We find that the dominant positive ions for the negative trigger voltage studies are the same as those observed for the positive trigger voltage studies, i.e. He⁺, H₂O⁺, OH⁺ and H^+ . The comparison between their spatial profiles (figure 15) shows that the distribution is quite similar for all positive ions with the density being highest along the axis of the streamer tail, similar to the results observed previously for low positive voltage (see section 3.2). However, figures 15(c) and (d) show two peaks of ions densities which is not observed for the positive trigger voltage (compare with figure 7). Moreover, the plasma density is more uniform in the streamer body. This is due to the fact that the entire structure of streamer discharge for negative voltage studies is very different from that of positive voltage. Namely, for the negative voltage, we see either avalanche and streamer or two streamers moving in the opposite directions rather than just one streamer moving toward the cathode (which was observed for the positive voltage studies). We conclude from figures 15 and 16 that the main contribution to the plasma is by the cathode-directed streamer. For the positive trigger voltage this anode directed avalanche propagates through the gas seeded with the electrons having density $\sim 10^{12}$ m⁻³. For the negative trigger voltage, anodedirected streamer propagates through the gas ionized by the avalanche moving toward the anode having density $\sim 10^{18}$ m⁻³. Therefore, more electrons participate in the cathode-directed streamer propagation.

The dominant excited neutrals for the negative trigger voltage are OH, H and O radicals with the density of OH and H radicals exceeding that of O by an order of magnitude (figure 16). This is explained by the fact that OH radicals are generated directly from the primary species H₂O by the electron impact (H₂O + $e \rightarrow$ OH + H + e), while O is generated from OH in dissociation reaction OH + $e \rightarrow$ O + e. The rate

of the latter reaction is much smaller than the rate of water dissociation reaction due to much smaller density of OH than the density of H_2O .

As compared to the positive trigger voltage of 2 kV, we find that the density of OH radicals is ~2 orders of magnitude smaller for negative trigger voltage (compare figures 15(a) and 8(a)). OH radicals are mainly generated in reaction (5), (see table A1) whose rate for a fixed density of H₂O depends on n_e and T_e . The comparison between figures 13(b) and 5(b) shows smaller T_e in the streamer body for the negative trigger voltage which is due to different structure of the electric field in the body of the streamers originated at the pin and flat electrodes. The rate coefficients of the electron impact ionization and dissociation reactions of He and H₂O increase exponentially for $T_e < 10 \,\text{eV}$. Therefore, even small changes in T_e result in the drastic changes in the rate coefficients of the electron impact reactions. This explains significant difference of OH density obtained for two polarities of the pin electrode.

For oxygen O_2 , we see a similar trend (figure 17) with the density being negligible in the body of the discharge with majority of oxygen concentrated at the surface of the bubble near the anode. This indicates that the main contribution to the production of oxygen is surface reactions such as destruction of ions and neutrals at the bubble surface, rather than the volumetric production of oxygen through recombination of O atoms. The main difference between the negative and positive trigger voltage is that the oxygen density for the negative voltage is ~2 orders of magnitude lower than that obtained for the positive trigger voltage. This is explained by smaller densities of O and OH radicals. Indeed, the simulation results have shown that the main contribution to the generation of O_2 comes from OH, O, H_2O^+ and heavier $H_{11}O_5^+$ and $H_{13}O_6^+$. Among the dominant neutral species, the flux of OH radicals is an order of magnitude higher than the flux of O radicals (figure 18).

The dominant water complex species found for the negative trigger voltage are the heavier species $H_9O_4^+$, $H_{11}O_5^+$ and $H_{13}O_6^+$ with the number density of these species reaching values ~10¹⁸ m⁻³ after 3.5 ns. These values are an order of magnitude smaller than those obtained for the positive trigger voltage. These species are generated from H_2O^+ whose density is ~1 order of magnitude smaller for the negative trigger voltage (compare figures 7 and 15). The dominant negative ions are $H_5O_3^-$ with the density an order of magnitude higher than that of OH⁻. The densities of negative ions are much smaller than the densities of positive ions. The presence of these ions does not affect the streamer dynamics and hence is not shown here.

4. Summary

The plasma dynamics and chemical kinetics of the streamers generated in the atmospheric-pressure bubbles suspended in the distilled water were studied by the axi-symmetric fluid model. This work was primarily motivated by the experiments reported in [26]. All the studies were conducted at saturated vapour pressure conditions, noting that the results were not sensitive for water vapour mole fractions of in the range 0-10%.

We find that, for positive trigger voltages, the streamer discharge evolves axially at low voltages but prefers surface propagation mode at high voltages, while no surface propagation mode was found for negative trigger voltages. The polarity of the trigger voltages substantially changes the dynamic characteristics of the discharge. For a positive trigger voltage, the discharge progresses through a single cathodedirected streamer from the point of origin in the vicinity of the pin anode. For a negative trigger voltage of the pin electrode, the discharge evolves through either an avalanche and streamer mode or two streamers propagating opposite to each other. The regime depends on the value of the applied negative voltage. A comparison between active species generated for the negative and positive trigger voltage showed larger number densities of active species in the latter case but more uniform distribution of active species in the former case. We also observe that the presence of water vapor in the bubble leads to water complex ions dominating the concentration of negative ions and OH radicals dominating the concentration of excited neutrals.

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Appendix

Table A1. Chemical reactions included in the model [36].

No.	Reaction ^a	Rate coefficient ^b
Electron	n impact ionization	
1	$e + \text{He} \rightarrow 2e + \text{He}^+$	$f(T_{\rm e})$
2	$e + { m He}^* ightarrow 2e + { m He}^+$	$f(T_{\rm e})$
3	$e + H_2 O \rightarrow 2e + H_2 O^+$	$f(T_{\rm e})$
4	$e + H \rightarrow 2e + H^+$	$5.08 \times 10^{-9} T_{e}^{0.6} \exp(-13.6/T_{e})$
5	$e + \mathrm{H}_2 \rightarrow 2e + \mathrm{H}_2^+$	$9.1 * 10^{-9} T_{\rm e}^{0.5} \exp(-15.4/T_{\rm e})$

(Continued)

No.	Reaction ^a	Rate coefficient ^b	
6	$e + \Omega \rightarrow 2e + \Omega^+$	$0.0 \times 10^{-9} T^{0.7} \cos(-12.6/T)$	
7	$a + 0 \rightarrow 2a + 0^+$	$7.0 \times 10^{-10} T_e^{2.0} \exp(-12.6/T_e)$	
8	$e + O_2 \rightarrow 2e + O_2$	$9.0 \times 10^{-10} T_e^{-1} \exp(-12.0/T_e)$	
9	$e + O_2(a) \rightarrow 2e + O_2^{-1}$	$9.0 \times 10^{-10} I_e^{-10} \exp(-11.6/I_e)$	
Floatron im	$e + OH \rightarrow 2e + OH$	$2.0 * 10^{-10} T_{\rm e}^{1.76} \exp(-13.8/T_{\rm e})$	
10	$a + He \rightarrow a + He^*$	$f(T_{-})$	
11	$e + H_2 O \rightarrow H + OH + e$	$f(T_{e})$	
12	$a + H_2 O \rightarrow H_2 + O(^1D) + a$	$f(T_e)$	
13	$e + H_2 O \rightarrow H_2 + O(D) + e$ $e + H_2 O \rightarrow H_2 + OH(A) + e$	$f(T_{e})$	
14	$e + H_2 \rightarrow 2H + e$	$8.73 \times 10^{-8}T^{0.5} \exp(-11.7/T)$	
15	$a \pm 0 \rightarrow 0({}^{l}D) \pm a$	$4.5 \times 10^{-9} \exp(-2.29/T)$	
16	$e + 0 \rightarrow 0(D) + e$ $e + 0 \rightarrow 20 + e$	$4.5 \times 10^{-9} \exp(-2.29/T_e)$	
17	$c + o_2 + 2o + c$	$7.1 \times 10^{-8} \exp(-8.0/T_e)$	
10	$e + O_2 \rightarrow e + O + O(D)$	$4.0 \times 10^{-10} \exp(-8.4/T_e)$	
10	$e + O_2 \rightarrow e + O_2(b)$	$3.24 \times 10^{-10} \exp(-2.218/I_{\rm e})$	
20	$e + O_2 \rightarrow e + O_2(a)$	$1.7 \times 10^{-9} \exp(-3.1/T_{\rm e})$	
20	$e + O_2(a) \rightarrow e + O_2$	$5.6 * 10^{-9} \exp(-2.2/T_e)$	
21	$e + O_2(b) \rightarrow e + O + O(^{1}D)$	$3.49 * 10^{-\circ} \exp(-4.29/T_{\rm e})$	
22	$e + OH \rightarrow e + O + H$	$2.08 * 10^{-7} T_{\rm e}^{-0.76} \exp(-6.9/T_{\rm e})$	
23	$e + HO_2 \rightarrow H + O_2 + e$	$3.1 * 10^{-9}$	
24	$e + H_2O_2 \rightarrow 2OH + e$	$2.36 * 10^{-9}$	
25	$e + H_2O_2 \rightarrow H + HO_2 + e$	$3.1 * 10^{-11}$	
26	$e + \mathcal{O}_3 \rightarrow \mathcal{O} + \mathcal{O}_2 + e$	$5.88 * 10^{-9}$	
Electron imp	pact attachment and dissociative attachment		
27	$e + H_2 O \rightarrow OH + H^-$	$f(T_{\rm e})$	
28	$e + H_2 O \rightarrow H_2 + O^-$	$f(I_e)$	
30	$e + H_2 O \rightarrow OH + H_2$	$J(I_e)$	
31	$e + HO \rightarrow HO + O^{-}$	5.1×10^{-10}	
22	$e + H_2O_2 \rightarrow H_2O + O$	$1.57 \times 10^{-10} T_{\rm e}^{-0.55}$	
52 D' ' ' '	$e + H_2O_2 \rightarrow OH + OH$	$2.7 * 10^{-10} T_{e}^{-0.5}$	
Dissociative	recombination	$5.5.10^{-30}$ m^{-2} 0	
24	$e + He + He \rightarrow He + He$	$6.6 \times 10^{-50} T_e^{2.5}$	
54 25	$e + \text{He}_2^+ + \text{He} \rightarrow \text{He}^* + 2\text{He}$	$3.5 * 10^{-27}$	
35	$e + \mathrm{H}_{5}\mathrm{O}_{2}^{+} \rightarrow 2\mathrm{H}_{2}\mathrm{O} + \mathrm{H}$	$1.62 * 10^{-6} T_{e}^{-0.15}$	
36	$e + \mathrm{H}_4\mathrm{O}_2^+ \to \mathrm{H}_2\mathrm{O} + \mathrm{OH} + \mathrm{H}$	$9.6 * 10^{-7} T_{\rm e}^{-0.2}$	
37	$e + \mathrm{H}_7\mathrm{O}_3^+ \to 3\mathrm{H}_2\mathrm{O} + \mathrm{H}$	$2.24 * 10^{-6} T_{\rm e}^{-0.08}$	
38	$e + H_9O_4^+ \rightarrow 4H_2O + H$	$3.6 * 10^{-6}$	
39	$e + H_{11}O_5^+ \rightarrow 5H_2O + H$	$4.0 * 10^{-6}$	
40	$e + H_{13}O_6^+ \rightarrow 6H_2O + H$	$4.0 * 10^{-6}$	
Ion molecule reactions			
41	$\mathrm{H}^- + \mathrm{He} \rightarrow \mathrm{He} + \mathrm{H} + e$	$8.0 * 10^{-12}$	
42	$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$	$1.4 * 10^{-31}$	
43	$He^+ + H_2 O \rightarrow H^+ + OH + He$	$2.04 * 10^{-10}$	
44	$He^+ + H_2 O \rightarrow H + OH^+ + He$	$2.86 * 10^{-10}$	
45	$\mathrm{He^{\!\!+}} + \mathrm{H_2O} \! \rightarrow \! \mathrm{H_2O^{\!\!+}} + \mathrm{He}$	$6.05 * 10^{-11}$	
46	$\text{HeH}^+ + \text{H} \rightarrow \text{H}_2^+ + \text{He}$	$9.1 * 10^{-10}$	
47	$\text{HeH}^+ + \text{H}_2 \text{O} \rightarrow \text{H}_3 \text{O}^+ + \text{He}$	$4.3 * 10^{-10}$	
48	$\text{He}_2^+ + \text{H}_2 \text{O} \rightarrow \text{HeH}^+ + \text{He} + \text{OH}(A)$	$1.3 * 10^{-10}$	
49	$He_2^+ + H_2 O \rightarrow O^+ + H_2 + 2He$	$2.1 * 10^{-10}$	

 Table A1. (Continued)

(Continued)

No.	Reaction ^a	Rate coefficient ^b
50	$He_2^+ + H_2 O \rightarrow OH^+ + H + 2He$	$2.1 * 10^{-10}$
51	$\operatorname{He}_2^+ + \operatorname{H}_2\operatorname{O} \rightarrow \operatorname{H}^+ + \operatorname{OH} + 2\operatorname{He}$	$2.1 * 10^{-10}$
52	$\text{He}_2^+ + \text{H}_2\text{O} \rightarrow \text{HeH}^+ + \text{OH} + \text{He}$	$2.1 * 10^{-10}$
53	$He_2^+ + H_2 O \rightarrow H_2^+ + O + 2He$	$2.1 * 10^{-10}$
54	$H^+ + H_2 O \rightarrow H_2 O^+ + H$	$6.9 * 10^{-9}$
55	$H^- + H_2 O \rightarrow OH^- + H_2$	$3.8 * 10^{-9}$
56	$H_2^+ + He \rightarrow HeH^+ + H$	$1.3 * 10^{-10}$
57	$H_2^+ + H_2 O \rightarrow H_2 O^+ + H_2$	$3.9 * 10^{-9}$
58	$H_2^+ + H_2 O \rightarrow H_3 O^+ + H$	$3.4 * 10^{-9}$
59	$O^+ + H_2 O \rightarrow H_2 O^+ + O$	$2.6 * 10^{-9}$
60	$\mathrm{O}^- + \mathrm{H}_2 \mathrm{O} \to \mathrm{OH}^- + \mathrm{OH}$	$1.4 * 10^{-9}$
61	$OH^+ + O \rightarrow O_2^+ + H$	$7.1 * 10^{-10}$
62	$OH^+ + H_2 O \rightarrow H_2 O^+ + OH$	$1.5 * 10^{-9}$
63	$OH^+ + H_2 O \rightarrow H_3O^+ + O$	$1.3 * 10^{-9}$
64	$\rm H_2O^+ + OH \rightarrow \rm H_3O^+ + O$	$6.9 * 10^{-10}$
65	$\mathrm{H_2O^+} \ + \ \mathrm{H_2O^+} \ + \ \mathrm{OH}$	$1.85 * 10^{-9}$
66	$O_2^+ + H_2 O + M \rightarrow H_2 O_3^+ + M$	$2.6 * 10^{-28} (T_{\rm g}/300)^{-4}$
67	$H_2O^+ + O_2 \rightarrow H_2O + O_2^+$	$3.3 * 10^{-10}$
68	$H_2O_3^+ + H_2O \rightarrow H_4O_2^+ + O_2$	$1.0 * 10^{-9}$
69	$H_2O_3^+ + H_2O \rightarrow H_3O^+ + OH + O_2$	$3.0 * 10^{-10}$
70	$H_4O_2^+ + H_2O \rightarrow H_5O_2^+ + OH$	$1.4 * 10^{-9}$
71	$H_3O^+ + H_2O + M \rightarrow H_5O_2^+ + M$	$3.2 * 10^{-27} (T_{\rm g}/300)^{-4}$
72	$H_5O_2^+ + H_2O + M \rightarrow H_7O_3^+ + M$	$7.4 * 10^{-27} (T_g/300)^{-7.5}$
73	$H_7O_3^+ + H_2O + M \rightarrow H_9O_4^+ + M$	$2.5 * 10^{-27} (T_g/300)^{-8.1}$
74	$H_9O_4^+ + M \rightarrow H_7O_3^+ + H_2O + M$	$2.0 * 10^{18} T_g^{-8.1} \exp(-8360/T_g)$
75	$H_9O_4^+ + H_2O + M \rightarrow H_{11}O_5^+ + M$	$3.3 * 10^{-28} (T_g/300)^{-14}$
76	$H_{11}O_5^+ + M \rightarrow H_9O_4^+ + H_2O + M$	$6.3 * 10^{30} T_{a}^{-14} \exp(-5750/T_{a})$
77	$H_{11}O_5^+ + H_2O + M \rightarrow H_{13}O_6^+ + M$	$4.0 * 10^{-29} (T_{\rm e}/300)^{-15.3}$
78	$H_{13}O_{6}^{+} + M \rightarrow H_{11}O_{5}^{+} + H_{2}O + M$	$2.62 * 10^{33} T^{-15.3} \exp(-5000/T_{e})$
79	$O^- + H_2O + M \rightarrow H_2O_2^- + M$	$1.3 * 10^{-28}$
80	$OH^- + H_2O + M \rightarrow H_3O_2^- + M$	$2.5 * 10^{-28}$
81	$H_2O_2^- + H_2O \rightarrow H_3O_2^- + OH$	$1.0 * 10^{-11}$
82	$H_3O_2^- + H_2O + M \rightarrow H_5O_3^- + M$	$3.5 * 10^{-28}$
83	$He^+ + OH^- + M \rightarrow OH + He + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$
84	$\text{He}_2^+ + \text{O}^- + M \rightarrow \text{O} + 2\text{He} + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
85	$He_2^+ + OH^- + M \rightarrow OH + 2He + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
86	$He_2^+ + H_2O_2^- + M \rightarrow O + 2He + 2H_2O + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
87	$\operatorname{He}_{2}^{+} + \operatorname{H}_{3}\operatorname{O}_{2}^{-} + M \rightarrow \operatorname{OH} + 2\operatorname{He} + \operatorname{H}_{2}\operatorname{O} + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
88	$\operatorname{He}_{2}^{+} + \operatorname{H}_{5}\operatorname{O}_{3}^{-} + M \rightarrow \operatorname{OH} + 2\operatorname{He} + 2\operatorname{H}_{2}\operatorname{O} + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$
89	$OH^+ + O^- \rightarrow HO_2$	$2.0 * 10^{-7} (T_{\rm g}/300)^{-0.5}$
90	$OH^+ + H_2O_2^- + M \rightarrow O + OH + 2H_2O + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$
91	$OH^+ + H_5O_3^- + M \rightarrow 2OH + 2H_2O + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
92	$H_2O^+ + OH^- + M \rightarrow OH + H_2O^+ M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
93	$H_2O^+ + O^- + M \rightarrow O + H_2O + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
94	$\mathrm{H_2O^+} + \mathrm{H_2O_2^-} + M \rightarrow \mathrm{O} + 2\mathrm{H_2O} + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
95	$\mathrm{H_2O^+} + \mathrm{H_3O_2^-} + M \rightarrow \mathrm{OH} + 2\mathrm{H_2O} + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$
96	$\mathrm{H_2O^+} + \mathrm{H_5O_3^-} + M \rightarrow \mathrm{OH} + 3\mathrm{H_2O} + M$	$2.0 * 10^{-25} (T_g/300)^{-2.5}$

 Table A1. (Continued)

(Continued)

	Table A1. (Continued)				
No.	Reaction ^a	Rate coefficient ^b			
97	$H_2O_3^+ + H_5O_3^- + M \rightarrow OH + 3H_2O + O_2 + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$			
98	$H_9O_4^+ + H_2O_2^- + M \rightarrow OH + 5H_2O + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$			
99	$H_9O_4^+ + H_5O_3^- + M \rightarrow 7H_2O + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$			
100	$H_{11}O_5^+ + H_2O_2^- + M \rightarrow 6H_2O + OH + M$	$2.0 * 10^{-25} (T_{\rm g}/300)^{-2.5}$			
101	$H_1Q_5^+ + H_5Q_2^- + M \rightarrow 8H_2Q + M$	$2.0 * 10^{-25} (T_{\rm c}/300)^{-2.5}$			
102	$H_{12}O_{c}^{+} + H_{2}O_{2}^{-} + M \rightarrow OH + 7H_{2}O + M$	$2.0 * 10^{-25} (T_c/300)^{-2.5}$			
103	$H_{12}O_{0}^{+} + H_{2}O_{2}^{-} + M \rightarrow 9H_{2}O + M$	$2.0 * 10^{-25} (T_c/300)^{-2.5}$			
Neutral rea	ctions	_10 · 10 (1g, 200)			
104	$2\text{He}^* \rightarrow \text{He}_2^+ + e$	$2.03 * 10^{-9} (T_g/300)^{0.5}$			
105	$2\text{He}^* \rightarrow \text{He}^+ + \text{He} + e$	$8.7 * 10^{-10} (T_{\rm s}/300)^{0.5}$			
106	$\text{He}^* + \text{He}_2^* \rightarrow \text{He}^+ + 2\text{He} + e$	$5 * 10^{-10}$			
107	$\operatorname{He}^{*} + \operatorname{He}_{2}^{*} \rightarrow \operatorname{He}_{2}^{+} + \operatorname{He} + e$	$2 * 10^{-9}$			
108	$He^* + H \rightarrow H^+ + He + e$	$1.1 * 10^{-9}$			
109	$\text{He}^* + \text{H}_2 \rightarrow \text{H}_2^+ + \text{He} + e$	$2.9 * 10^{-11}$			
110	$He^* + O \rightarrow O^+ + He + e$	$3.96 * 10^{-10} (T_g/300)^{0.17}$			
111	$\text{He}^* + \text{O}_2 \rightarrow \text{O}_2^+ + \text{He} + e$	$2.54 * 10^{-10} (T_g/300)^{0.5}$			
112	$He^* + OH \rightarrow OH^+ + He^- + e^-$	7.8×10^{-10}			
113	$He^* + H_2O \rightarrow H_2O^+ + He + e$	$6.6 * 10^{-10}$			
114	$He^* + H_2O \rightarrow He + OH^+ + H + e$	$1.5 * 10^{-10}$			
115	$He^* + H_2O \rightarrow He + OH + H^+ + e$	2.6×10^{-10}			
116	$He^* + H_2O \rightarrow HeH^+ + OH + e$	8.5×10^{-12}			
117	$He^* + H_2O_2 \rightarrow He + OH^+ + OH + e$	7.8×10^{-10}			
118	$He_2^* + H_2 \rightarrow H_2^+ + 2He + e$	$2.2 * 10^{-10}$			
119	$He_2^2 + OH \rightarrow OH^+ + 2He + e$	$6 * 10^{-10}$			
120	$He_2^2 + H_2O \rightarrow H_2O^+ + 2He + e$	$6 * 10^{-10}$			
121	$He^* + 2He \rightarrow He^*_2 + He$	$2 * 10^{-34}$			
122	$He_2^* + M \rightarrow 2He + M$	$1.5 * 10^{-15}$			
123	$He + O(^{1}D) \rightarrow O + He$	1.0×10^{-13}			
124	$He + O(D) \rightarrow OH + He$	1.5×10^{-14}			
125	$He + H + O_2 \rightarrow He + HO_2$	$2.0 \times 10^{-32} (T_{-}/300)^{-0.8}$			
126	$He + H + OH \rightarrow He + H_2O$	$1.56 \times 10^{-31} (T_{\star}/300)^{-2.6}$			
127	$He + O + O_2 \rightarrow O_3 + He$	$3.4 \times 10^{-34} (T_c/300)^{-1.2}$			
128	$H + O_3 \rightarrow OH + O_2$	$2.71 \times 10^{-11} (T_2/300)^{-0.75}$			
129	$H + HO_2 \rightarrow O_2 + H_2$	$1.1 \times 10^{-12} T^{0.56} \exp(-346/T)$			
130	$H + HO_2 \rightarrow 2OH$	$2.35 \times 10^{-10} \exp(-373.7/T)$			
131	$O(^{1}D) + O \rightarrow O + O_{2}(b)$	$2.55 \times 10^{-11} \exp(-575.17 \log)$			
132	$O(D) + O_2 \rightarrow O + O_2(b)$ $O + OH \rightarrow H + O_2$	$(0, 10^{-11}T^{-0.186} \text{ cm} (-154/T))$			
133	$O + HO_2 \rightarrow OH + O_2$	$0.0 * 10^{-11} \exp(-154/I_g)$			
134	O(D) + U O = U O + O	$2.9 \times 10^{-10} \exp(200/T_g)$			
135	$O(D) + H_2O_2 \rightarrow H_2O_+O_2$	5.2×10^{-10}			
135	$O(D) + H_2 O \rightarrow 2OH$	$1.62 \times 10^{-10} \exp(64.95/I_g)$			
130	$O(^4D) + H_2 O \rightarrow O + H_2 O$	1.2×10^{-11}			
137	$O_2(b) + H_2 O \rightarrow O_2(a) + H_2 O$	$4.52 * 10^{-12} \exp(89/T_g)$			
130	$20\Pi \rightarrow \Pi_2 0 + 0$	$2.5 * 10^{-15} T_g^{1.14} \exp(-50/T_g)$			
139	$2 \cup H \rightarrow H_2 \cup_2$	$1.5 * 10^{-11} (T_g/300)^{-0.37}$			
140	$OH + HO_2 \rightarrow O_2 + H_2O$	$4.38 \times 10^{-11} \exp(110.9/T_g)$			
141	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$4.53 * 10^{-12} \exp(-288.9/T_g)$			
142	$OH(A) + H_2 O \rightarrow OH + H_2 O$	$4.9 * 10^{-10} (T_g/300)^{0.5}$			
143	$OH(A) + H_2O_2 \rightarrow HO_2 + H_2O$	$2.93 * 10^{-10}$			

 ${}^{a}f(T_{e})$ indicates that the rate coefficients is obtained using the Boltzman equation solver BOLSIG⁺ [34]. b Rate coefficients have the units of cm³ s⁻¹ for two-body reactions and cm⁶ s⁻¹ for three-body reactions; T_{e} has the units eV; T_{g} has the units K.

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