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Chemistry in glow discharges of H₂ / O₂ mixtures. Diagnostics and modelling

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Abstract

The chemistry of low pressure H₂ + O₂ discharges with different mixture ratios has been studied in a hollow cathode DC reactor. Neutral and positive ion distributions have been measured by mass spectrometry, and Langmuir probes have been used to provide charge densities and electron temperatures. A simple zero order kinetic model including neutral species and positive and negative ions, which takes into account gas-phase and heterogeneous chemistry, has been used to reproduce the global composition of the plasmas over the whole range of mixtures experimentally studied, and allows for the identification of the main physicochemical mechanisms that may explain the experimental results. To our knowledge, no combined experimental and modelling studies of the heavy species kinetics of low pressure H₂ + O₂ plasmas including ions has been reported before.

As expected, apart from the precursors, H₂O is detected in considerable amounts. The model also predicts appreciable concentrations of H and O atoms and the OH radical. The relevance of the metastable species O(¹D) and O₂(a¹_g) is analysed. Concerning the charged species, positive ion distributions are dominated by H₃O⁺ for a wide range of intermediate mixtures, while H₃⁺ and O₂⁺ are the major ions for the higher and lower H₂/O₂ ratios, respectively. The mixed ions OH⁺, H₂O⁺ and HO₂⁺ are also observed in small amounts. Negative ions are shown to have a limited relevance in the global chemistry; their main contribution is the reduction of the electron density available for electron impact processes.

1. Introduction

Low pressure plasmas in electrical discharges with H₂ and O₂ are of interest in a variety of fields. In astrochemistry, the formation of H₂O and H₃O⁺ is of great relevance as they can be detected in interstellar environments [1-3]. Ions containing oxygen and hydrogen are formed in interstellar clouds [4], and they are assumed to play an important role in gas phase chemical routes leading to the production of H₂O. The hydronium ion (H₃O⁺) has been observed in molecular clouds since the nineties [5]. The recent Herschel mission has led to the detection of OH⁺ [6] and H₂O⁺ [7] in the diffuse interstellar medium and their role as markers of regions with a small fraction of H₂ has been highlighted [8]. The HO₂⁺ ion remains unobserved to date. It has been repeatedly considered as a possible tracer for

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molecular oxygen [9-11] in a similar way as N_2H^+ is for N_2 , but the available thermodynamic and kinetic data suggest that the concentration of this ion in the ISM should be too small to be detectable [10]. In fusion research, discharge cleaning is used to eliminate the residual molecules in a vacuum vessel, of which oxygen and water are major components [12, 13], and oxygen-containing cold plasmas have been proposed for the removal of co-deposits at the reactor walls [14, 15]. Hydrogen and oxygen plasmas are also widely used in surface treatments, like chemical modification [16-18], decontamination [19] or functionalization of carbon nanotubes [20].

Previous studies on this kind of plasmas have been carried out under different conditions and with very different objectives. Atmospheric pressure discharges have been used in experimental and theoretical studies of $H_2 + O_2$ ignition [21], in the simulation of gas heating processes in $H_2 + O_2$ streamers [22], or in the modelling of production mechanisms of different neutral species [23, 24]. An extensive global model for mixtures of He with small fractions ($< 1\%$) of H_2O has been elaborated by Liu et al. [25], and the formation of OH radicals in plasma assisted combustion of H_2 / air mixtures has been studied experimentally and theoretically by Yin et al. [26]. Low pressure plasmas of $H_2 + O_2$, mostly in the mbar range, have been employed by various groups. They have been used in the infrared spectroscopy analysis of the spectrum of the H_3O^+ ion [27]. Nevertheless, kinetic studies of these plasmas are limited to the analysis of the neutral species, such as the determination of oxygen atom concentrations in microwave post discharges of He- H_2 - O_2 mixtures using NO titration [28], the modelling of neutral species in the afterglow of a $H_2 + O_2$ discharge [29], or the experimental study of the variation of the $O_2(a^1 \text{ g})$ concentration with the introduction of small amounts of H_2 in an Ar + O_2 microwave discharge [30].

In this work, we present a study of the chemistry of neutral and ionic species in H_2/O_2 plasmas based on the experimental diagnostics and kinetic modelling of hollow cathode discharges at a pressure of 8 Pa and mixture proportions ranging from pure H_2 to pure O_2 . For the pressure value selected, which lies toward the high pressure limit of the stable operating range of the discharge (1-10 Pa), the ion distributions in the plasma are largely determined by ion-molecule chemistry, which is the goal of the present study. For the lowest operating pressures, displaying higher electron temperatures, the ion distributions tend to be dominated by the products of direct electron impact ionization [31]. Previous experimental results for H_2/O_2 plasmas at similar conditions but restricted to low O_2 concentrations (up to 15%) were given in [32]. Langmuir probes provide values for the electron temperatures and densities, and neutral and positive ion concentrations are determined by mass spectrometry. The main surface and gas processes are identified by comparison of experimental data and model predictions, and their relative relevance under the different discharge conditions is analysed.

2. Experimental setup

The DC plasma reactor used for the experiments has been described in previous works [33, 34]. It consists of a stainless steel grounded hollow cathode reactor (34 cm length, 10 cm diameter) with a central anode. The vessel is pumped to a base pressure of 10^{-4} Pa by a 300 l/s turbomolecular pump backed by a dry pump. The reactor has additional ports for pressure

gauges, windows and coupling of the experimental techniques for the plasma diagnostics. Neutral species from the plasma are sampled with a quadrupole mass spectrometer with electron impact ionization (Balzers, Prisma QMS 200). A plasma process monitor (Balzers, PPM421), which includes an electrostatic focusing system, a cylindrical mirror energy analyzer and a quadrupole mass filter, is used to measure the mass and energy distributions of the positive ions hitting the cathode. Both of these instruments are installed in a differentially pumped vacuum chamber and sample neutrals or ions from the plasma through a diaphragm of $\sim 100 \mu\text{m}$ diameter. The pressure during plasma measurements in this chamber is $\sim 10^{-5}$ Pa.

Electron temperatures and charge densities are measured with double Langmuir probes made in our laboratory [35]. The electron mean temperature and total charge density in the reactor are obtained from the analysis of the characteristic curves of the double Langmuir probe measurements in each discharge. The condition of orbital limited motion in a collision-free probe sheath is considered to be met [36]. The use of a single probe was also attempted in our reactor, but it was not possible to reach the electron saturation current due to the appearance of a secondary glow discharge in the probe when its positive potential was increased above the plasma potential.

Mixtures of H_2/O_2 of different proportions (from pure H_2 to pure O_2), with a total pressure of 8 Pa, are used for plasma generation. Measurements are performed under continuous flow conditions, and the pressures in the chamber (measured by a capacitance manometer Leybold CTR90) are regulated by balancing the gas flow with needle valves at the entrance (one for each gas) and a butterfly valve at the exit of the reactor, whose position is kept fixed during the experiments. For neutral species, calibration of the different sensitivity of detection of the QMS 200 for each pure gas is performed by comparing the capacitance manometer readings at various known pressures and the mass spectrometer ones. The H_2O concentration is obtained by comparison with the calibration of the QMS for Ne (due to the similar mass), which is done in the same way as for O_2 and H_2 , but taking into account the necessary corrections due to the different ionization cross section and the isotopic abundance of Ne. Calibration of the PPM421 for ions is performed with the noble gases He, Ne and Ar. The plasma monitor is used in the neutral detection mode, and the signal of each gas is compared to the corrected readings of a Bayard-Alpert gauge located in the same chamber. Taking into account possible errors in the determination of efficiencies for the various neutrals and ions and the reproducibility of the measurements, the uncertainties in the experimental concentrations of the different species are estimated to be $\sim 20\%$.

The residence time of gases in the reactor is measured according to the method used in previous works [33], obtaining a value of 0.54 ± 0.10 s. Plasma currents of ~ 150 mA and voltages of 500–550 V (depending on the mixture ratio) are maintained during the experiments. An electron gun is used for plasma ignition and then turned off.

3. Model

A zero order kinetic model is employed for the interpretation of the experimental results. It is based on a set of coupled differential equations describing the time evolution of the

concentrations of both neutral and ionic species from the ignition of the discharge until the attainment of the steady state. Similar models applied to H_2+D_2 , H_2+N_2 and H_2+Ar discharges can be found in refs. [37-40]. The model accounts for the main physico-chemical processes: electron impact dissociation and ionization, ion-molecule and ion-ion reactions, neutralization at the wall and heterogeneous chemistry. The full set of considered reactions can be found in Tables 1 and 2.

Electron impact reactions have rate coefficients which depend on the electron temperature. These rate coefficients have been calculated from the corresponding cross sections assuming a Maxwellian distribution for the electron energy distribution function, with a temperature that is derived from the Langmuir probe measurements. Other parameters required by the model are charge density, residence time and H_2/O_2 ratio. Unless otherwise indicated, experimental values for all of these parameters have been used as input for the model.

The assumption of a Maxwellian distribution is only an approximation. The actual shape of the electron energy distribution function (eedf) is not known with precision in our plasmas. On the one hand, inelastic and reactive collisions can deplete the high energy tail of a thermal eedf [75-77]. On the other hand, a small amount of non-thermal electrons, with energies extending to that corresponding to the cathode-anode voltage, can also be present in the discharge [78-80]. Electron impact dissociative processes can give rise to hot atoms that are mostly thermalized within the glow. In the steady state, a small fraction of these hot atoms survives and can be detected either in the line profiles of Balmer emission lines of H atoms [81] or indirectly in the energy resolved mass spectra of H^+ and O^+ ions [81-83]. However, previous works carried out on this reactor for different gas mixtures at comparable pressures [33, 34, 36-39] have shown that the assumption of a Maxwellian distribution is not a bad approximation for the global kinetics, and we have adopted it here for lack of better information on the actual eedf. The limitations of this approximation should be taken into account in the interpretation of the results.

As in previous works, a gas temperature $T_g = 300 \text{ K}$ has been assumed in the model calculations for the cold plasmas in our room temperature reactor. Rotational temperature estimates, based on emission spectroscopy for comparable plasmas [81, 84], set an upper limit of 350-400 K for the gas temperature.

Both neutral and charged species have been included in the model. Among neutrals, we can make a distinction between stable neutral species (H_2 , O_2 and H_2O) and radicals. Experimental data is only available for the first group, allowing for comparison with the model. Two metastable species, $\text{O}(^1\text{D})$ and $\text{O}_2(\text{a}^1_g)$ (also referred to as $\text{O}_2(\text{a})$), have been included in the model due to the importance of their gas phase neutral reactions and their relevance in the formation of negative ions, respectively.

Vibrationally excited states of H_2 have not been contemplated explicitly in the model. In a previous study of pure H_2 plasmas in the same reactor, emission spectroscopy measurements in conjunction with a collisional radiative model [33] showed that the H_2 vibrational populations in our plasmas are concentrated in the lowest levels and can be roughly described by a vibrational temperature of $\sim 3000 \text{ K}$. For this vibrational temperature, the

population of $H_2(v=1)$ is $\sim 12\%$. Given the high threshold for electron impact dissociation of H_2 (~ 11 eV) as compared with the first vibrational quantum of H_2 (~ 0.5 eV), we do not expect a significant contribution of vibrationally excited molecules, $H_2(v)$, to the global electron impact dissociation of H_2 . The decrease in population with growing v is far more important than the increase in the rate coefficient due to the lower energy threshold.

Charged species comprise positive and negative ions and electrons, which have distinct destruction mechanisms. Positive ions are assumed to disappear from the plasma mainly due to diffusion through the sheath to the reactor walls, where they are neutralized with a probability of 1 (see ref [34] for details on the treatment of ion diffusion). To meet the electroneutrality condition, the flux of positive ions to the walls is balanced to match the net production of positive charge in the glow [33]. Other mechanisms such as electron impact neutralization and ion-ion recombination are also considered, but their importance is orders of magnitude lower. For negative ions, collisional detachment with neutrals is the main destruction process, although electron impact detachment has also been included along with the above mentioned ion-ion recombination. Negative ions are considered to be confined within the discharge by the space charge electric field and, as assumed in other models [45, 85] do not diffuse to the walls. Total charge density is assumed to remain constant, so the value for the electron density is obtained by subtracting the total negative ion density from it.

Neutral chemistry is driven mainly by electron impact dissociation and wall recombination, although some gas phase bimolecular reactions (often including $O(^1D)$) are also important. Heterogeneous processes at the wall surface are responsible for the formation of H_2O , apart from the regeneration of the parent molecules H_2 and O_2 . Table 2 shows the heterogeneous reactions included in the model, as well as the corresponding rate coefficients γ . The kinetic description for heterogeneous reactions follows the formulation employed in refs. [37, 38]. A detailed account of the treatment of diffusion of neutral species to the wall in the model can be found in ref. [34]. In agreement with these studies, the flux of atoms (O and H) and radicals (OH) to the surface wall dominate the heterogeneous chemistry including both adsorption and recombination via Eley-Rideal (ER) reactions. The γ_{ER} selected for H_2 is 3.5×10^{-3} (taken from reference [39]) and a value of 2.4×10^{-2} is estimated for O_2 , above the value considered for N_2 in [39]. This assumption is based on results from [86], where higher wall recombination coefficients are obtained from O radicals than from N radicals on stainless steel. Reactions W_8 to W_{10} are responsible for the formation of water at the reactor wall through ER reactions. Water production can require the formation of OH(s) firstly (W_6 - W_7), which is then removed by impinging H atoms (W_8); or it can be generated by direct abstraction of H(s) or O(s) atoms with OH radicals and H_2 molecules, respectively (W_9 and W_{10}). The related γ_{ER} values (not available in the literature) have been chosen for a best global agreement with the data measured in this work over the whole range of studied concentrations. Dissociative adsorption of O_2 at the walls, which has been experimentally studied by molecular beams and modelled on clean Fe surfaces [87, 88], has been tested with model simulations and has very small influence on the present H_2 / O_2 plasmas. In previous works [37-39], adsorptions of neutral molecules were considered negligible as compared with those of atoms and radicals. Literature calculations suggest that the

adsorption of water on surface iron atoms can take place without a barrier [89, 90]. However, model simulations with this assumption, including the subsequent reactions of adsorbed water, lead to relevant discrepancies with our experimental results, which are accounted for much better by assuming no H_2O adsorption. Likewise the Langmuir-Hinshelwood heterogeneous recombination of adsorbed reactants like $\text{OH(s)} + \text{H(s)}$ or 2OH(s) for water production, with predicted energy barriers of $\sim 1.1 \text{ eV}$ and $\sim 0.65 \text{ eV}$ [89], respectively, have been considered minor, as compared with the barrierless Eley-Rideal processes listed in table 2 and have not been included in the final modelling.

4. Results and discussion

The electron temperatures and densities measured with the Langmuir probe (along with the model values, which will be discussed below) can be found in figure 1. The values depend on the relative fraction of O_2 in the precursor mixture ($\text{O}_2/(\text{O}_2+\text{H}_2)$). Electron temperatures are stable through the range of mixtures investigated, with a mean value of $\sim 2.4 \text{ eV}$, except for the pure hydrogen discharge, where it falls to $\sim 1.7 \text{ eV}$. The special behaviour of the pure H_2 discharge is also reproduced for the electron densities, where for pure hydrogen the value is higher than those for the rest of the mixtures. The higher electron temperatures measured for the mixtures containing O_2 indicate that the high energy tail of the eedf is more populated. This results in a higher ionization efficiency and, as a consequence, less electrons would be needed to maintain the discharge, as observed. On the other hand, it seems that, once a small amount of O_2 is present in the mixture, electron temperature and density are determined by the total gas pressure rather than by the H_2/O_2 proportion. The reasons for this behavior are not obvious and in any case lay beyond the scope of this work.

The experimental results for the relative concentrations of the neutral stable species O_2 , H_2 and H_2O , normalized to the sum of concentrations of just these species (which are the only three that can be detected by our experimental set-up) are represented as symbols in figure 2. Water is produced in the discharge in appreciable amounts, reaching a maximum of $\sim 30\%$ of the total neutral concentration for a mixture with $\sim 40\% \text{ O}_2$, close to what would be expected from a stoichiometric point of view, which would correspond to maximum water formation for a fraction of oxygen of 33% . The oxygen precursor is depleted at high H_2 fractions, as it is mostly dissociated and then recombined at the wall to form H_2O . The H_2 precursor is also depleted at high oxygen fractions, but in a smaller proportion. Other neutral stable species, such as O_3 , were not detected in our discharges.

Model simulations for these species are displayed as lines in figure 2. The agreement with the experimental results is good, reproducing the behaviour of the three molecules reasonably well. Water is shown to have a maximum concentration of $\sim 35\%$, which is slightly higher than the experimental value ($\sim 30\%$) and corresponds also to the $40\% \text{ O}_2$ mixture. This slight overestimation of water formation happens for all the simulated conditions, leading to marginally higher depletions of the precursors H_2 and O_2 than those measured, especially for the extreme mixtures.

Steady state concentrations of H_2O are given by the equilibrium between the dissociation of the precursor gases and the recombination of radicals at the wall. These radicals have not

been measured experimentally, but their concentrations can be simulated with the model. Figure 3 shows the predicted relative concentrations of all the neutral species considered, normalized to the sum of concentrations of all of them. As could be expected, the stable neutral species dominate the distributions, but radicals appear in considerable amounts. Atomic hydrogen, produced mainly through dissociation of H_2 , has concentrations of $\sim 5\%$ for most of the mixtures, decreasing below this value only for mixtures containing $< 10\%$ H_2 . Oxygen atoms in the ground state show comparable concentrations to those of atomic hydrogen, but reach higher densities for O_2 -rich mixtures (up to 30% $O(^3P)$ for pure oxygen) and tend to decrease with growing H_2 content. The other main radical, OH, is formed mainly from the dissociation of water molecules and thus follows a similar behaviour to this species, reaching concentrations up to 10% for high oxygen conditions. Ozone and HO_2 are hardly formed in the plasma and their relevance to the chemistry is limited.

The two excited species included in the model, $O_2(a^1_g)$ and $O(^1D)$, have very different effects in the chemistry of the discharge. Concentrations of $O_2(a^1_g)$ are comparatively high, typically $\sim 5\%$ of the O_2 concentration, almost reaching 10% of the total neutral concentration for the pure oxygen plasma. Despite these high values, the impact in the chemistry of the discharge is limited, its main role being the production of O^- ions through dissociative attachment. On the other hand, the amounts of $O(^1D)$ in the discharge are very low, three or four orders of magnitude below the concentration of $O(^3P)$, but with a heavier role in the neutral chemistry of the discharge. The reactions of $O(^1D)$ with H_2 and H_2O (G_{11} and G_{15}) have high rate coefficients for a homogeneous neutral process, and become a main source for OH radicals when the concentration of $O(^1D)$ is high enough (80% - 90% O_2 mixtures).

Figure 4 shows the measured positive ion distributions for the different considered mixtures, as well as their model predictions. Due to the high density of data, the different species have been arranged in two panels for clarity. Hydrogenic ions (H^+ , H_2^+ , H_3^+) are only dominant for mixtures with nearly no oxygen, where H_3^+ is clearly the dominant ion. As soon as oxygen is added to the mixture, water is formed and H_3O^+ quickly becomes the major ion, while the concentration of H_3^+ decreases. This situation is maintained through mixtures with approximately $4\% < O_2 < 70\%$, with H_3O^+ accounting for $\sim 50\text{--}60\%$ of the positive charge. In this range, the pure oxygenic ions O^+ and O_2^+ increase with the O_2 fraction, while mixed ions (H_2O^+ , OH^+ , HO_2^+) are roughly stable. At $\sim 80\%$ O_2 fraction, O_2^+ becomes the major ion, with H_3O^+ sinking, following the decrease in neutral H_2O available in the gas phase. Between 90% and 100% O_2 , all hydrogen-containing ions abruptly disappear from the plasma as expected, with only O_2^+ and O^+ in a 2:1 ratio remaining in the pure oxygen discharge.

The global behaviour of the major ions is reasonably well reproduced by the model, although there are some discrepancies with the experimental observations. At the lowest O_2 concentration, H_3^+ is the dominant ion, with an important contribution of H_3O^+ and H^+ , which replicates the experimental results. However, the value for the electron temperature used for this simulation is 2.4 eV, as opposed to the 1.7 eV value measured with the Langmuir probe (see Fig. 1). Using the measured value as an input for the model leads to an

important overestimation of the H_3O^+ concentration. The use of a higher value for the electron temperature is supported by previous measurements in pure hydrogen plasmas at the same pressure [33, 37, 38]. The rest of the model simulations have been carried out using the experimental values for the electron temperatures and densities.

The addition of oxygen to the mixture makes H_3O^+ quickly become the major ion. In H_2 -rich plasmas, the main mechanism for the formation of this ion is the proton transfer from H_3^+ to H_2O (reaction T_{12}), whose high rate coefficient can be justified by taking into account the difference in proton affinity of the species involved (691.0 kJ/mol for H_2O and 422.3 kJ/mol for H_2). As the oxygen ratio grows, other ions become important in the mixture while H_3^+ sinks, diversifying the production processes for H_3O^+ . For intermediate mixtures, these include charge transfer reactions involving H_2O^+ (reactions T_{21} and T_{22}) and OH^+ (T_{19}), all of which have high rate coefficients. When the hydrogen present in the mixture is lowered, the concentration of hydronium decreases and O_2^+ , which is mainly produced from the direct ionization of O_2 molecules, becomes the major ion. For the pure oxygen plasma, only this ion and O^+ from the dissociative ionization of O_2 remain, but the ratio between them (3:1) is different from the experimental one (2:1). This ratio is highly dependent on the electron temperature, so a rise in this parameter would help reproduce the experimental results.

The three mixed ions OH^+ , H_2O^+ and HO_2^+ have concentrations of the order of $\sim 1\text{--}3\%$ for most of the mixtures studied with H_2O^+ tending to be slightly more abundant. This behaviour reproduces qualitatively the experimental observations. H_2O^+ is produced mainly through the ionization of water molecules (I_8), and then destroyed through collisions with H_2 (T_{21}) and H_2O (T_{22}), as mentioned earlier. In the case of OH^+ , it is produced mainly from the dissociative ionization of H_2O (I_9), and destroyed through collisions with all of the major molecular species in the plasma, H_2 (T_{17}), O_2 (T_{20}) and H_2O (T_{18} and T_{19}). For HO_2^+ , the reaction with H_2 to form H_3^+ is nearly thermoneutral, with the forward (T_{25}) and backward (T_{13}) rate coefficients being comparable, and this equilibrium determines its concentration for H_2 -rich mixtures. When oxygen is the major component of the mixture, reaction T_{24} becomes the main source of HO_2^+ , while the destruction mechanism is still the same.

It is interesting to observe at this point that the relative concentrations of the H_3O^+ , H_2O^+ and OH^+ ions are similar to those predicted in astrochemical models for the interior of dark clouds [8], where the chemistry leading to the formation of these ions has some similitude with that of our discharge. It starts also with the ionization of molecular hydrogen and proceeds through proton transfer reactions involving H_3^+ . In diffuse clouds, where OH^+ and H_2O^+ have been detected [6, 7], H_2 is scarce, and the abundant electrons neutralize H_3^+ . In these regions other mechanisms starting with the ionization of atomic hydrogen become prevalent and produce an inverse ordering of the ionic relative abundances [8] ($[\text{OH}^+] > [\text{H}_2\text{O}^+] > [\text{H}_3\text{O}^+]$). The concentration of the O_2H^+ ion found in our plasmas is similar to that of OH^+ , which suggests that this ion might be found, as a minor species, inside dark clouds.

Purely hydrogenic ions obviously dominate for pure H_2 conditions but decrease abruptly with the addition of oxygen to the mixture, especially H_3^+ , falling orders of magnitude from

their initial values. The experimental data shows the same decrease but with a smoother slope, with H_3^+ only going below 1% concentration for a ~ 60% O_2 mixture, while in the model simulations it occurs for a mere 10% O_2 . In the case of H_2^+ , its concentration is underestimated by almost an order of magnitude through the whole range of mixtures, and for H^+ the behaviour is only reproduced for high H_2 and high O_2 conditions.

The concentrations of these ions depend strongly on the electron temperature, as both H^+ and H_2^+ are produced by electron impact ionization of H_2 (reactions I_5 and I_6 , respectively), and H_3^+ is produced from H_2^+ in a charge transfer reaction with H_2 (T_5). A higher electron temperature would enhance the production of these ions, leading to a better agreement between the experiment and the model. However, for the majority of mixtures studied, rising the electron temperature would lead to an important increase in certain species, such as H_2O^+ and OH^+ , which are already well reproduced by the model, effectively altering the behaviour of the major ions in the discharge. Figure 5 displays the simulated relative concentrations of positive ions for two electron temperatures: 2 eV and 3 eV. The variations commented on above can be appreciated.

The results of the simulations for the negative charge carriers can be seen in figure 6. The distribution is dominated by electrons for all mixture ratios, with negative ions making up at most 25% of the total negative charge. In the pure H_2 plasma, negative ions are hardly present, with a relative concentration of $\text{H}^- \sim 0.1\%$. However, the addition of small amounts of O_2 to the mixture makes its concentration rise up to 10%, due to the high cross section for the dissociative attachment of H_2O (reaction A_2), which is being formed in the discharge. As the oxygen ratio grows, H^- ions are lost due to collisional detachment with O_2 (Dt_4), whereas O^- and OH^- ions increase in concentration, O^- being produced from the dissociative attachment of water (A_5) and then transformed into OH^- through collisions with H_2 and H_2O (T_{26} and T_{27}). OH^- is the major negative ion for mixtures from 40% to 80% O_2 . For higher oxygen concentrations, the amount of H_2 and H_2O in the discharge is not enough to maintain an efficient formation of OH^- , so it decreases quickly. In these conditions, O^- is formed from the dissociative attachment of O_2 (reaction A_1) and $\text{O}_2(\text{a}^1_g)$ (reaction A_4).

The relevance of the negative ion processes in the global chemistry of the discharge is low, as they are not involved in any main mechanism for production or destruction of positive ions or neutrals. In our discharge, ion-ion neutralization, which is the main gas phase process involving positive ions, is far less important than the neutralization at the cathode walls. The main contribution of negative ions is in fact the decrease in the electron density, which lowers the rate of electron impact processes but, given that their concentration never exceeds 25% of the total negative charge, this effect is not large.

5. Summary and conclusions

A combined diagnostics and modelling of low pressure $\text{H}_2 + \text{O}_2$ plasmas with different mixture ratios, generated in a hollow cathode DC reactor, has been presented. The results of the model simulations have allowed the identification of the main processes determining the observed neutral and ion distributions. To our knowledge, no combined experimental and

modelling studies of the kinetics of low pressure $\text{H}_2 + \text{O}_2$ plasmas including ions had been reported before.

Water formation is observed in the discharge for the whole range of mixtures, up to a maximum of $\sim 30\%$ relative concentration. These results are well reproduced by the kinetic model, which predicts slightly higher concentrations (up to 35%) of water. The concentrations of other neutrals, including radicals and excited species that could not be experimentally observed, have been also simulated with the model. Atomic oxygen and hydrogen are formed in appreciable amounts, with relative concentrations of the order of 10% when the presence of their molecular precursors is significant. The OH radical is formed from the dissociation of water, showing a similar behaviour over the range of mixtures, with a peak value of $\sim 10\%$ of the total neutral concentration. The excited species $\text{O}_2(\text{a}^1_g)$ and $\text{O}(\text{D})$ are formed in different proportions in the discharge, with $\text{O}_2(\text{a}^1_g)$ reaching up to 10% relative concentration but having a limited impact in the chemistry. In contrast, $\text{O}(\text{D})$ is produced in smaller amounts (up to $\sim 0.1\%$) but has a great relevance in the chemistry due to the high cross sections for its reactions with neutrals. The other neutral species considered, O_3 and HO_2 , are hardly formed in our plasmas.

The experimental ion distributions are dominated by hydrogenic ions only for mixtures with nearly no oxygen. As soon as H_2O is formed in the plasma, H_3O^+ becomes the major ion, remaining as such for mixtures with $4\% < \text{O}_2 < 70\%$. For higher O_2 fractions, pure oxygen ions become dominant, with O_2^+ as the major ion for these mixtures. The concentrations of the mixed minor ions H_2O^+ , OH^+ , HO_2^+ are stable through a wide range of H_2/O_2 ratios, only sinking for the extreme mixtures. A comparison of the relative abundances of these ions with the predictions of astrochemical models suggests that HO_2^+ might be present as a minor component in the interior of dark interstellar clouds. Model simulations reproduce the behaviour of the ions reasonably well. For the pure H_2 discharge, H_3^+ is the dominant ion, and when oxygen is added to the mixture, H_3O^+ concentration grows due to proton transfer between H_3^+ and H_2O , becoming the major ion. For high O_2 ratios, direct ionization of this precursor causes O_2^+ to prevail in the plasma.

The main discrepancy between measurements and simulations is found for the pure hydrogenic ions, whose predicted decrease upon oxygen addition to the mixture is much more abrupt than experimentally observed. This is due to the low electron temperature, which causes the charge transfer processes to prevail over electron impact. As soon as oxygen is added to the mixture, water is formed and H_3^+ is destroyed through charge transfer to H_2O . A higher value for the electron temperature would increase the concentration of hydrogenic ions through the direct ionization of H_2 and subsequent charge transfer; however, this would lead to a great change in the concentrations of other ions. A non-maxwellian electron energy distribution function could justify a different balance of these processes, by increasing or decreasing the population of the high energy tail.

The concentrations of negative charge carriers have been simulated with the model. The distribution is dominated by electrons for all mixture ratios, with negative ion concentrations reaching up to 25% . H^- and O^- are the major negative ions for the H-rich and O-rich discharges, respectively, while OH^- prevails for the intermediate mixtures. The relevance of

negative ions to the global chemistry is limited. Their main function is decreasing the electron density available for electron impact processes.

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Figure 1.

Electron temperature (a) and electron density (b) measured with a double Langmuir probe. The values used in the model are the same as the experimental ones except for the pure H₂ discharge, where an electron temperature of 2.4 eV is employed (see text).

Figure 2. Relative concentrations for the stable neutrals as a function of O₂ fraction, normalized to the sum of concentrations of the three stable species. Symbols: experimental data. Lines: values obtained from model simulations.

Figure 3. Simulated relative concentrations for all the neutral species considered in the model, normalized to the sum of concentrations of all of them. They are split in two panels for clarity.

Figure 4.

Symbols: experimental relative concentrations of positive ions in the discharge for the different mixtures studied, normalized to the sum of concentrations of all positive ions. The narrow dotted lines are only to guide the eye. Continuous lines: model results for the relative concentrations of positive ions. The data have been split in two panels for clarity.

Figure 5.

Model predictions of relative concentrations of positive ions in the discharge at two electron temperatures, 2 eV and 3 eV, normalized to the sum of concentrations of all positive ions.

Figure 6.

Model simulations for relative concentrations of negative charge carrier normalized to the sum of concentrations of all of them.

Table 1

Gas phase reactions included in the model.

	Process	Rate coefficient (cm ³ s ⁻¹)	Reference
Electron impact ionization			
I ₁	$e + O \rightarrow O^+ + 2e$	$1.03 \times 10^{-8} T_e^{0.5} \exp(-14.3/T_e)$	[41]
I ₂	$e + O_2 \rightarrow O^+ + O + 2e$	$4.84 \times 10^{-9} T_e^{0.5} \exp(-22.5/T_e)$	[42]
I ₃	$e + O_2 \rightarrow O_2^+ + 2e$	$7.07 \times 10^{-9} T_e^{0.5} \exp(-13.1/T_e)$	[42]
I ₄	$e + H \rightarrow H^+ + 2e$	$6.50 \times 10^{-9} T_e^{0.49} \exp(-12.89/T_e)$	[33]
I ₅	$e + H_2 \rightarrow H^+ + H + 2e$	$3.00 \times 10^{-8} T_e^{0.44} \exp(-37.72/T_e)$	[33]
I ₆	$e + H_2 \rightarrow H_2^+ + 2e$	$3.12 \times 10^{-8} T_e^{0.17} \exp(-20.07/T_e)$	[33]
I ₇	$e + OH \rightarrow OH^+ + 2e$	$1.48 \times 10^{-8} T_e^{0.5} \exp(-12.6/T_e)$	[43]
I ₈	$e + H_2O \rightarrow H_2O^+ + 2e$	$9.87 \times 10^{-9} T_e^{0.5} \exp(-13.3/T_e)$	[44]
I ₉	$e + H_2O \rightarrow OH^+ + H + 2e$	$2.88 \times 10^{-9} T_e^{0.5} \exp(-17.7/T_e)$	[44]
I ₁₀	$e + H_2O \rightarrow H^+ + OH + 2e$	$1.77 \times 10^{-9} T_e^{0.5} \exp(-20.0/T_e)$	[44]
I ₁₁	$e + H_2O \rightarrow O^+ + H_2 + 2e$	$3.03 \times 10^{-10} T_e^{0.5} \exp(-23.5/T_e)$	[44]
I ₁₂	$e + O_2(a) \rightarrow O_2^+ + 2e$	$9.0 \times 10^{-10} T_e^{2.0} \exp(-11.6/T_e)$	[45]
Electron impact dissociation			
D ₁	$e + H_2 \rightarrow 2H + e$	$1.75 \times 10^{-7} T_e^{-1.24} \exp(-12.59/T_e)$	[33]
D ₂	$e + O_2 \rightarrow 2O + e$	$4.2 \times 10^{-9} \exp(-5.56/T_e)$	[46]
D ₃	$e + O_2 \rightarrow O + O^1D + e$	$5.0 \times 10^{-8} \exp(-8.40/T_e)$	[46]
D ₄	$e + OH \rightarrow O + H + e$	K_{D4}^a	[47]
D ₅	$e + H_2O \rightarrow OH + H + e$	K_{D5}^b	[44]
D ₆	$e + H_2O \rightarrow O^1D + H_2 + e$	$2.0 \times 10^{-9} T_e^{0.5} \exp(-7.0/T_e)$	[44]
D ₇	$e + O_2(a) \rightarrow 2O + e$	$4.2 \times 10^{-9} \exp(-4.6/T_e)$	[45]
Electron impact neutralization			
N ₁	$H_2^+ + e \rightarrow H + H$	K_{N1}^c	[33]
N ₂	$H_3^+ + e \rightarrow 3H$	$0.5 \times K_{N2}^d$	[33]
N ₃	$H_3^+ + e \rightarrow H_2 + H$	$0.5 \times K_{N2}^d$	[33]
N ₄	$O_2^+ + e \rightarrow O + O$	$4.9 \times 10^{-8} (0.026/T_e)^{0.7}$	[48]
N ₅	$O_2^+ + e \rightarrow O + O^1D$	$1.06 \times 10^{-7} (0.026/T_e)^{0.7}$	[48]
N ₆	$O_2^+ + e \rightarrow O^1D + O^1D$	$7.56 \times 10^{-8} (0.026/T_e)^{0.7}$	[48]
N ₇	$OH^+ + e \rightarrow O + H$	$3.75 \times 10^{-8} (0.026/T_e)^{0.5}$	[49]
N ₈	$H_2O^+ + e \rightarrow OH + H$	$8.6 \times 10^{-8} (0.026/T_e)^{0.5}$	[50]
N ₉	$H_2O^+ + e \rightarrow O + H_2$	$3.9 \times 10^{-8} (0.026/T_e)^{0.5}$	[50]

	Process	Rate coefficient (cm ³ s ⁻¹)	Reference
Electron impact ionization			
N ₁₀	H ₂ O ⁺ + e → O + H + H	3.05 × 10 ⁻⁷ (0.026/T _e) ^{0.5}	[50]
N ₁₁	H ₃ O ⁺ + e → OH + H + H	2.85 × 10 ⁻⁷ (0.026/T _e) ^{0.5}	[51]
N ₁₂	H ₃ O ⁺ + e → O + H ₂ + H	5.6 × 10 ⁻⁹ (0.026/T _e) ^{0.5}	[51]
N ₁₃	H ₃ O ⁺ + e → OH + H ₂	6.02 × 10 ⁻⁸ (0.026/T _e) ^{0.5}	[51]
N ₁₄	H ₃ O ⁺ + e → H ₂ O + H	1.08 × 10 ⁻⁷ (0.026/T _e) ^{0.5}	[51]
N ₁₅	HO ₂ ⁺ + e → O ₂ + H	3 × 10 ⁻⁷ (0.026/T _e) ^{0.5}	[52]
Neutral homogeneous			
G ₁	H + O ₃ → O + HO ₂	7.51 × 10 ⁻¹³	[53]
G ₂	H + HO ₂ → H ₂ O + O	9.18 × 10 ⁻¹¹ exp(-971.9/T _g)	[54]
G ₃	H + HO ₂ → H ₂ O + O(¹ D)	4.8 × 10 ⁻¹⁶ T _g ^{1.55} exp(80.58/T _g)	[53]
G ₄	H + HO ₂ → O ₂ + H ₂	1.1 × 10 ⁻¹² T _g ^{0.56} exp(-346/T _g)	[54]
G ₅	H + HO ₂ → 2OH	2.35 × 10 ⁻¹⁰ exp(-373.7/T _g)	[54]
G ₆	O(¹ D) + HO ₂ → OH + O ₂	2.9 × 10 ⁻¹¹ exp(200/T _g)	[54]
G ₇	O ² (a) + HO ₂ → OH + O + O ₂	1.66 × 10 ⁻¹¹	[55]
G ₈	H + O ₃ → OH + O ₂	2.71 × 10 ⁻¹¹ (T _g /300) ^{0.75}	[53]
G ₉	O(¹ D) + O ₃ → 2O ₂	1.2 × 10 ⁻¹⁰	[53]
G ₁₀	O(¹ D) + O ₃ → 2O + O ₂	1.2 × 10 ⁻¹⁰	[53]
G ₁₁	O(¹ D) + H ₂ → OH + H	1.1 × 10 ⁻¹⁰	[54]
G ₁₂	O(¹ D) + O ₂ → O + O ₂	4.8 × 10 ⁻¹² exp(67/T _g)	[56]
G ₁₃	O(¹ D) + O ₂ → O + O ₂ (a)	1.6 × 10 ⁻¹² exp(67/T _g)	[57]
G ₁₄	O(¹ D) + OH → H + O ₂	6 × 10 ⁻¹¹ T _g ^{-0.186} exp(-154/T _g)	[54]
G ₁₅	O(¹ D) + H ₂ O → 2OH	1.62 × 10 ⁻¹⁰ exp(64.95/T _g)	[53]
G ₁₆	O(¹ D) + H ₂ O → O + H ₂ O	1.2 × 10 ⁻¹¹	[58]
Ion-molecule			
T ₁	H ⁺ + O → O ⁺ + H	3.75 × 10 ⁻¹⁰	[59]
T ₂	H ⁺ + H ₂ O → H ₂ O ⁺ + H	8.20 × 10 ⁻⁹	[59]
T ₃	H ⁺ + O ₂ → O ₂ ⁺ + H	1.17 × 10 ⁻⁹	[59]
T ₄	H ₂ ⁺ + H → H ₂ + H ⁺	6.40 × 10 ⁻¹⁰	[59]
T ₅	H ₂ ⁺ + H ₂ → H ₃ ⁺ + H	2.00 × 10 ⁻⁹	[59]
T ₆	H ₂ ⁺ + H ₂ O → H ₂ O ⁺ + H ₂	0.53 × 7.30 × 10 ⁻⁹ = 3.87 × 10 ⁻⁹	[59]
T ₇	H ₂ ⁺ + H ₂ O → H ₃ O ⁺ + H	0.47 × 7.30 × 10 ⁻⁹ = 3.43 × 10 ⁻⁹	[59]
T ₈	H ₂ ⁺ + O ₂ → O ₂ ⁺ + H ₂	0.29 × 2.70 × 10 ⁻⁹ = 7.83 × 10 ⁻¹⁰	[59]
T ₉	H ₂ ⁺ + O ₂ → HO ₂ ⁺ + H	0.71 × 2.70 × 10 ⁻⁹ = 1.92 × 10 ⁻⁹	[59]
T ₁₀	H ₃ ⁺ + O → OH ⁺ + H ₂	0.70 × 1.20 × 10 ⁻⁹ = 8.40 × 10 ⁻¹⁰	[59]

	Process	Rate coefficient ($\text{cm}^3 \text{s}^{-1}$)	Reference
Electron impact ionization			
T ₁₁	$\text{H}_3^+ + \text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}$	$0.30 \times 1.20 \times 10^{-9} = 3.60 \times 10^{-10}$	[59]
T ₁₂	$\text{H}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2$	5.30×10^{-9}	[59]
T ₁₃	$\text{H}_3^+ + \text{O}_2 \rightarrow \text{HO}_2^+ + \text{H}_2$	6.70×10^{-10}	[59]
T ₁₄	$\text{O}^+ + \text{H} \rightarrow \text{H}^+ + \text{O}$	6.40×10^{-10}	[59]
T ₁₅	$\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$	1.62×10^{-9}	[59]
T ₁₆	$\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{O}$	2.60×10^{-9}	[59]
T ₁₇	$\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H}$	9.70×10^{-10}	[59]
T ₁₈	$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{OH}$	$0.55 \times 2.89 \times 10^{-9} = 1.59 \times 10^{-9}$	[59]
T ₁₉	$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}$	$0.45 \times 2.89 \times 10^{-9} = 1.30 \times 10^{-9}$	[59]
T ₂₀	$\text{OH}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{OH}$	3.80×10^{-10}	[59]
T ₂₁	$\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H}$	7.60×10^{-10}	[59]
T ₂₂	$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$	1.85×10^{-9}	[59]
T ₂₃	$\text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O}$	3.30×10^{-10}	[59]
T ₂₄	$\text{O}_2^+ + \text{H}_2 \rightarrow \text{HO}_2^+ + \text{H}$	4.00×10^{-11}	[59]
T ₂₅	$\text{HO}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{O}_2$	3.30×10^{-10}	[59]
T ₂₆	$\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$	3×10^{-11}	[60]
T ₂₇	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}$	1.4×10^{-9}	[61]
Electron impact attachment			
A ₁	$\text{e} + \text{O}_2 \rightarrow \text{O}^- + \text{O}$	$1.07 \times 10^{-9} T_e^{-1.391} \exp(-6.26/T_e)$	[62]
A ₂	$\text{e} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^-$	$3.54 \times 10^{-9} T_e^{-1.5} \exp(-6.66/T_e)$	[44]
A ₃	$\text{e} + \text{H}_2 \rightarrow \text{H}^- + \text{H}$	$5.6 \times 10^{-13} T_e^{0.5} \exp(-5.5/T_e)$	[63]
A ₄	$\text{e} + \text{O}_2(\text{a}) \rightarrow \text{O} + \text{O}^-$	$2.28 \times 10^{-10} \exp(-2.29/T_e)$	[45]
A ₅	$\text{e} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}^-$	$7.08 \times 10^{-10} T_e^{-1.3} \exp(-8.61/T_e)$	[44]
A ₆	$\text{e} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}$	$1.24 \times 10^{-10} T_e^{-1.3} \exp(-7.32/T_e)$	[44]
Detachment			
Dt ₁	$\text{e} + \text{H}^- \rightarrow \text{H} + 2\text{e}$	$2.32 \times 10^{-8} T_e^2 \exp(-0.13/T_e)$	[64]
Dt ₂	$\text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e}$	1.3×10^{-9}	[65]
Dt ₃	$\text{H}^- + \text{O} \rightarrow \text{OH} + \text{e}$	1×10^{-9}	[65]
Dt ₄	$\text{H}^- + \text{O}_2 \rightarrow \text{HO}_2 + \text{e}$	1.2×10^{-9}	[66]
Dt ₅	$\text{OH}^- + \text{H} \rightarrow \text{H}_2\text{O} + \text{e}$	1.8×10^{-9}	[67]
Dt ₆	$\text{OH}^- + \text{O} \rightarrow \text{HO}_2 + \text{e}$	2×10^{-10}	[67]
Dt ₇	$\text{e} + \text{OH}^- \rightarrow \text{OH} + 2\text{e}$	$9.67 \times 10^{-6} T_e^{-1.9} \exp(-12.1/T_e)$	[68]
Dt ₈	$\text{O}^- + \text{O}_2(\text{a}) \rightarrow \text{O}_3 + \text{e}$	1.9×10^{-10}	[69]
Dt ₉	$\text{O}^- + \text{H} \rightarrow \text{OH} + \text{e}$	5×10^{-10}	[60]

	Process	Rate coefficient ($\text{cm}^3 \text{s}^{-1}$)	Reference
Electron impact ionization			
Dt ₁₀	$\text{O}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{e}$	$6 \times 10^{-10} (\text{T}_\text{g}/300)^{-0.24}$	[70]
Dt ₁₁	$\text{O}^- + \text{O} \rightarrow \text{O}_2 + \text{e}$	2.3×10^{-10}	[69]
Electron impact excitation and deexcitation			
X ₁	$\text{e} + \text{O}_2 \rightarrow \text{O}_2(\text{a}) + \text{e}$	$1.7 \times 10^{-9} \exp(-3.1/\text{T}_\text{e})$	[45]
X ₂	$\text{e} + \text{O} \rightarrow \text{O}(\text{^1D}) + \text{e}$	$4.5 \times 10^{-9} \exp(-2.29/\text{T}_\text{e})$	[45]
Dx ₁	$\text{e} + \text{O}_2(\text{a}) \rightarrow \text{O}_2 + \text{e}$	$5.6 \times 10^{-9} \exp(-2.2/\text{T}_\text{e})$	[45]
Ion-ion neutralization			
IN ₁	$\text{H}^+ + \text{H}^- \rightarrow 2\text{H}$	$1.8 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[21]
IN ₂	$\text{H}_2^+ + \text{H}^- \rightarrow \text{H} + \text{H}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[71]
IN ₃	$\text{H}_3^+ + \text{H}^- \rightarrow 2\text{H}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[72]
IN ₄	$\text{O}^+ + \text{H}^- \rightarrow \text{H} + \text{O}$	$2.3 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[60]
IN ₅	$\text{O}_2^+ + \text{H}^- \rightarrow \text{H} + \text{O}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₆	$\text{OH}^+ + \text{H}^- \rightarrow \text{H}_2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₇	$\text{H}_2\text{O}^+ + \text{H}^- \rightarrow \text{H} + \text{H}_2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₈	$\text{H}_3\text{O}^+ + \text{H}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$	$2.3 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[60]
IN ₉	$\text{H}^+ + \text{O}^- \rightarrow \text{H} + \text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₀	$\text{H}_2^+ + \text{O}^- \rightarrow \text{H}_2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₁	$\text{H}_3^+ + \text{O}^- \rightarrow \text{OH} + \text{H}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₂	$\text{O}^+ + \text{O}^- \rightarrow 2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-1}$	[57]
IN ₁₃	$\text{O}_2^+ + \text{O}^- \rightarrow \text{O}_2 + \text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[73]
IN ₁₄	$\text{OH}^+ + \text{O}^- \rightarrow \text{HO}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₅	$\text{H}_2\text{O}^+ + \text{O}^- \rightarrow \text{O} + \text{H}_2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₆	$\text{H}_3\text{O}^+ + \text{O}^- \rightarrow \text{H}_2\text{O} + \text{OH}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₇	$\text{H}_2^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}$	1×10^{-7}	[56]
IN ₁₈	$\text{H}_3^+ + \text{OH}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₁₉	$\text{O}^+ + \text{OH}^- \rightarrow \text{HO}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₂₀	$\text{O}_2^+ + \text{OH}^- \rightarrow \text{OH} + \text{O}_2$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₂₁	$\text{OH}^+ + \text{OH}^- \rightarrow 2\text{OH}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₂₂	$\text{H}_2\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OH}$	$2 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[56]
IN ₂₃	$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$	$4 \times 10^{-7} (\text{T}_\text{g}/300)^{-0.5}$	[21]

T_g is given in K.

T_e is given in eV.

$$^a \text{K}_{\text{D4}} = -2.82402 \times 10^{-11} \text{T}_\text{e} + 3.38111 \times 10^{-11} \text{T}_\text{e}^2 - 7.01504 \times 10^{-12} \text{T}_\text{e}^3 + 6.09826 \times 10^{-13} \text{T}_\text{e}^4 - 1.96671 \times 10^{-14} \text{T}_\text{e}^5$$

$${}^b_{\text{KD5}} = 1.67959 \times 10^{-10} T_e - 1.22568 \times 10^{-11} T_e^2 + 2.19508 \times 10^{-11} T_e^3 - 3.01892 \times 10^{-12} T_e^4 + 1.2549 \times 10^{-13} T_e^5$$

$${}^c_{\text{KN1}} = 7.51 \times 10^{-9} - 1.12 \times 10^{-9} T_e + 1.03 \times 10^{-10} T_e^2 - 4.15 \times 10^{-12} T_e^3 + 5.86 \times 10^{-14} T_e^4$$

$${}^d_{\text{KN2}} = 8.39 \times 10^{-9} + 3.02 \times 10^{-9} T_e - 3.80 \times 10^{-10} T_e^2 + 1.31 \times 10^{-11} T_e^3 + 2.42 \times 10^{-13} T_e^4 - 2.30 \times 10^{-14} T_e^5 + 3.55 \times 10^{-16} T_e^6$$

Table 2

Wall reactions for positive ions (neutralization) and neutrals (adsorption and recombination)

Wall neutralization		γ
K ₁	$\text{H}^+ + \text{Wall} \rightarrow \text{H}$	1
K ₂	$\text{H}_2^+ + \text{Wall} \rightarrow \text{H}_2$	1
K ₃	$\text{H}_3^+ + \text{Wall} \rightarrow \text{H}_2 + \text{H}$	1
K ₄	$\text{O}^+ + \text{Wall} \rightarrow \text{O}$	1
K ₅	$\text{O}_2^+ + \text{Wall} \rightarrow \text{O}_2$	1
K ₆	$\text{OH}^+ + \text{Wall} \rightarrow \text{OH}$	1
K ₇	$\text{H}_2\text{O}^+ + \text{Wall} \rightarrow \text{H}_2\text{O}$	1
K ₈	$\text{H}_3\text{O}^+ + \text{Wall} \rightarrow \text{H}_2\text{O} + \text{H}$	1
K ₉	$\text{HO}_2^+ + \text{Wall} \rightarrow \text{O}_2 + \text{H}$	1

	Heterogeneous reactions	γ	Ref.
W ₁	$\text{H} + \text{F}_s \rightarrow \text{H(s)}$	1	<i>e</i>
W ₂	$\text{H(s)} + \text{H} \rightarrow \text{H}_2 + \text{F}_s$	0.0035	[39]
W ₃	$\text{O} + \text{F}_s \rightarrow \text{O(s)}$	1	<i>f</i>
W ₄	$\text{O(s)} + \text{O} \rightarrow \text{O}_2 + \text{F}_s$	0.024	<i>f</i>
W ₅	$\text{OH} + \text{F}_s \rightarrow \text{OH(s)}$	1	<i>e</i>
W ₆	$\text{H(s)} + \text{O} \rightarrow \text{OH(s)}$	0.006	<i>f</i>
W ₇	$\text{H} + \text{O(s)} \rightarrow \text{OH(s)}$	0.002	<i>f</i>
W ₈	$\text{OH(s)} + \text{H} \rightarrow \text{H}_2\text{O} + \text{F}_s$	0.004	<i>f</i>
W ₉	$\text{OH} + \text{H(s)} \rightarrow \text{H}_2\text{O} + \text{F}_s$	0.005	<i>f</i>
W ₁₀	$\text{O(s)} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{F}_s$	0.00005	<i>f</i>
W ₁₁	$\text{O(^1D)} + \text{wall} \rightarrow \text{O}$	1	[57]
W ₁₂	$\text{O}_2(\text{a}) + \text{wall} \rightarrow \text{O}_2$	0.007	[74]

F_s stands for a free surface site and X(s) refers to adsorbed species.*e* : Adsorption of atoms and radicals is assumed to have a probability of 1*f* : Assumed in this work