Numerical simulation of the effect of water admixtures on the evolution of a helium/dry air discharge

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Abstract

In this study, a one-dimensional plasma fluid model is used to shed light into the evolution of a He/dry air (500 ppm, 79% N₂ and 21% O₂) dielectric barrier discharge (DBD) under different levels of water admixtures (20 to 2000 ppm). The model considers the analytical chemistry between helium, nitrogen, oxygen and water species and it is verified with experimental results to ensure its correctness. The simulation results show that water admixtures highly affect the discharge characteristics and the dominant ions in the mixture. In particular, it was observed that the increase of water in the mixture up to 600 ppm causes the reduction of the breakdown voltage, while above 600 ppm the breakdown voltage increases. Furthermore, the simulation results show that the most important positive ion in the mixture is H₂O⁺ for 20 - 100 ppm of water admixtures and H₁₁O₅⁺ for 100 - 2000 ppm of admixtures. The most abundant negative charged species is found to be electrons for the range of water admixtures considered in this study. To interpret these results and to get an insight into the discharge evolution the main reaction pathways of ion production are investigated and analyzed.

1. Introduction

Atmospheric pressure plasma sources have received much attention in the last decades, due to low production cost, easy implementation and applications ranging from surface modification [1,2], plasma medicine [3,4], sterilization [5,6] etc. For applications used in temperature-sensitive materials, plasma sources usually operate with inert gases such as argon [7,8], neon [9–11] or helium [12–15], and their electrodes are covered with dielectric layers in order to prevent arcs [16,17]. The inert gases require low power, remain at low temperatures yet are still able to produce a wide range of excited and reactive species.

Helium dielectric barrier discharges (DBD) at atmospheric pressure have shown very promising results in the mentioned applications and particularly in biomedical applications, such as wound healing [18], treatment of cancer [19], bacterial inactivation etc. [6]. In such discharges the presence of water impurities is unavoidable and has been shown to highly affect the plasma chemistry and dynamic evolution [20–33]. In practice, water impurities are due to the operation of the plasma in the ambient humid air and also due to the plasma interaction with biotic surfaces in wet and moist environments. The significant effect of the impurities on the ion composition of a helium atmospheric pressure discharge is presented by Große-Kreul et al. [33]. In particular in this work, the ions composition in the mixture is investigated through mass spectrometry, with and without considering any purification methods. It was observed that without any purification methods the most important ion in the mixture are the water clusters H⁺(H₂O)_n. On the other hand, with purification methods, the ion composition is still affected

by the residual trace gases. Furthermore, the presence of the water vapours into the gas discharge increases the removal efficiency of the volatile organic compounds as shown by Chipier et al [34]. As the discharge evolution is mainly determined by the ions, understanding the effect of the water admixtures on the ion composition is a prerequisite for effective utilization of these devices.

Due to the very complex chemistry behind this type of discharges (dozens of species and hundreds to thousands of reaction channels), mainly zero dimensional global models are used for these simulations. These models are computationally efficient, but have limitations, as they do not consider the spatial evolution (diffusion and convective transport) of the different species in the mixture. The effect of water admixtures on helium discharges through global models has been investigated by several researchers [35–40]. Particularly, Liu et al. [38] investigated the plasma chemistry of a He/H₂O mixture. The main species and dominant reaction pathways over a wide range of water admixtures (0-3000 ppm) were highlighted. The simulation results showed that water charged species dominate over helium charged species for levels of water admixtures above 30 ppm. It was shown that the electronegativity of the discharge increases as the level of water increases in the helium mixture. In addition, Liu et al. [39] investigated the effect of H₂O admixtures on the chemistry of a He+O₂ plasma. It was observed that even at low concentrations of water in the mixture, hydrated ions are abundant. In that study, the ratio between water and oxygen was kept constant at 0.5%. It was found that the ratio H₂O/O₂ of around one provides the highest amount of reactive species in the mixture. The effect of humid air on the plasma composition of a He+O₂ (0.5%) plasma was investigated by Murakami et al. [35–37]. It was found that as the level of humid air increases in the mixture, the electronegativity of the plasma composition increases while the concentration of reactive oxygen species decreases. Recently, through a global model, Schröter et al. [40] showed the importance of the surface reaction probabilities (for the species H, O and OH) and the reactor geometry on the composition of the reactive species in the mixture for a He+H₂O plasma. It was observed that the surface reaction probabilities especially for low mass species (such as H) influence significantly the concentration levels of the reactive species in the mixture. It was also found that as the size of the reactor cross section increases, the densities of H, O and OH increase with H experiencing the most dramatic increase due to its high diffusion and therefore lower surface losses.

As shown by global models, even at low levels of water admixtures in the helium plasma, the hydrated ions become dominant. However, hydration changes the mass of ions and consequently their transport coefficients. Global models cannot capture this effect on the plasma dynamics. In this study, a one-dimensional plasma fluid model is developed for the description of helium DBD in the presence of air admixtures (nitrogen, oxygen and water species). The model considers 56 species and 496 reaction channels and it is verified with experimental results in order to ensure its correctness. Subsequently, the level of dry air (79% N₂ and 21% O₂) is kept constant at 500 ppm (a plausible value for atmospheric pressure discharges without any vacuum equipment) and the effect of water admixtures (20 to 2000 ppm) on the discharge evolution is investigated. The simulation results show that the level of water in the mixture significantly affects the plasma chemistry, the discharge characteristics, and the concentration of ion species in the mixture. Hence, it is very important to understand these effects, in order to be able to optimize helium DBDs for specific applications.

The paper is organized as follows. The experimental setup is described in section 2 and the simulation model with its input parameters in section 3. The comparison of the simulation model with the experimental data and the effect of water admixtures on the evolution of the helium DBD are presented in section 4. Conclusions are presented in section 5.

2. Experimental setup

In order to ensure the correctness of the numerical model, experimental data are compared with simulation results. The experimental setup is shown in Figure 1. It consists of two parallel plate copper electrodes (10.4 cm x 5.0 cm) deposited on a dielectric layer of a glass ($\epsilon_r=8$) with thickness of 1.2 mm each. The distance between the dielectrics is kept constant at 5.0 mm. A high-voltage amplifier (Trek, Inc., model PD07016) driven by an arbitrary waveform generator

(Tektronix, model AFG3022C) is used to operate the discharge. This feeds the upper electrode, through a current limiting resistor (5 kOhms), with a sinusoidal voltage of 2.5 kV amplitude peak to peak and frequency of 10 kHz. The other electrode is grounded. The electrode-dielectrics assembly, forming the discharge gap is placed in the centre of a stainless steel chamber, connected to the vacuum system and the helium flowmeter output [41]. Before conducting the experiments, the stainless steel chamber is heated and pumped down to 10^{-5} torr. The flow of helium (4.6 spectral purity, Linde) is controlled using a mass flow controller (MKS 1179A coupled) and is kept constant at 2.2 l/min (0.7 s residence time inside the gap). The pressure is kept slightly higher than ambient, at 780 torr to reduce the possibility of air intake into the chamber due to leakage.

The applied voltage, measured close to the HV electrode using a high-voltage probe (Tektronix P6015A), and the current measured on the ground line by a current monitor (Pearson 6585), are displayed and stored using a digital oscilloscope (Tektronix TDS 5034B, 350 MHz Bandwidth and 5 GS/s Sample Rate). The average of 50 consecutive acquisitions is considered here. The gas temperature is estimated using the rotational distribution in the emission spectrum of the first negative system of N_2^+ ($(B^2\Sigma_u^+, v_B=0) \rightarrow (X^2\Sigma_g^+, v_X=0)$), by the Boltzmann plot method, under the assumption that the rotational temperature reflects that of the gas molecules inside the plasma [42,43]. Using this method, the gas temperature is estimated to be around 300 K. The experimental setup is shown in Figure 1 and operational parameters are summarized in Table 1.

Figure 1: Detail of experimental DBD configuration, not to scale.

Table 1: Operational parameters of the experimental setup.

Relative permittivity (ϵ_r)	8
Gap between dielectrics (mm)	5.0
Dielectric thickness (mm)	1.2
Electrode area (cm ²)	52
Gas pressure (torr)	780
Gas temperature (K)	300
Voltage _{p-p} (kV)	2.5
Voltage waveform	sinusoidal
Frequency (kHz)	10
Helium gas purity (%)	99.996
Total gas flow rate (l/min)	2.2

3. Simulation model and input parameters

In this study the plasma fluid model (PFM) [44,45] is used for the description of a helium DBD in the presence of nitrogen, oxygen and water species. The model equations and boundary conditions are presented in detail in previous work [46] and for this reason they will only be

briefly mentioned here. For electron and electron energy the continuity equation in the drift diffusion approximation is used as follows:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \vec{\Gamma}_e = S_e \quad (1)$$

$$\frac{\partial n_\varepsilon}{\partial t} + \nabla \cdot \vec{\Gamma}_\varepsilon = -e\vec{\Gamma}_e \cdot \vec{E} + S_\varepsilon \quad (2)$$

where n_e and n_ε is the electron and electron energy density respectively, $\vec{\Gamma}_e$ and $\vec{\Gamma}_\varepsilon$ is the flux of electron and electron energy respectively, S_e is the source term for the production-destruction of electrons, S_ε is the source term that accounts for the energy gain or loss in elastic and inelastic collisions of electrons with the heavy species in the mixture, $\vec{E}$ is the electric field and $\vec{\Gamma}_e \cdot \vec{E}$ accounts for the contribution of Joule heat. For the heavy species (neutral, excited and ion species) the multi-component diffusion equation is used.

$$\rho \frac{\partial}{\partial t} (\omega_i) + \rho (u \cdot \nabla) \omega_i = \nabla \cdot \vec{j}_i + S_i, \quad i = 1, \dots, Q - 1 \quad (3)$$

where ρ is the density of the mixture, ω_i the mass fraction of species i , $\vec{j}_i$ the diffusive flux vector, S_i the source term and Q is the number of heavy species in the mixture. The density of the background gas (helium) is calculated from the equation $\omega = 1 - \sum_{i=1}^{Q-1} \omega_i$. The above equations (1-3) are coupled with Poisson's equation for the description of the electric field. The boundary condition considered for the electrons is that when they reach the dielectric they are adsorbed. On the other hand, secondary electrons are emitted from the dielectric surface, due to the bombardment of the dielectric surface by heavy species. For the heavy species in the mixture, it is considered that when heavy species reach the dielectric surface (due to their random motion and the motion from the electric field) they are converted to their ground state as shown in Table 4. The model considers also the charge deposited on the dielectric surfaces. The plasma chemistry of the model considers 56 species and 496 reaction channels. The species considered in the model and the reactions channels are presented in Table 2 and Table A1 (in Appendix A) respectively. The rate coefficients of the reactions 1-3, 25-38, 63-78, 159-169 and the transport properties of the electrons and electron energy are calculated from the solution of the Boltzmann equation in the two term approximation [44]. This procedure is described in detail in previous work [46]. The mobilities of the species He^+ , He_2^+ , N_2^+ , N_4^+ , O_2^+ , O_4^+ , O^- , O_2^- , O_3^- , H_2O^+ , H_3O^+ , H_5O_2^+ , H_7O_3^+ , H_9O_4^+ , $\text{H}_{11}\text{O}_5^+$, $\text{H}_{13}\text{O}_6^+$, $\text{H}_{15}\text{O}_7^+$, $\text{H}_{17}\text{O}_8^+$, $\text{H}_{19}\text{O}_9^+$, H^- , OH^- , H_3O_2^- , H_5O_3^- , H^+ , H_2^+ , OH^+ , H_4O_2^+ , H_2O_3^+ , HeH^+ are taken from [28,47]. The diffusion coefficients for the species He , O_2 , O_3 , H_2O , H_2 , HO_2 , H , H_2O_2 and H_2O_2^- are calculated from the kinetic theory [48,49] and the diffusion coefficient for the He_m , He_2^* , N , N_2 , $\text{N}_2(\text{v})$, $\text{N}_2(\text{A})$, $\text{N}_2(\text{B})$, $\text{N}_2(\text{a})$, $\text{N}_2(\text{C})$, O , $\text{O}(\text{I}^{\text{S}})$, $\text{O}(\text{I}^{\text{D}})$, $\text{O}_2(\text{v})$, $\text{O}_2(\text{a})$, $\text{O}_2(\text{b})$, OH and $\text{OH}(\text{A})$ are taken from literature [50,28].

The air impurities considered in the model (for comparison purposes with the experiment of section 2) are presented in Table 3, unless otherwise stated. These are due to the air remaining in the discharge chamber after its heating and pumping down to 10^{-5} Torr, and air impurities from the helium bottle. The low level of relative humidity (10%) considered in the air remaining in the discharge chamber, is due to the heating of the discharge chamber. The levels of N_2 , O_2 and H_2O impurities from the helium bottle were lower than the maximum values given by the producer because a brand-new full helium bottle was used and the heavier N_2 , O_2 and H_2O species have a lower probability of being exported from the bottle compared to He . In summary, the heating and pumping of the chamber, the continuous flow and the higher pressure of helium than atmosphere in the chamber ensures a high helium purity in the discharge chamber. The numerical model confirmed this, as a low level of air impurities (as seen in Table 3) was required for matching with the experimental results.

The surface reactions, reaction probabilities, secondary electron emission coefficient (SEEC) and mean energy of secondary electrons (MESE) considered on the dielectric surfaces are given in Table 4. The surface reactions and reaction probabilities are taken from

[51,38,52,28,40]. The SEEC is set to 0.015 because it gives the best agreement with the experimental results. It is noted that such coefficients in simulation models are adjusted [53,54] to match the experimental results.

For all the species in the mixture, a uniform initial density of 10^{13} m^{-3} was set (except for the He which is the background gas, and the densities of N_2 , O_2 and H_2O which are defined based on the level of air content in the mixture (see Table 3). It is noted that different initial densities have also been used in the range of $10^{11} - 10^{14} \text{ m}^{-3}$ yielding similar simulation results.

The equations of the plasma fluid model are solved using the plasma module of the COMSOL multiphysics simulation package [55] on an Intel Xenon E5-2667 V4 3.2 kHz (with 16 core) server. These equations are discretized by the Galerkin finite element method using linear element shape functions. The resulting system is solved using the direct solver PARDISO [56]. For the time integration, the backward Euler method is used. The model considers 554 elements and 26556 degrees of freedom, with the smaller mesh size of $10 \text{ }\mu\text{m}$ located in the region of the plasma and the larger mesh size of $50 \text{ }\mu\text{m}$ located in the dielectrics. Each simulation was run for 12 voltage cycles and it required about two (2) days to be performed.

Table 2: Species included in the model chemistry.

Species		
Electrons		e^-
Helium	Ions	$\text{He}^+, \text{He}_2^+$
	Neutrals	$\text{He}, \text{He}_m, \text{He}_2^*$
Nitrogen	Ions	$\text{N}_2^+, \text{N}_4^+$
	Neutrals	$\text{N}, \text{N}_2, \text{N}_2(v), \text{N}_2(A), \text{N}_2(B), \text{N}_2(a), \text{N}_2(C)$
Oxygen	Ions	$\text{O}_2^+, \text{O}_4^+, \text{O}^-, \text{O}_2^-, \text{O}_3^-$
	Neutrals	$\text{O}, \text{O}_2, \text{O}_3, \text{O}(^1\text{S}), \text{O}(^1\text{D}), \text{O}_2(v), \text{O}_2(a), \text{O}_2(b)$ $\text{H}_2\text{O}^+, \text{H}_2\text{O}_3^+, \text{H}_3\text{O}^+, \text{H}_4\text{O}_2^+, \text{H}_5\text{O}_2^+, \text{H}_7\text{O}_3^+, \text{H}_9\text{O}_4^+,$
Water	Ions	$\text{H}_{11}\text{O}_5^+, \text{H}_{13}\text{O}_6^+, \text{H}_{15}\text{O}_7^+, \text{H}_{17}\text{O}_8^+, \text{H}_{19}\text{O}_9^+, \text{H}_3\text{O}_2^-,$ H_5O_3^-
	Neutrals	H_2O
Others	Ions	$\text{H}^+, \text{H}_2^+, \text{OH}^+, \text{HeH}^+, \text{H}^-, \text{OH}^-, \text{H}_2\text{O}_2^-$
	Neutrals	$\text{H}, \text{H}_2, \text{OH}, \text{OH}(A), \text{HO}_2, \text{H}_2\text{O}_2$

He_m represents $\text{He}(2^3\text{S})$ and $\text{He}(2^1\text{S})$; He_2^* represents $\text{He}_2(a^3\Sigma_u^+)$; $\text{N}_2(v)$ represents the vibrational excited states of $\text{N}_2(v = 1 - 10)$; $\text{N}_2(A)$ represents $\text{N}_2(A^3\Sigma_u^+ (v = 0 - 4))$, $\text{N}_2(A^3\Sigma_u^+ (v = 5 - 9))$ and $\text{N}_2(A^3\Sigma_u^+ (v > 9))$; $\text{N}_2(B)$ represents $\text{N}_2(B^3\Pi_g), \text{N}_2(W^3\Delta_u)$ and $\text{N}_2(B^3\Sigma_u^-)$; $\text{N}_2(a)$ represents $\text{N}_2(a^1\Sigma_u^-), \text{N}_2(a^1\Pi_g)$ and $\text{N}_2(W^1\Delta_u)$; $\text{N}_2(C)$ represents $\text{N}_2(C^3\Pi_u), \text{N}_2(E^3\Sigma_g^+)$ and $\text{N}_2(a^1\Sigma_g^+)$; $\text{O}_2(a)$ represents $\text{O}_2(a^1\Delta_g)$; $\text{O}_2(b)$ represents $\text{O}_2(b^1\Sigma_g^+)$; $\text{O}_2(v)$ represents the vibrational excited states of $\text{O}_2(v = 1 - 4)$.

Table 3: Air impurities considered for the comparison of the simulation model with the experiment results of section 2.

Species	Discharge Chamber (ppm) ^a	Helium Bottle (ppm) ^b	Total (ppm)
N_2	15.8 (79% of air)	10	25.8
O_2	4.2 (21% of air)	1	5.2
H_2O	0.05 (10% relative humidity)	1.5	1.55

^a) Air impurities (20 ppm) remaining in the chamber after heating and pumping down to 10^{-5} Torr.

^b) Air impurities in the helium bottle. The suppliers quote maximum impurity levels in the 99.996% grade helium as being N_2 20 ppm, O_2 5 ppm and H_2O 5 ppm.

Table 4: Surface reactions, reaction probabilities, SEEC and MESE.

No	Surface Reaction ^{a)}	Reaction probability ^{a)}	SEEC	MESE
1	$\text{He}_m + \text{Surface} \rightarrow \text{He}$	1	1.5e-2	5
2	$\text{He}_2^* + \text{Surface} \rightarrow 2\text{He}$	1	1.5e-2	5
3	$\text{He}^+ + \text{Surface} \rightarrow \text{He}$	1	1.5e-2	5
4	$\text{He}_2^+ + \text{Surface} \rightarrow 2\text{He}$	1	1.5e-2	5
5	$\text{N} + \text{Surface} \rightarrow 0.5\text{N}_2$	0.01	0	0
6	$\text{N}_2(A) + \text{Surface} \rightarrow \text{N}_2$	0.5	1.5e-2	1
7	$\text{N}_2(B) + \text{Surface} \rightarrow \text{N}_2$	0.5	1.5e-2	1
8	$\text{N}_2(a) + \text{Surface} \rightarrow \text{N}_2$	0.5	1.5e-2	1
9	$\text{N}_2(C) + \text{Surface} \rightarrow \text{N}_2$	0.5	1.5e-2	1
10	$\text{N}_2^+ + \text{Surface} \rightarrow \text{N}_2$	1	1.5e-2	3
11	$\text{N}_4^+ + \text{Surface} \rightarrow 2\text{N}_2$	1	1.5e-2	3
12	$\text{O} + \text{Surface} \rightarrow 0.5\text{O}_2$	0.02	0	0
13	$\text{O}(^1D) + \text{Surface} \rightarrow \text{O}$	1	0	0
14	$\text{O}(^1S) + \text{Surface} \rightarrow \text{O}$	1	0	0
15	$\text{O}_2(v) + \text{Surface} \rightarrow \text{O}_2$	0.2	0	0
16	$\text{O}_2(a) + \text{Surface} \rightarrow \text{O}_2$	0.0004	0	0
17	$\text{O}_2(b) + \text{Surface} \rightarrow \text{O}_2$	0.02	0	0
18	$\text{O}_3 + \text{Surface} \rightarrow \text{O}_3$	1	0	0
19	$\text{O}^- + \text{Surface} \rightarrow 0.5\text{O}_2$	1	0	0
20	$\text{O}_2^- + \text{Surface} \rightarrow \text{O}_2$	1	0	0
21	$\text{O}_3^- + \text{Surface} \rightarrow \text{O}_3$	1	0	0
22	$\text{O}_2^+ + \text{Surface} \rightarrow \text{O}_2$	1	1.5e-2	3
23	$\text{O}_4^+ + \text{Surface} \rightarrow 2\text{O}_2$	1	1.5e-2	3
24	$\text{H} + \text{Surface} \rightarrow 0.5\text{H}_2$	0.03	0	0
25	$\text{H}^+ + \text{Surface} \rightarrow \text{H}$	1	1.5e-2	3
26	$\text{H}^- + \text{Surface} \rightarrow \text{H}$	1	0	0
27	$\text{H}_2^+ + \text{Surface} \rightarrow \text{H}_2$	1	1.5e-2	3
28	$\text{OH}(a) + \text{Surface} \rightarrow \text{OH}$	1	0	0
29	$\text{OH} + \text{Surface} \rightarrow 0.5\text{H}_2\text{O}_2$	0.03	0	0
30	$\text{OH}^+ + \text{Surface} \rightarrow \text{OH}$	1	1.5e-2	3
31	$\text{OH}^- + \text{Surface} \rightarrow \text{OH}$	1	0	0
32	$\text{HeH}^+ + \text{Surface} \rightarrow \text{He} + \text{H}$	1	1.5e-2	3
33	$\text{H}_2\text{O}^+ + \text{Surface} \rightarrow \text{H}_2\text{O}$	1	1.5e-2	3
34	$\text{H}_2\text{O}_3^+ + \text{Surface} \rightarrow \text{H}_2\text{O} + \text{O}_2$	1	1.5e-2	3
35	$\text{H}_3\text{O}^+ + \text{Surface} \rightarrow \text{H} + \text{H}_2\text{O}$	1	1.5e-2	3
36	$\text{H}_4\text{O}_2^+ + \text{Surface} \rightarrow 2\text{H}_2\text{O}$	1	1.5e-2	3
37	$\text{H}_5\text{O}_2^+ + \text{Surface} \rightarrow \text{H} + 2\text{H}_2\text{O}$	1	1.5e-2	3
38	$\text{H}_7\text{O}_3^+ + \text{Surface} \rightarrow \text{H} + 3\text{H}_2\text{O}$	1	1.5e-2	3
39	$\text{H}_9\text{O}_4^+ + \text{Surface} \rightarrow \text{H} + 4\text{H}_2\text{O}$	1	1.5e-2	3
40	$\text{H}_{11}\text{O}_5^+ + \text{Surface} \rightarrow \text{H} + 5\text{H}_2\text{O}$	1	1.5e-2	3
41	$\text{H}_{13}\text{O}_6^+ + \text{Surface} \rightarrow \text{H} + 6\text{H}_2\text{O}$	1	1.5e-2	3
42	$\text{H}_2\text{O}_2^- + \text{Surface} \rightarrow \text{H}_2\text{O}_2$	1	0	0
43	$\text{H}_3\text{O}_2^- + \text{Surface} \rightarrow \text{OH} + \text{H}_2\text{O}$	1	0	0
44	$\text{H}_5\text{O}_3^- + \text{Surface} \rightarrow \text{OH} + 2\text{H}_2\text{O}$	1	0	0

^a ref [51,38,52,28,40]

4. Results and discussion

4.1. Comparison of the simulation model with the experimental results

In order to ensure the validity of the numerical model, the simulation results are compared with experimental measurements. The comparison is based on the electrical characteristics as taken from the experiment and the numerical model. Figure 2 presents the discharge current and the applied voltage as measured from the experimental configuration presented in section

2 and the simulation model with level of air impurities (31 ppm) as determined in Table 3. The experimental results were obtained for DBD working in continuous He flow at 780 Torr. From Figure 2, it can be observed that the measured voltage presents a collapse during the discharge current. Similar collapse is also observed in other experimental studies [57]. For the simulation, the applied voltage presented in the figure is the input sinusoidal voltage on the upper electrode.

As it can be observed, there is good agreement between the experimental discharge current and simulation results, with an error on the peak value less than 10%. The experimental discharge current consists of a single narrow current pulse, of relatively large peak value (about 60 mA) per half-cycle of the external voltage fact which is attributed to the homogenous mode of DBD, thus the discharge can be treated as one-dimensional. Furthermore, in both cases the discharge current occurs at the same time during the rising and falling part of the applied voltage. The above analysis gives us confidence on the ability of the model to capture the physics behind these kind of discharges and can be used to study the effect of water admixtures on the evolution of He/air discharges.

Figure 2: Comparison between simulation and measured discharge characteristics (current and voltage).

In order to investigate the discharge development, the spatio-temporal evolution of the total ionization rate in logarithmic scale is presented in Figure 3. The polarity of the applied voltage is illustrated in the graph. As it can be seen, during the rising part of the applied voltage, the ionization wave begins from the anode and propagates towards the cathode, which is characteristic of a glow discharge. The maximum of the ionization rate occurs at the peak of the discharge current and close to the cathode. After the breakdown, charges accumulate on the dielectric surface, creating an electric field in the opposite direction to that of the applied voltage. The reduced voltage in the gap causes the ionization rate to reduce as well after breakdown. During the falling part of the applied voltage, the voltage polarity in the gap changes (as can be seen from Figure 3), and the ionization wave propagates in the opposite direction. The maximum of the ionization rate occurs at the peak of the discharge current and close to the cathode, indicating that the discharge exhibits glow characteristics.

Figure 3: Simulation results of (a) the applied voltage and discharge current, and (b) the spatio-temporal evolution of the total ionization rate in logarithmic scale over a voltage cycle.

4.2. Effect of water admixtures on the discharge characteristics of a He/dry air (500 ppm) DBD

In this section, the level of water admixtures is varied in the range of 20-2000 ppm and its effect on the discharge characteristics of a helium/dry air discharge is investigated. The level of dry air in the helium DBD is considered to be 500 ppm (79% N_2 and 21% O_2), as this is a plausible value for atmospheric pressure discharges without any vacuum equipment [37]. In the range of water admixtures considered in this study, the discharge exhibits symmetric characteristics. Figure 4 presents the discharge characteristics (applied voltage, gap voltage and discharge current) for two different levels of water admixtures (50 and 500 ppm). As can be seen, in both cases the discharge characteristics are symmetric, with one current pulse per half voltage cycle, at the same absolute amplitude and shape. After the breakdown, the gap voltage reduces significantly due to the charge accumulation on the dielectric surfaces shielding the electric field of the applied voltage [46]. As the applied voltage increases and just prior to its maximum, there is a second peak of the gap voltage. However, that gap voltage is not sufficient to ignite a second discharge.

Comparing the discharge characteristics for these two cases of water admixtures (50 and 500 ppm), two differences can be observed regarding the discharge current and the gap voltage. The amplitude of the discharge current is higher for the case of 500 ppm water admixture, however, its current pulse width is narrower. On the other hand, the breakdown voltage is lower

for the case of 500 ppm, while, its secondary gap voltage peak is higher. Similar observations have been made in literature [58].

Figure 4: Simulation results of the discharge characteristics (applied voltage, gap voltage and discharge current) for (a) 50 ppm and (b) 500 ppm of water admixtures in a He/dry air (500 ppm) DBD.

In order to further investigate the effect of water admixtures on the discharge characteristics, the breakdown voltage, the amplitude of the discharge current and the second peak of the gap voltage at different levels of water admixtures are presented in Figure 5. As it can be seen, the breakdown voltage reduces as the level of water increases in the mixture (up to ~ 600 ppm). This is due to the enhancement of water-related reactions (such as the Penning ionization reaction, charge transfer reaction, etc.). From the schematic diagram of Figure 8 it can be seen that the ion production is initiated by the increase of He_m and He^+ (this is consistent with our previous work [46]). Although the energy threshold for the production of He_m and He^+ is higher in comparison to the direct ionization of N_2 , O_2 and H_2O , direct ionization is not important for low levels of impurities, as can be seen in Figure 10. For low levels of impurities, the ionization of these species is mainly due to Penning ionization with He_m . The discharge is ignited when the He_m and He^+ reach the necessary values for the production of adequate ions which are able to trigger breakdown. By increasing the concentration of water in the mixture, the reactions associated with water, (i.e. reactions ..., 221, 222, 223, ... 286, 287, 288, ...) also benefit, and as a result a lower concentration of He_m and He^+ is required for ion production. Since the concentration of He_m and He^+ depends on the gap voltage, the reduction in He_m and He^+ will result in a lower breakdown voltage. As the water impurities increase (higher than 600 ppm) the attachment of electrons becomes important, and the breakdown voltage starts increasing.

From Figure 5 it can be observed that the amplitude of the discharge current has a sharp increase for up to 600 ppm of water and at higher levels it starts approaching a constant value. The sharp increase of the discharge current peak is caused by the benefit of H_2O -related reactions that increases the ionization rate and consequently the amplitude of the discharge current. However, above 600 ppm of water, the attachment of electrons becomes important. The two effects balance each other out resulting in a somewhat constant current above 600 ppm.

The second peak of the gap voltage shows a similar behaviour to the discharge current amplitude (see Figure 5). Specifically, it shows a sharp increase for up to 600 ppm water in the mixture, while for higher levels it approaches a constant value. This behaviour can be explained by the surface charge accumulation on the dielectrics during the breakdown. In particular, as the level of water increases in the mixture (up to 600 ppm), the amplitude of the discharge current increases but its pulse width becomes narrower (see Figure 4). Due to the narrower width, the total charge accumulation on the dielectrics and the shielding of the applied voltage decreases (see Figure 6, presenting the surface charge density on the dielectrics at different levels of water admixtures over a voltage cycle). For that reason, the gap voltage increases significantly. However, above 600 ppm of water, the discharge current pulse amplitude, width

and charge accumulation generally remain constant. This results in somewhat constant shielding and therefore, constant second peak of the gap voltage.

Figure 5: Simulation results of the breakdown voltage, second peak of the gap voltage and amplitude of the discharge current at different levels of water in a He/dry air (500 ppm) DBD. The amplitude and frequency of the sinusoidal applied voltage are 2.5 kV peak to peak and 10 kHz respectively.

Figure 6: Simulation results of the surface charge density on the dielectrics at different levels of water admixtures (50, 500 and 1000 ppm) over a voltage cycle. GND refers to the dielectric covering the ground electrode and HV to the dielectric covering the high voltage electrode.

4.3. Effect of water admixtures on the ion composition of a He/dry air (500 ppm) DBD

In Figure 7, the average concentrations of the positive ions during the breakdown are presented, for different levels of water admixtures (20 - 2000 ppm). As can be observed, the dominant positive ion from 20 to 100 ppm of water is H_2O^+ , while from 100 - 2000 ppm it is $\text{H}_{11}\text{O}_5^+$. It is noted that at 2000 ppm of water, the concentrations of $\text{H}_{11}\text{O}_5^+$ and $\text{H}_{13}\text{O}_6^+$ coincide. At this level, the concentrations of $\text{H}_{11}\text{O}_5^+$ and $\text{H}_{13}\text{O}_6^+$ have a negative and positive slope respectively, indicating that $\text{H}_{13}\text{O}_6^+$ will become the dominant ion in the mixture after 2000 ppm.

To analyze the evolution of positive ions concentrations, the most important reaction pathways for ion production are presented in the schematic diagram of Figure 8. It is noted that the simulation results shown that the relative intensities of the different electron sources do not change considerably in time. Furthermore, the analysis of the simulation results shown that Penning ionization processes (associated with He_m) are the most important reactions for ion production.

At low levels of water in the mixture (up to 50 ppm), He_m species are mainly lost in the Penning ionization reactions 52, 59 and 115 (see Figure 10 that presents the most important reactions for electron production) for the production of nitrogen and oxygen positive ions. However, the nitrogen and oxygen ions are quickly converted to H_2O^+ and H_2O_3^+ and for that reason are not the dominant ions, even at these low levels of water in the mixture. As the level of water further increases in the mixture, the amount of He_m lost in Penning ionization reactions with H_2O species increases (reactions 283, 285, 286, 287, 288 and 289, see Figure 10), and particularly through reaction 286. For the above reasons, H_2O^+ is the dominant ion in the range of 20 - 100 ppm. The concentration of H_2O^+ (OH^+ , H^+ and HeH^+ , the other ions produced through Penning ionization reactions of He_m with water species), presents a maximum and then decreases as the level of water admixtures increases. This occurs due to the hydration of these species or their conversion to higher order cluster ions. In particular, above ~ 90 ppm of water in the mixture, OH^+ and H^+ are quickly converted to H_2O^+ . Similarly, H_2O^+ and HeH^+ , after 60 and 300 ppm respectively are converted to H_3O^+ . However, the concentration of H_3O^+ does not become the dominant one at any level of water in the mixture, because it is immediately converted to H_5O_2^+ . Similar behavior is also observed for H_5O_2^+ and H_7O_3^+ . In particular, the H_5O_2^+ is immediately converted to H_7O_3^+ which it then immediately converted to H_9O_4^+ . As the level of water increases in the mixture (100-2000 ppm), the most dominant ion becomes $\text{H}_{11}\text{O}_5^+$ due to the fast hydration of the lightest water clusters. Similar results were also observed in the global model [38,27].

Figure 7: Average concentrations of the positive ions during the breakdown, for different levels of water admixtures in the helium/dry air (500 ppm) discharge. The amplitude and frequency of the sinusoidal applied voltage are 2.5 kV peak to peak and 10 kHz respectively.

Figure 8: Schematic diagram of the most important reaction pathways for positive ion production.

The effect of water admixtures on the concentration of the negative charge species is presented in Figure 9. As it can be seen, electrons are the most important negative species in the mixture for the range of water admixtures considered in this study. The concentration of negative ions is at least one order of magnitude lower. Furthermore, it can be observed that the concentration of the negative ions H_5O_3^- , H_2O_2^- , OH^- , H_3O_2^- and H^- exhibit an upward trend as the level of water increases in the mixture, that shows an increase of the electronegative character of the plasma. On the other hand, the oxygen negative ions (O^- and O_3^-) show a downward trend as the level of water increases in the mixture, similar to the results presented in [37], while the concentration of O_2^- remains generally constant for the different levels of water in the mixture.

Figure 9: Average concentrations of the electrons and the negative ions during the breakdown, for different levels of water admixtures in the helium/dry air (500 ppm) discharge. The amplitude and frequency of the sinusoidal applied voltage are 2.5 kV peak to peak and 10 kHz respectively.

As electrons are the most abundant in the mixture, it is important to investigate the reaction pathways behind their production and destruction. The average reaction rates for electron production during the breakdown are presented in Figure 10. As it can be seen, at low levels of water in the mixture (up to 50 ppm), the most important reactions for electron production are the Penning ionization of He_m with N_2 and O_2 (reactions 52, 59 and 115), similar to prior work [46]. However, as the level of water increases in the mixture (>50 ppm), the loss of He_m in Penning ionization reactions with H_2O species increases and hence reaction 286 (H_2O^+ production) becomes the dominant reaction for electron production. The other Penning ionization reactions of He_m with H_2O (for the production of OH^+ , H^+ and HeH^+ , reactions 287, 288 and 289) have a similar trend to reaction 286 but to a lesser extent. The increase of loss of He_m species with water species (through Penning reactions) reduces the amount lost with the rest ground state species in the mixture (such as He , N_2 and O_2). For that reason, the Penning ionization reactions 52, 59 and 115 (associated with N_2 and O_2 species) decrease as the level of water increases in the mixture. Similar behavior occurs for reactions 53 and 117, as He_2^* is mainly produced through He_m species and He species.

Regarding the direct ionization processes, it can be seen that the direct ionization of He , N_2 and O_2 (reactions 3, 38 and 78 respectively) present an almost constant value for the different levels of water in the mixture. Furthermore, these reactions are less important in comparison to the Penning ionization reactions (associated with He_m species). On the other hand, as expected, the direct ionization of H_2O (reaction 167) increases as the level of water increases. Finally, it is noted that only the detachment collisional reaction 188 approaches the contribution of reaction 286 (most important Penning ionization reaction of electron production) at high levels of water in the mixture (> 1500 ppm). Similar trend is also present for the detachment collisional reaction 189 but to a lesser extent.

Figure 10: Simulation results of the average reaction rates of electron production during the breakdown, for different levels of water admixtures in the helium/dry air (500 ppm) discharge. The amplitude and frequency of the sinusoidal applied voltage are 2.5 kV peak to peak and 10 kHz respectively.

The average reaction rates for electron destruction during the breakdown are presented in Figure 11. The most important reaction for electron destruction up to 70 ppm of water admixtures, is the dissociative recombination of electrons with H_9O_4^+ positive ions (reaction 182), while from 70 and up to 1500 the dissociative recombination with $\text{H}_{11}\text{O}_5^+$ (reaction 183). As the level of water increases more than 1500 ppm, it can be observed that the dissociative attachment of electrons with H_2O molecules (reaction 160, for the production of H^-) becomes the dominant reaction for electron destruction. It is noted that H^- is quickly converted to OH^- (through reaction 211) which is then converted to H_3O_2^- (through reaction 240) and which is finally converted to H_5O_3^- (through the reaction 242). For that reason for high levels of water in the mixture, H_5O_3^- is the next most important negative species in the mixture after electrons (see Figure 9).

Figure 11: Simulation results of the average reaction rates of electron destruction during the breakdown, for different levels of water admixtures in the helium/dry air (500 ppm) discharge.

The amplitude and frequency of the sinusoidal applied voltage are 2.5 kV peak to peak and 10 kHz respectively.

5. Conclusions

In this study a one-dimensional plasma fluid model is used to investigate the effect of water admixtures on the evolution of a helium/dry air (500 ppm, 79% N₂ and 21% O₂) DBD. The level of water in the mixture is varied in the range of 20-2000 ppm. The simulation results show that water admixtures highly affect the discharge characteristics and the dominant ions in the mixture. In particular, the increase of water in the mixture benefits the H₂O-related reactions. This causes the discharge current peak to increase, and the discharge to ignite at lower voltages (up to 600 ppm of water). However, the further increase of water (above 600 ppm) enhances the attachment of electrons with water molecules which causes the discharge to ignite at higher voltages. Despite the higher breakdown voltage, the discharge current peak remains almost constant, due to the high attachment of electrons with water molecules. Furthermore, the increase of water in the mixture causes the discharge current pulse width to become narrower. This reduces the total charge accumulation on the dielectrics and consequently the shielding of the applied voltage.

The simulation results show that the dominant ion for water admixtures in the range of 20 to 100 ppm is H₂O⁺. By further increasing the water in the mixture, the water ion clusters are quickly converted to heavier water ion clusters. For that reason, from 100 ppm of water and up to 2000 ppm, the H₁₁O₅⁺ is the most abundant ion in the mixture. The processes behind ion production and interaction are summarized in a schematic diagram. This diagram provides a simple yet complete picture for ion evolution and the dependence on the level of admixtures in the He discharge. Finally, from 20 to 2000 ppm of water admixtures, the most important negative charge species are found to be electrons. It is also observed that as the level of water increases in the mixture the electronegative character of the plasma increases.

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Appendix A

Table A1: Rate coefficients for helium, nitrogen, oxygen and water reactions.

No.	Reaction equation ^{a)}	Rate constant ^{b)}	Threshold (eV)	Ref
1	$e^- + \text{He} \rightarrow e^- + \text{He}$	$f(\varepsilon)$	0	[59]
2	$e^- + \text{He} \rightarrow e^- + \text{He}_m$	$f(\varepsilon)$	19.82	[59]
3	$e^- + \text{He} \rightarrow 2e^- + \text{He}^+$	$f(\varepsilon)$	24.58	[59]
4	$e^- + \text{He}_m \rightarrow 2e^- + \text{He}^+$	$2.254 \times 10^{-13} T_e^{-0.1241} e^{-5.725/T_e}$	4.78	[60]
5	$e^- + \text{He}_m \rightarrow e^- + \text{He}$	2.9×10^{-15}	-19.82	[61,62]
6	$e^- + \text{He}_2^+ \rightarrow e^- + 2\text{He}$	3.8×10^{-15}	-17.9	[61]
7	$2e^- + \text{He}^+ \rightarrow e^- + \text{He}_m$	6×10^{-32}	-4.78	[63]
8	$2e^- + \text{He}_2^+ \rightarrow \text{He}_m + \text{He} + e^-$	2.8×10^{-32}	0	[61]
9	$e^- + \text{He} + \text{He}_2^+ \rightarrow \text{He}_m + 2\text{He}$	3.5×10^{-39}	0	[61]
10	$2e^- + \text{He}_2^+ \rightarrow \text{He}_2^+ + e^-$	1.2×10^{-33}	0	[61]
11	$e^- + \text{He} + \text{He}_2^+ \rightarrow \text{He}_2 + \text{He}$	1.5×10^{-39}	0	[61]
12	$\text{He}_m + \text{He}_m \rightarrow \text{He}_2^+ + e^-$	$2.03 \times 10^{-15} (T_g/300)^{0.5}$	-18.2	[64]
13	$\text{He}_m + \text{He}_m \rightarrow \text{He}^+ + \text{He} + e^-$	$8.7 \times 10^{-16} (T_g/300)^{0.5}$	-15.8	[64]
14	$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$	$1.4 \times 10^{-43} (T_g/300)^{-0.6}$	0	[64]
15	$\text{He}_m + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$	2×10^{-46}	0	[64]
16	$\text{He}_m + \text{He}_2^+ \rightarrow \text{He}^+ + 2\text{He} + e^-$	$5 \times 10^{-16} (T_g/300)^{0.5}$	-13.5	[61]

17	$\text{He}_m + \text{He}_2^* \rightarrow \text{He}_2^+ + \text{He} + \text{e}^-$	$2 \times 10^{-15} (T_g/300)^{0.5}$	-15.9	[61]
18	$\text{He}_2^* + \text{He}_2^* \rightarrow \text{He}^+ + 3\text{He} + \text{e}^-$	$3 \times 10^{-16} (T_g/300)^{0.5}$	-11.3	[61]
19	$\text{He}_2^* + \text{He}_2^* \rightarrow \text{He}_2^+ + 2\text{He} + \text{e}^-$	$1.2 \times 10^{-15} (T_g/300)^{0.5}$	-13.7	[61]
20	$\text{He}_2^* + \text{He} \rightarrow 2\text{He} + \text{He}$	1.5×10^{-21}	0	[65,66]
21	$\text{e}^- + \text{He} + \text{He}^+ \rightarrow \text{He}_m + \text{He}$	$7.4 \times 10^{-47} (T_e/T_g)^{-2}$	0	[63]
22	$\text{e}^- + \text{He}_2^+ \rightarrow \text{He} + \text{He}_m$	$7.12 \times 10^{-21} (T_e/T_g)^{-1.5}$	0	[65]
23	$\text{He}_m + 2\text{He} \rightarrow 3\text{He}$	2×10^{-46}	0	[65]
24	$\text{e}^- + \text{He}_2^* \rightarrow \text{He}_2^+ + 2\text{e}^-$	$9.75 \times 10^{-16} T_e^{0.71} e^{-3.4/T_e}$	3.4	[64]
			0.3, 0.6, 0.9,	
25	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2 (v = 1 \text{ to } 10)$	$f(\varepsilon)$	1.1, 1.4, 1.7, 2, 2.2, 2.5,	[67]
			2.7	
26	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{A})$	$f(\varepsilon)$	6.2	[67]
27	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{A})$	$f(\varepsilon)$	7	[67]
28	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{B})$	$f(\varepsilon)$	7.4	[67]
29	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{B})$	$f(\varepsilon)$	7.4	[67]
30	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{A})$	$f(\varepsilon)$	7.8	[67]
31	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{B})$	$f(\varepsilon)$	8.2	[67]
32	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{a})$	$f(\varepsilon)$	8.4	[67]
33	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{a})$	$f(\varepsilon)$	8.6	[67]
34	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{a})$	$f(\varepsilon)$	8.9	[67]
35	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{C})$	$f(\varepsilon)$	11	[67]
36	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{C})$	$f(\varepsilon)$	11.9	[67]
37	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2(\text{C})$	$f(\varepsilon)$	12.3	[67]
38	$\text{e}^- + \text{N}_2 \rightarrow 2\text{e}^- + \text{N}_2^+$	$f(\varepsilon)$	15.5	[67]
39	$\text{e}^- + \text{N}_2 \rightarrow \text{e}^- + \text{N} + \text{N}$	$1 \times 10^{-14} T_e^{0.5} e^{-16/T_e}$	9.757	[68]
40	$\text{e}^- + \text{N}_4^+ \rightarrow 2\text{N}_2$	3×10^{-13}	0	[69]
41	$2\text{e}^- + \text{N}_4^+ \rightarrow 2\text{N}_2 + \text{e}^-$	3.17×10^{-42}	0	[60]
42	$2\text{e}^- + \text{N}_2^+ \rightarrow \text{e}^- + \text{N}_2$	3.17×10^{-42}	0	[70]
43	$\text{e}^- + \text{N}_2^+ \rightarrow 2\text{N}$	$2.54 \times 10^{-12} T_e^{-0.5}$	0	[50]
44	$\text{N}_2(\text{A}) + \text{N}_2(\text{a}) \rightarrow \text{e}^- + \text{N}_4^+$	5×10^{-17}	0	[71]
45	$\text{N}_2(\text{a}) + \text{N}_2(\text{a}) \rightarrow \text{e}^- + \text{N}_4^+$	2×10^{-16}	0	[71]
46	$\text{N}_2(\text{B}) + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2(\text{A})$	3×10^{-17}	0	[72]
47	$\text{N}_2(\text{C}) + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2(\text{a})$	1×10^{-17}	0	[72]
48	$\text{N}_2(\text{a}) \rightarrow \text{N}_2 + h\nu (117 \text{ nm})$	1×10^2	0	[73]
49	$\text{N}_2(\text{A}) \rightarrow \text{N}_2 + h\nu (293 \text{ nm})$	0.5	0	[73]
50	$\text{N}_2(\text{B}) \rightarrow \text{N}_2(\text{A}) + h\nu (1045 \text{ nm})$	1.34×10^5	0	[73]
51	$\text{N}_2(\text{C}) \rightarrow \text{N}_2(\text{B}) + h\nu (336 \text{ nm})$	2.45×10^7	0	[73]
52	$\text{He}_m + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2^+ + \text{He}$	5×10^{-17}	0	[60]
53	$\text{He}_2^* + \text{N}_2 \rightarrow \text{e}^- + \text{N}_2^+ + 2\text{He}$	5×10^{-17}	0	[60]
54	$\text{He}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{He}$	1.2×10^{-15}	0	[74]
55	$\text{He}_2^+ + \text{N}_2 \rightarrow \text{N}_2^+ + 2\text{He}$	1.1×10^{-15}	0	[74]
56	$\text{N}_2^+ + \text{He} + \text{N}_2 \rightarrow \text{N}_4^+ + \text{He}$	$8.9 \times 10^{-42} (T_g/300)^{-1.54}$	0	[74]
57	$\text{He}^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_2^+ + 2\text{He}$	1.1×10^{-41}	0	[74]
58	$\text{He}_2^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_2^+ + 3\text{He}$	1.6×10^{-41}	0	[74]
59	$\text{He}_m + \text{N}_2 + \text{He} \rightarrow \text{N}_2^+ + 2\text{He} + \text{e}^-$	3.3×10^{-42}	0	[75]
60	$\text{He}_2^* + \text{N}_2 \rightarrow 2\text{He} + \text{N}_2$	1.5×10^{-21}	0	[35]
61	$\text{N}_2^+ + 2\text{N}_2 \rightarrow \text{N}_4^+ + \text{N}_2$	5×10^{-41}	0	[76]
62	$\text{N}_4^+ + \text{N}_2 \rightarrow \text{N}_2^+ + 2\text{N}_2$	2.5×10^{-21}	0	[76]
63	$\text{e}^- + \text{O}_2 \rightarrow \text{e}^- + \text{O}_2 (v = 1 \text{ to } 4)$	$f(\varepsilon)$	0.19, 0.38, 0.6, 0.8	[67]
64	$\text{e}^- + \text{O}_2 \rightarrow \text{O} + \text{O}^-$	$f(\varepsilon)$	0	[67]
65	$\text{e}^- + \text{O}_2(b) \rightarrow \text{O} + \text{O}^-$	$f(\varepsilon)$	0	[59]
66	$\text{e}^- + \text{O}_2(a) \rightarrow \text{O} + \text{O}^-$	$f(\varepsilon)$	0	[59]
67	$\text{e}^- + \text{O}_2(v) \rightarrow \text{O} + \text{O}^-$	$f(\varepsilon)$	0	[77]
68	$\text{e}^- + \text{O}_2 \rightarrow \text{e}^- + \text{O}_2(a)$	$f(\varepsilon)$	0.977	[67]
69	$\text{e}^- + \text{O}_2(a) \rightarrow \text{e}^- + \text{O}_2$	$f(\varepsilon)$	-0.977	b)

70	$e^- + O_2 \rightarrow e^- + O_2(b)$	$f(\varepsilon)$	1.627	[67]
71	$e^- + O \rightarrow e^- + O(^1D)$	$f(\varepsilon)$	1.968	[78]
72	$e^- + O \rightarrow e^- + O(^1S)$	$f(\varepsilon)$	4.192	[59]
73	$e^- + O_2 \rightarrow e^- + 2O$	$f(\varepsilon)$	6	[67]
74	$e^- + O_2(b) \rightarrow e^- + O(^1D) + O$	$f(\varepsilon)$	6.77	[77]
75	$e^- + O_2 \rightarrow e^- + O + O(^1D)$	$f(\varepsilon)$	8.4	[67]
76	$e^- + O_2 \rightarrow e^- + O + O(^1S)$	$f(\varepsilon)$	9.97	[67]
77	$e^- + O_2(a) \rightarrow 2e^- + O_2^+$	$f(\varepsilon)$	11.1	[77]
78	$e^- + O_2 \rightarrow 2e^- + O_2^+$	$f(\varepsilon)$	12.1	[67]
79	$e^- + O_3 \rightarrow e^- + O_2 + O$	5.88×10^{-15}	0	[79]
80	$e^- + O_2^+ \rightarrow 2O$	$1.2 \times 10^{-14} T_e^{-0.7}$	0	[80]
81	$e^- + O + O_2 \rightarrow O^- + O_2$	1×10^{-43}	0	[81]
82	$e^- + O_2 + O_2 \rightarrow O_2^- + O_2$	$2.26 \times 10^{-42} (T_g/300)^{-0.5}$	0	[82]
83	$e^- + O_2^+ + O_2 \rightarrow 2O_2$	$2.49 \times 10^{-41} (T_e)^{-1.5}$	0	[81]
84	$2e^- + O_2^+ \rightarrow e^- + O_2$	$7.18 \times 10^{-39} (T_e)^{-4.5}$	0	[71]
85	$O^- + O_2 + O_2 \rightarrow O_3^- + O_2$	$1.1 \times 10^{-42} (T_g/300)^{-1}$	0	[51]
86	$O_2^- + O \rightarrow O^- + O_2$	$1.5 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
87	$O_2^- + O_3 \rightarrow O_3^- + O_2$	$6 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
88	$O_2^+ + O_3^- + O_2 \rightarrow O_2 + O_3 + O_2$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
89	$O_4^+ + O^- + O_2 \rightarrow 2O_2 + O + O_2$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
90	$O_4^+ + O_2^- + O_2 \rightarrow 3O_2 + O_2$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
91	$O_4^+ + O_3^- + O_2 \rightarrow 2O_2 + O_3 + O_2$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
92	$O + O^- \rightarrow e^- + O_2$	$2 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
93	$O^- + O_2(b) \rightarrow e^- + O_2 + O$	$6.9 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
94	$O^- + O_2(a) \rightarrow e^- + O_3$	$3 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
95	$O_3^- + O \rightarrow O_2^- + O_2$	$2.5 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
96	$O_4^+ + O \rightarrow O_2^+ + O_3$	3×10^{-16}	0	[71]
97	$O_4^+ + O_2 \rightarrow O_2^+ + 2O_2$	$3.3 \times 10^{-12} (T_g/300)^{-4} e^{(-5030/T_g)}$	0	[71]
98	$O(^1D) + O_2 \rightarrow O_2 + O$	$4.8 \times 10^{-18} e^{(67/T_g)}$	0	[83]
99	$O(^1D) + O_2 \rightarrow O_2(a) + O$	$1.6 \times 10^{-18} e^{(67/T_g)}$	0	[83]
100	$O(^1D) + O_2 \rightarrow O_2(b) + O$	$2.56 \times 10^{-17} e^{(67/T_g)}$	0	[83]
101	$O(^1S) + O_2(a) \rightarrow O + O_2$	1.1×10^{-16}	0	[80]
102	$O_2(b) + O_3 \rightarrow 2O_2 + O$	$7.33 \times 10^{-18} (T_g/300)^{0.5}$	0	[80]
103	$e^- + O_4^+ \rightarrow 2O_2$	$2.25 \times 10^{-13} T_e^{-0.5}$	0	[71]
104	$e^- + O + He \rightarrow O^- + He$	1×10^{-43}	0	[51]
105	$e^- + O_3 + He \rightarrow O_3^- + He$	1×10^{-43}	0	[51]
106	$He_2^* + O_2 \rightarrow 2He + O_2$	1.5×10^{-21}	0	[65]
107	$O_2(v) + M \rightarrow O_2 + M$	$1 \times 10^{-20} (T_g/300)^{0.5}$	0	[80]
108	$O^- + O_2 + He \rightarrow O_3^- + He$	$1.1 \times 10^{-42} (T_g/300)^{-1}$	0	[51]
109	$O_2^+ + O_3^- + He \rightarrow O_2 + O_3 + He$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
110	$O_4^+ + O^- + He \rightarrow 2O_2 + O + He$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
111	$O_4^+ + O_2^- + He \rightarrow 3O_2 + He$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
112	$O_4^+ + O_3^- + He \rightarrow 2O_2 + O_3 + He$	$2 \times 10^{-37} (T_g/300)^{-2.5}$	0	[51,71]
113	$e^- + O_2 + He \rightarrow He + O_2^-$	1×10^{-43}	0	[84]
114	$O_2^+ + O_2 + He \rightarrow O_4^+ + He$	$5.8 \times 10^{-43} (T_g/300)^{-3.1}$	0	[85]
115	$He_m + O_2 \rightarrow O_2^+ + He + e^-$	$2.54 \times 10^{-16} (T_g/300)^{0.5}$	0	[80]
116	$He + He_m + O_2 \rightarrow O_2^+ + 2He + e^-$	1.6×10^{-43}	0	[86]
117	$He_2^* + O_2 \rightarrow O_2^+ + 2He + e^-$	$1 \times 10^{-16} (T_g/300)^{0.5}$	0	[87]
118	$O_2 + O + He \rightarrow O_3 + He$	$1.1 \times 10^{-46} e^{(510/T_g)}$	0	[84]

119	$\text{He}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{He}$	$1 \times 10^{-15}(T_g/300)^{0.5}$	0	[88]
120	$\text{O}(^1D) + \text{He} \rightarrow \text{O} + \text{He}$	1×10^{-19}	0	[80]
121	$\text{O}_2^+ + \text{O}^- + \text{M} \rightarrow \text{O}_2 + \text{O} + \text{M}$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
122	$\text{O}_2^+ + \text{O}_2^- + \text{M} \rightarrow 2\text{O}_2 + \text{M}$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
123	$\text{O}_2^+ + \text{O}^- + \text{N}_2 \rightarrow \text{O}_3 + \text{N}_2$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
124	$\text{O}_2^+ + \text{O}_3^- + \text{N}_2 \rightarrow \text{O}_2 + \text{O}_3 + \text{N}_2$	$1 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
125	$\text{O}_4^+ + \text{O}^- + \text{N}_2 \rightarrow 2\text{O}_2 + \text{O} + \text{N}_2$	$1 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
126	$\text{O}_4^+ + \text{O}_2^- + \text{N}_2 \rightarrow 3\text{O}_2 + \text{N}_2$	$1 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
127	$\text{O}_4^+ + \text{O}_3^- + \text{N}_2 \rightarrow 2\text{O}_2 + \text{O}_3 + \text{N}_2$	$1 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
128	$\text{N}_2^+ + \text{O}^- + \text{O}_2 \rightarrow \text{N}_2 + \text{O} + \text{O}_2$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
129	$\text{N}_2^+ + \text{O}^- + \text{N}_2 \rightarrow \text{N}_2 + \text{O} + \text{N}_2$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
130	$\text{N}_2^+ + \text{O}_2^- + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2 + \text{O}_2$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
131	$\text{N}_2^+ + \text{O}_2^- + \text{N}_2 \rightarrow \text{N}_2 + \text{O}_2 + \text{N}_2$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,35]
132	$\text{N}_2^+ + \text{O}_2 + \text{e}^- \rightarrow \text{O}_2 + \text{N}_2$	$6 \times 10^{-39}(T_e/T_g)^{-1.5}$	0	[35]
133	$\text{O}_2^+ + \text{N}_2 + \text{e}^- \rightarrow \text{O}_2 + \text{N}_2$	$6 \times 10^{-39}(T_e/T_g)^{-1.5}$	0	[35]
134	$\text{O}_2 + \text{N} + \text{N} \rightarrow \text{O}_2 + \text{N}_2$	3.9×10^{-45}	0	[35]
135	$\text{O} + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_3 + \text{N}_2$	$1.1 \times 10^{-46} \exp(510/T_g)$	0	[35]
136	$\text{O} + \text{O} + \text{N}_2 \rightarrow \text{O}_2 + \text{N}_2$	$6.49 \times 10^{-47} \exp(1039/T_g)$	0	[35]
137	$\text{O} + \text{O} + \text{N} \rightarrow \text{O}_2 + \text{N}$	$3.2 \times 10^{-45}(T_g/300)^{-0.41}$	0	[35]
138	$\text{O}_3 + \text{N}_2 \rightarrow \text{O} + \text{O}_2 + \text{N}_2$	$1.6 \times 10^{-15} \exp(-11400/T_g)$	0	[35]
139	$\text{O}(^1S) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	5×10^{-23}	0	[35]
140	$\text{O}(^1D) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	$1.8 \times 10^{-17} \exp(107/T_g)$	0	[35]
141	$\text{N}_4^+ + \text{O}(^1D) \rightarrow \text{O} + \text{N}_2 + \text{N}_2^+$	1×10^{-16}	0	[35]
142	$\text{N}_4^+ + \text{O}_2 \rightarrow \text{O}_2 + \text{N}_2 + \text{N}_2^+$	2.5×10^{-16}	0	[35]
143	$\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2^+$	$1.04 \times 10^{-15} T_g^{-0.5}$	0	[89]
144	$\text{N}_4^+ + \text{O}_2 \rightarrow 2\text{N}_2 + \text{O}_2^+$	4×10^{-16}	0	[90]
145	$\text{O}_4^+ + \text{N}_2 \rightarrow \text{O}_2 + \text{N}_2 + \text{O}_2^+$	$1 \times 10^{-11}(T_g/300)^{-4.2} \exp(-5400/T_g)$	0	[35]
146	$\text{O}^- + \text{O}_2 + \text{N}_2 \rightarrow \text{N}_2 + \text{O}_3^-$	$1 \times 10^{-42}(T_g/300)^{-1}$	0	[71]
147	$\text{e}^- + \text{O}_2 + \text{N}_2 \rightarrow \text{N}_2 + \text{O}_2^-$	$1.24 \times 10^{-43}(T_g/300)^{-0.5}$	0	[51]
148	$\text{e}^- + \text{O} + \text{N}_2 \rightarrow \text{N}_2 + \text{O}^-$	1×10^{-43}	0	[51]
149	$\text{O}_2^- + \text{N}_2(\text{A}) \rightarrow \text{e}^- + \text{O}_2 + \text{N}_2$	2.1×10^{-15}	0	[72]
150	$\text{O}_2^- + \text{N}_2(\text{B}) \rightarrow \text{e}^- + \text{O}_2 + \text{N}_2$	2.5×10^{-15}	0	[71]
151	$\text{O}^- + \text{N}_2(\text{A}) \rightarrow \text{e}^- + \text{O} + \text{N}_2$	2.2×10^{-15}	0	[72]
152	$\text{O}^- + \text{N}_2(\text{B}) \rightarrow \text{e}^- + \text{O} + \text{N}_2$	1.9×10^{-15}	0	[71]
153	$\text{N}_2(\text{A}) + \text{O}_2 \rightarrow 2\text{O} + \text{N}_2$	1.7×10^{-18}	0	[72]
154	$\text{N}_2(\text{A}) + \text{O}_2 \rightarrow \text{O}_2(\alpha) + \text{N}_2$	7.5×10^{-19}	0	[72]
155	$\text{N}_2(\text{A}) + \text{O} \rightarrow \text{O}(^1S) + \text{N}_2$	2.3×10^{-17}	0	[72]
156	$\text{N}_2(\text{B}) + \text{O}_2 \rightarrow 2\text{O} + \text{N}_2$	1.1×10^{-16}	0	[72]
157	$\text{N}_2(\text{a}) + \text{O}_2 \rightarrow 2\text{O} + \text{N}_2$	2.8×10^{-17}	0	[72]
158	$\text{N}_2(\text{C}) + \text{O}_2 \rightarrow \text{O} + \text{O}(^1S) + \text{N}_2$	3×10^{-16}	0	[72]
159	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H}_2\text{O}$	$f(\varepsilon)$	0	[59]
160	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^-$	$f(\varepsilon)$	0	[59]
161	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}^-$	$f(\varepsilon)$	0	[59]
162	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^-$	$f(\varepsilon)$	0	[59]
163	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H} + \text{OH}$	$f(\varepsilon)$	7	[59]
164	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H}_2 + \text{O}(^1D)$	$f(\varepsilon)$	7.4	[91]
165	$\text{e}^- + \text{H}_2 \rightarrow \text{e}^- + 2\text{H}$	$f(\varepsilon)$	8.9	[92]
166	$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H} + \text{OH}(\text{A})$	$f(\varepsilon)$	9	[92]
167	$\text{e}^- + \text{H}_2\text{O} \rightarrow 2\text{e}^- + \text{H}_2\text{O}^+$	$f(\varepsilon)$	12.61	[59]
168	$\text{e}^- + \text{H} \rightarrow 2\text{e}^- + \text{H}^+$	$f(\varepsilon)$	13.6	[67]
169	$\text{e}^- + \text{H}_2 \rightarrow 2\text{e}^- + \text{H}_2^+$	$f(\varepsilon)$	15.4	[67]

170	$e^- + OH \rightarrow e^- + O + H$	$2.08 \times 10^{-13} T_e^{-0.76} \exp(-6.9/T_e)$	6.9	[93]
171	$e^- + OH \rightarrow 2e^- + OH^+$	$2 \times 10^{-16} T_e^{1.78} \exp(-13.8/T_e)$	13.8	[93]
172	$e^- + HO_2 \rightarrow e^- + O_2 + H$	3.1×10^{-15}	0	[79]
173	$e^- + H_2O_2 \rightarrow e^- + 2OH$	2.36×10^{-15}	0	[79]
174	$e^- + H_2O_2 \rightarrow e^- + HO_2 + H$	3.1×10^{-17}	0	[79]
175	$e^- + OH + He \rightarrow He + OH^-$	3×10^{-43}	0	[94]
176	$e^- + O_2 + H_2O \rightarrow O_2^- + H_2O$	1.4×10^{-41}	0	[81]
177	$e^- + H_2O_2 \rightarrow H_2O + O^-$	$1.57 \times 10^{-16} T_e^{-0.55}$	0	[95]
178	$e^- + H_2O_2 \rightarrow OH + OH^-$	$2.7 \times 10^{-16} T_e^{-0.5}$	0	[95]
179	$e^- + H_5O_2^+ \rightarrow 2H_2O + H$	$1.62 \times 10^{-12} T_e^{-0.15}$	0	[96]
180	$e^- + H_4O_2^+ \rightarrow H_2O + OH + H$	$9.6 \times 10^{-13} T_e^{-0.2}$	0	[96]
181	$e^- + H_7O_3^+ \rightarrow 3H_2O + H$	$2.24 \times 10^{-12} T_e^{-0.08}$	0	[97]
182	$e^- + H_9O_4^+ \rightarrow 4H_2O + H$	3.6×10^{-12}	0	[97]
183	$e^- + H_{11}O_5^+ \rightarrow 5H_2O + H$	4×10^{-12}	0	[98]
184	$e^- + H_{13}O_6^+ \rightarrow 6H_2O + H$	4×10^{-12}	0	[98]
185	$e^- + H_{15}O_7^+ \rightarrow 7H_2O + H$	4×10^{-12}	0	[98]
186	$e^- + H_{17}O_8^+ \rightarrow 8H_2O + H$	4×10^{-12}	0	[98]
187	$e^- + H_{19}O_9^+ \rightarrow 9H_2O + H$	4×10^{-12}	0	[98]
188	$H^- + He \rightarrow He + H + e^-$	$8 \times 10^{-18} (T_g/300)^{0.5}$	0	[51]
189	$H^- + O_2 \rightarrow HO_2 + e^-$	1.2×10^{-15}	0	[99]
190	$He^+ + H_2O \rightarrow H^+ + OH + He$	2.04×10^{-16}	0	[66]
191	$He^+ + H_2O \rightarrow OH^+ + H + He$	2.86×10^{-16}	0	[66]
192	$He^+ + H_2O \rightarrow H_2O^+ + He$	6.05×10^{-17}	0	[66]
193	$HeH^+ + H \rightarrow H_2^+ + He$	9.1×10^{-16}	0	[66]
194	$HeH^+ + H_2O \rightarrow H_3O^+ + He$	4.3×10^{-16}	0	[100]
195	$He_2^+ + H_2O \rightarrow HeH^+ + He + OH(A)$	1.3×10^{-16}	0	[101]
196	$He_2^+ + H_2O \rightarrow OH^+ + H + 2He$	2.1×10^{-16}	0	[51]
197	$He_2^+ + H_2O \rightarrow H^+ + OH + 2He$	2.1×10^{-16}	0	[51]
198	$He_2^+ + H_2O \rightarrow HeH^+ + OH + He$	2.1×10^{-16}	0	[51]
199	$He_2^+ + H_2O \rightarrow H_2^+ + O + 2He$	2.1×10^{-16}	0	[51]
200	$O_2^+ + H_2O + N_2 \rightarrow H_2O_3^+ + N_2$	$2.6 \times 10^{-40} (T_g/300)^{-4}$	0	[96]
201	$O_2^+ + H_2O + He \rightarrow H_2O_3^+ + He$	$2.6 \times 10^{-40} (T_g/300)^{-4}$	0	[96]
202	$O_2^+ + H_2O + O_2 \rightarrow H_2O_3^+ + O_2$	$2.6 \times 10^{-40} (T_g/300)^{-4}$	0	[102]
203	$O_4^+ + H_2O + N_2 \rightarrow H_2O_3^+ + O_2 + N_2$	$1.5 \times 10^{-40} (T_g/300)^2$	0	[96]
204	$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$	3.3×10^{-16}	0	[103]
205	$H_2O_3^+ + O_2 \rightarrow O_4^+ + H_2O$	$2 \times 10^{-16} \exp(-2300/T_g)$	0	[103]
206	$O_4^+ + H_2O \rightarrow O_2 + H_2O_3^+$	1.7×10^{-15}	0	[103]
207	$N_2^+ + H_2O \rightarrow N_2 + H_2O^+$	3×10^{-15}	0	[102]
208	$N_4^+ + H_2O \rightarrow 2N_2 + H_2O^+$	2.4×10^{-15}	0	[104]
209	$H^+ + O_2 \rightarrow H + O_2^+$	2×10^{-15}	0	[66]
210	$H^+ + H_2O \rightarrow H + H_2O^+$	6.9×10^{-15}	0	[66]
211	$H^- + H_2O \rightarrow OH^- + H_2$	3.8×10^{-15}	0	[66]
212	$H_2^+ + He \rightarrow HeH^+ + H$	1.3×10^{-16}	0	[66]
213	$H_2^+ + O_2 \rightarrow O_2^+ + H_2$	8×10^{-16}	0	[66]
214	$H_2^+ + H_2O \rightarrow H_2O^+ + H_2$	3.9×10^{-15}	0	[66]
215	$H_2^+ + H_2O \rightarrow H_3O^+ + H$	3.4×10^{-15}	0	[66]
216	$O^- + H_2O \rightarrow OH^- + OH$	1.4×10^{-15}	0	[105]
217	$OH^+ + O \rightarrow O_2^+ + H$	7.1×10^{-16}	0	[66]
218	$OH^+ + O_2 \rightarrow O_2^+ + OH$	3.8×10^{-16}	0	[81]
219	$OH^+ + H_2O \rightarrow H_2O^+ + OH$	1.5×10^{-15}	0	[106]
220	$OH^+ + H_2O \rightarrow H_3O^+ + O$	1.3×10^{-15}	0	[107]
221	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	1.85×10^{-15}	0	[81]
222	$H_2O_3^+ + H_2O \rightarrow H_4O_2^+ + O_2$	1×10^{-15}	0	[96]
223	$H_2O_3^+ + H_2O \rightarrow H_3O^+ + OH + O_2$	3×10^{-16}	0	[105]
224	$H_4O_2^+ + H_2O \rightarrow H_5O_2^+ + OH$	1.4×10^{-15}	0	[96]
225	$H_3O^+ + H_2O + M \rightarrow H_5O_2^+ + M$	$3.2 \times 10^{-39} (T_g/300)^{-4}$	0	[104]

226	$\text{H}_5\text{O}_2^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_7\text{O}_3^+ + M$	$7.4 \times 10^{-39}(T_g/300)^{-7.5}$	0	[104]
227	$\text{H}_7\text{O}_3^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_9\text{O}_4^+ + M$	$2.5 \times 10^{-39}(T_g/300)^{-8.1}$	0	[104]
228	$\text{H}_9\text{O}_4^+ + M \rightarrow \text{H}_7\text{O}_3^+ + \text{H}_2\text{O} + M$	$2 \times 10^{12}T_g^{-8.1}\exp(-8360/T_g)$	0	[104]
229	$\text{H}_9\text{O}_4^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_{11}\text{O}_5^+ + M$	$3.3 \times 10^{-40}(T_g/300)^{-14}$	0	[104]
230	$\text{H}_{11}\text{O}_5^+ + M \rightarrow \text{H}_9\text{O}_4^+ + \text{H}_2\text{O} + M$	$6.3 \times 10^{24}T_g^{-14}\exp(-5750/T_g)$	0	[104]
231	$\text{H}_{11}\text{O}_5^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_{13}\text{O}_6^+ + M$	$4 \times 10^{-41}(T_g/300)^{-15.3}$	0	[104]
232	$\text{H}_{13}\text{O}_6^+ + M \rightarrow \text{H}_{11}\text{O}_5^+ + \text{H}_2\text{O} + M$	$2.62 \times 10^{27}T_g^{-15.3}\exp(-5000/T_g)$	0	[104]
233	$\text{H}_{13}\text{O}_6^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_{15}\text{O}_7^+ + M$	$4.5 \times 10^{-42}(T_g/300)^{-16}$	0	[104]
234	$\text{H}_{15}\text{O}_7^+ + M \rightarrow \text{H}_{13}\text{O}_6^+ + \text{H}_2\text{O} + M$	$1.98 \times 10^{29}T_g^{-16}\exp(-5000/T_g)$	0	[104]
235	$\text{H}_{15}\text{O}_7^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_{17}\text{O}_8^+ + M$	$4.5 \times 10^{-42}(T_g/300)^{-16}$	0	[104]
236	$\text{H}_{17}\text{O}_8^+ + M \rightarrow \text{H}_{15}\text{O}_7^+ + \text{H}_2\text{O} + M$	$1.98 \times 10^{29}T_g^{-16}\exp(-5000/T_g)$	0	[104]
237	$\text{H}_{17}\text{O}_8^+ + \text{H}_2\text{O} + M \rightarrow \text{H}_{19}\text{O}_9^+ + M$	$4.5 \times 10^{-42}(T_g/300)^{-16}$	0	[104]
238	$\text{H}_{19}\text{O}_9^+ + M \rightarrow \text{H}_{17}\text{O}_8^+ + \text{H}_2\text{O} + M$	$1.98 \times 10^{29}T_g^{-16}\exp(-5000/T_g)$	0	[104]
239	$\text{O}^- + \text{H}_2\text{O} + M \rightarrow \text{H}_2\text{O}_2^- + M$	1.3×10^{-40}	0	[108]
240	$\text{OH}^- + \text{H}_2\text{O} + M \rightarrow \text{H}_3\text{O}_2^- + M$	2.5×10^{-40}	0	[108]
241	$\text{H}_2\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^- + \text{OH}$	1×10^{-17}	0	[108]
242	$\text{H}_3\text{O}_2^- + \text{H}_2\text{O} + M \rightarrow \text{H}_5\text{O}_3^- + M$	3.5×10^{-40}	0	[108]
243	$\text{He}^+ + \text{OH}^- + M \rightarrow \text{OH} + \text{He} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
244	$\text{He}_2^+ + \text{O}^- + M \rightarrow \text{O} + 2\text{He} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
245	$\text{He}_2^+ + \text{OH}^- + M \rightarrow \text{OH} + 2\text{He} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
246	$\text{He}_2^+ + \text{H}_2\text{O}_2^- + M \rightarrow 2\text{He} + \text{O} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
247	$\text{He}_2^+ + \text{H}_3\text{O}_2^- + M \rightarrow 2\text{He} + \text{OH} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
248	$\text{He}_2^+ + \text{H}_5\text{O}_3^- + M \rightarrow 2\text{He} + \text{OH} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
249	$\text{O}_2^+ + \text{OH}^- \rightarrow \text{O}_2 + \text{OH}$	$2 \times 10^{-13}(T_g/300)^{-0.5}$	0	[38]
250	$\text{O}_2^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{O}_2 + \text{O} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
251	$\text{O}_2^+ + \text{H}_3\text{O}_2^- + M \rightarrow \text{O}_2 + \text{OH} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
252	$\text{O}_2^+ + \text{H}_5\text{O}_3^- + M \rightarrow \text{O}_2 + \text{OH} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
253	$\text{OH}^+ + \text{O}^- \rightarrow \text{HO}_2$	$2 \times 10^{-13}(T_g/300)^{-0.5}$	0	[38]
254	$\text{OH}^+ + \text{O}_2^- \rightarrow \text{OH} + \text{O}_2$	$2 \times 10^{-13}(T_g/300)^{-0.5}$	0	[38]
255	$\text{OH}^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{O} + \text{OH} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
256	$\text{OH}^+ + \text{H}_5\text{O}_3^- + M \rightarrow 2\text{OH} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
257	$\text{H}_2\text{O}^+ + \text{O}^- + M \rightarrow \text{O} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
258	$\text{H}_2\text{O}^+ + \text{OH}^- + M \rightarrow \text{OH} + \text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
259	$\text{H}_2\text{O}^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{O} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
260	$\text{H}_2\text{O}^+ + \text{H}_3\text{O}_2^- + M \rightarrow \text{OH} + 2\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
261	$\text{H}_2\text{O}^+ + \text{H}_5\text{O}_3^- + M \rightarrow \text{OH} + 3\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
262	$\text{H}_2\text{O}_3^+ + \text{O}^- + M \rightarrow \text{H}_2\text{O} + \text{O} + \text{O}_2 + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
263	$\text{H}_2\text{O}_3^+ + \text{O}_2^- + M \rightarrow \text{H}_2\text{O} + 2\text{O}_2 + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
264	$\text{H}_2\text{O}_3^+ + \text{H}_5\text{O}_3^- + M \rightarrow 3\text{H}_2\text{O} + \text{OH} + \text{O}_2 + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
265	$\text{H}_9\text{O}_4^+ + \text{H}_2\text{O}_2^- + M \rightarrow 5\text{H}_2\text{O} + \text{OH} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
266	$\text{H}_9\text{O}_4^+ + \text{H}_5\text{O}_3^- + M \rightarrow 7\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
267	$\text{H}_{11}\text{O}_5^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{OH} + 6\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
268	$\text{H}_{11}\text{O}_5^+ + \text{H}_5\text{O}_3^- + M \rightarrow 8\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
269	$\text{H}_{13}\text{O}_6^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{OH} + 7\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
270	$\text{H}_{13}\text{O}_6^+ + \text{H}_5\text{O}_3^- + M \rightarrow 9\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]

271	$\text{H}_{15}\text{O}_7^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{OH} + 8\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
272	$\text{H}_{15}\text{O}_7^+ + \text{H}_5\text{O}_3^- + M \rightarrow 10\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
273	$\text{H}_{17}\text{O}_8^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{OH} + 9\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
274	$\text{H}_{17}\text{O}_8^+ + \text{H}_5\text{O}_3^- + M \rightarrow 11\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
275	$\text{H}_{19}\text{O}_9^+ + \text{H}_2\text{O}_2^- + M \rightarrow \text{OH} + 10\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
276	$\text{H}_{19}\text{O}_9^+ + \text{H}_5\text{O}_3^- + M \rightarrow 12\text{H}_2\text{O} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[71,109]
277	$\text{H}_9\text{O}_4^+ + \text{O}^- + M \rightarrow 4\text{H}_2\text{O} + \text{OH} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
278	$\text{H}_9\text{O}_4^+ + \text{O}_2^- + M \rightarrow 4\text{H}_2\text{O} + \text{O}_2 + \text{H} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
279	$\text{H}_{11}\text{O}_5^+ + \text{O}^- + M \rightarrow 5\text{H}_2\text{O} + \text{OH} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
280	$\text{H}_{11}\text{O}_5^+ + \text{O}_2^- + M \rightarrow 5\text{H}_2\text{O} + \text{O}_2 + \text{H} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
281	$\text{H}_{13}\text{O}_6^+ + \text{O}^- + M \rightarrow 6\text{H}_2\text{O} + \text{OH} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
282	$\text{H}_{13}\text{O}_6^+ + \text{O}_2^- + M \rightarrow 6\text{H}_2\text{O} + \text{O}_2 + \text{H} + M$	$2 \times 10^{-37}(T_g/300)^{-2.5}$	0	[38]
283	$\text{He}_m + \text{H} \rightarrow \text{H}^+ + \text{He} + \text{e}^-$	1.1×10^{-15}	0	[110]
284	$\text{He}_m + \text{H}_2 \rightarrow \text{H}_2^+ + \text{He} + \text{e}^-$	2.9×10^{-17}	0	[111]
285	$\text{He}_m + \text{OH} \rightarrow \text{OH}^+ + \text{He} + \text{e}^-$	7.8×10^{-16}	0	[38]
286	$\text{He}_m + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{He} + \text{e}^-$	6.6×10^{-16}	0	[100]
287	$\text{He}_m + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^+ + \text{He} + \text{e}^-$	1.5×10^{-16}	0	[100]
288	$\text{He}_m + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ + \text{He} + \text{e}^-$	2.6×10^{-17}	0	[100]
289	$\text{He}_m + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HeH}^+ + \text{e}^-$	8.5×10^{-18}	0	[100]
290	$\text{He}_m + \text{H}_2\text{O}_2 \rightarrow \text{He} + \text{OH}^+ + \text{OH} + \text{e}^-$	7.8×10^{-16}	0	[38]
291	$\text{He}_2^* + \text{H}_2 \rightarrow \text{H}_2^+ + 2\text{He} + \text{e}^-$	2.2×10^{-16}	0	[112]
292	$\text{He}_2^* + \text{OH} \rightarrow \text{OH}^+ + 2\text{He} + \text{e}^-$	6×10^{-16}	0	[38]
293	$\text{He}_2^* + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + 2\text{He} + \text{e}^-$	6×10^{-16}	0	[113]
294	$\text{He}_2^* + \text{H}_2\text{O} \rightarrow 2\text{He} + \text{H}_2\text{O}$	1.5×10^{-21}	0	[66]
295	$\text{He} + \text{OH(A)} \rightarrow \text{He} + \text{OH}$	1.5×10^{-20}	0	[101]
296	$\text{He} + \text{H} + \text{O}_2 \rightarrow \text{He} + \text{HO}_2$	$2 \times 10^{-44}(T_g/300)^{-0.8}$	0	[114]
297	$\text{He} + \text{H} + \text{OH} \rightarrow \text{He} + \text{H}_2\text{O}$	$1.56 \times 10^{-43}(T_g/300)^{-2.6}$	0	[115]
298	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$2.71 \times 10^{-17}(T_g/300)^{0.75}$	0	[116]
299	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	$1.1 \times 10^{-18}T_g^{0.56}\exp(-346/T_g)$	0	[81]
300	$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	$2.35 \times 10^{-16}\exp(-373.7/T_g)$	0	[81]
301	$\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2$	$6 \times 10^{-17}T_g^{-0.186}\exp(-154/T_g)$	0	[81]
302	$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	$2.9 \times 10^{-17}\exp(200/T_g)$	0	[81]
303	$\text{O}(^1D) + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	5.2×10^{-16}	0	[81]
304	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$1.62 \times 10^{-16}\exp(64.95/T_g)$	0	[116]
305	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{O} + \text{H}_2\text{O}$	1.2×10^{-17}	0	[83]
306	$\text{O}_2(b) + \text{H}_2\text{O} \rightarrow \text{O}_2(a) + \text{H}_2\text{O}$	$4.52 \times 10^{-18}\exp(89/T_g)$	0	[117]
307	$2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$2.5 \times 10^{-21}T_g^{1.14}\exp(-50/T_g)$	0	[116]
308	$2\text{OH} \rightarrow \text{H}_2\text{O}_2$	$1.5 \times 10^{-17}(T_g/300)^{-0.37}$	0	[114]
309	$\text{OH} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$4.38 \times 10^{-17}\exp(110.9/T_g)$	0	[81]
310	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$4.53 \times 10^{-18}\exp(-288.9/T_g)$	0	[81]
311	$\text{OH(A)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{OH}$	$4.9 \times 10^{-16}(T_g/300)^{0.5}$	0	[118]
312	$\text{OH(A)} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	2.93×10^{-16}	0	[119]
313	$\text{OH(A)} \rightarrow \text{OH} + h\nu$	1.25×10^6	0	[101]

Note: ^{a)} M represents the background gases Helium atom, Nitrogen and Oxygen molecule. ^{b)} Rate coefficients have units of s^{-1} , m^3s^{-1} , m^6s^{-1} for one, two and three body reactions respectively; T_e has units of eV; T_g has units of K. $f(\epsilon)$ indicates the rate coefficient as a function of the mean electron energy calculated from the solution of Boltzmann equation. The reference indicates the database of the cross section used. ^{b)} The cross sections are calculated by detailed balancing.

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