A critical review of the reaction set for a low pressure oxygen processing discharge

by

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Abstract

This report contains a collection of reaction rate coefficients for the reactions in a low pressure oxygen processing discharge. The rate coefficient are reviewed, evaluated and revised. We assume the electron energy distribution to be Maxwellian and the fit to the rate coefficient for electron impact is valid for electron temperature in the range 1 – 7 eV.

1 Introduction

Oxygen plasmas play a crucial role in industrial applications as well as in atmospheric physics. Low pressure oxygen discharges have been applied in plasma processing for decades with applications such as ashing of photoresist (Tolliver, 1984), removing polymide and organic films and oxidation or deposition of thin film oxides (Carl et al., 1990). Oxygen discharges have also been proposed as a sterilization source (Bol'shakov et al., 2004). Low pressure oxygen discharges are weakly electronegative and the negative ions are expected to contribute significantly to the overall charge balance in oxygen plasma. The presence of negative ions alters the overall discharge phenomena with additional volume recombination loss and a particular spatial distribution of the negative ions which affects the ion flux loss to the wall (Lichtenberg et al., 1994; Chung, 1999). Oxygen is a simple diatomic gas that has been particularly well studied. However, even in a relatively simple oxygen discharge a number of species can be formed. Data sets for oxygen exists, including rate coefficients for many of the relevant reactions (Eliasson and Kogelshatz, 1986a; Kossyi et al., 1992; Slinker and Ali, 1982; Lieberman and Lichtenberg, 1994; Herron and Green, 2001). However, many of the cross sections for binary processes among these species have not been carefully measured or calculated (Lieberman and Lichtenberg, 1994, p. 251) and there is still some uncertainty regarding the absolute values of the electron impact cross sections. Furthermore, there are available collections of excitation and ionization cross sections for electron impact on atomic oxygen (Laher and Gilmore, 1990) and oxygen molecule (Itikawa et al., 1989). There have been several attempts to model the oxygen plasma in a low pressure (1 – 100 mTorr) inductive discharge (Lee et al., 1994; Lee and Lieberman, 1995; Patel, 1998; Gudmundsson et al., 2000a, 2001; Meeks et al., 1998; Kiehlbauch and Graves, 2003), parallel plate capacitive discharge in the range 5 – 200 mTorr (Stoffels et al., 1995), glows in the range of a few Torrs (Thompson, 1961; Gordiets et al., 1995), and in flowing rf discharges at pressures of few tens of Torr for $O_2(a^1\Delta_g)$ production (Stafford and Kushner, 2004). The most extensive collections (Eliasson and Kogelshatz, 1986a; Kossyi et al., 1992) were mainly intended for atmospheric research. Reaction sets for applications to low pressure processing discharges have also been compiled (Lieberman and Lichtenberg, 1994; Lee et al., 1994; Lee, 1995; Lee and Lieberman, 1995; Patel, 1998; Gudmundsson et al., 2000a, 2001; Meeks et al., 1998; Kiehlbauch and Graves, 2003). In a low pressure processing discharge O^- is found to be the dominant

negative ion (Gudmundsson et al., 2001) and ion-ion recombination is suggested to play an important role at pressures below 10 mTorr (Gudmundsson, 2004). The aim of this work is to evaluate and revise the rate coefficients in oxygen processing discharges, $\mathrm{T_e} \approx 1-7$ V and $T_\mathrm{i} \ll T_\mathrm{e}$, were T_e is the electron temperature and T_i is the ion temperature. The rate coefficients for electron impact excitation, electron impact ionization and elastic scattering of electrons for argon, oxygen atom and oxygen molecule are reviewed separately (Gudmundsson, 2002). Throughout the text we use the roman typeface symbol T for the voltage equivalent of the temperature. The rate coefficients for electron impact collisions were calculated assuming Maxwellian electron energy distribution and fit over an electron temperature range 1 – 7 V.

2 Rate coefficients

The rate coefficient for an electron impact collision is obtained by integrating the cross sections over an assumed Maxwellian distribution

$$k = \langle \sigma(v) v \rangle_v = 4\pi \int_0^\infty \sigma(v) v^3 f(v) dv \tag{1}$$

where σ is the collision cross section, v the electron velocity and

$$f(v) = \left(\frac{m_\mathrm{e}}{2\pi e T_\mathrm{e}} \right)^{3/2} \exp\left(-\frac{m_\mathrm{e} v^2}{2 e T_\mathrm{e}} \right) \tag{2}$$

is the Maxwellian velocity distribution, m_e is the electron mass, e is the electron charge and T_e is the electron temperature. Using the relationship for the velocity and kinetic energy of a particle

$$\mathcal{E} = \frac{m_\mathrm{e} v^2}{2e} \tag{3}$$

we find

$$f(\mathcal{E}) = \frac{2}{\sqrt{\pi}} \frac{1}{T_\mathrm{e}^{3/2}} \exp\left(-\frac{\mathcal{E}}{T_\mathrm{e}} \right) \tag{4}$$

to be the normalized Maxwellian electron energy distribution. Thus

$$k = \int_0^\infty \sigma(\mathcal{E}) \left(\frac{8 e T_\mathrm{e}}{\pi m_\mathrm{e}} \right)^{1/2} \frac{\mathcal{E}}{T_\mathrm{e}} \exp\left(-\frac{\mathcal{E}}{T_\mathrm{e}} \right) \frac{d\mathcal{E}}{T_\mathrm{e}} \tag{5}$$

is the rate coefficient. The rate coefficients where then fit to an Arrhenius form

$$k = A \mathrm{T}_\mathrm{e}^B \exp(-C/\mathrm{T_e}) \tag{6}$$

in the range 1 – 7 eV where A, B and C are constants.

2.1 Electron impact ionization of oxygen molecule

Electron impact ionization of the oxygen molecule in the ground state

$$e + O_2 \longrightarrow O_2^+ + 2e$$

has rate coefficient of

$$2.34 \times 10^{-15} T_e^{1.03} \exp(-12.29/T_e) \qquad m^3/s$$

is calculated from the cross section measured by Krishnakumar and Srivastava (1992). The commonly used rate coefficient for electron impact ionization of oxygen molecule $9.0 \times 10^{-16} T_e^2 \exp(-12.6/T_e)$ m^3/s (Lee et al., 1994; Lieberman and Lichtenberg, 1994) was based on the data set of Eliasson and Kogelshatz (1986a).

For electron impact ionization of the metastable oxygen molecule $O_2(a^1\Delta_g)$

$$e + O_2(a^1\Delta_g) \longrightarrow O_2^+ + 2e$$

we assume that the same process takes place except the threshold energy is lowered by 0.98 eV and the rate coefficient is

$$2.34 \times 10^{-15} T_e^{1.03} \exp(-11.31/T_e) \qquad m^3/s.$$

2.2 Electron impact dissociative ionization of oxygen molecule

Electron impact dissociative ionization of the oxygen molecule

$$e + O_2 \longrightarrow O^+ + O + 2e$$

has rate coefficient of

$$1.88 \times 10^{-16} T_e^{1.699} \exp(-16.81/T_e) \qquad m^3/s$$

which is calculated from the cross section measured by Krishnakumar and Srivastava (1992). This recently measured cross section is in excellent agreement with the early measurements of Rapp et al. (1965).

For electron impact dissociative ionization of the metastable oxygen molecule $O_2(a^1\Delta_g)$

$$e + O_2(a^1\Delta_g) \longrightarrow O^+ + O + 2e$$

we assume that the same process takes place except the threshold energy is lowered by 0.98 eV which gives a rate coefficient of

$$1.88 \times 10^{-16} T_e^{1.699} \exp(-15.83/T_e) \qquad m^3/s.$$

2.3 Ion-pair formation by electron impact of the oxygen molecule

The cross section for ion-pair formation by electron impact of the oxygen molecule

$$e + \mathrm{O_2} \longrightarrow \mathrm{O^+} + \mathrm{O^-} + e$$

was measured by Rapp and Briglia (1965). The rate coefficient based on these measurements is

$$7.1 \times 10^{-17} \mathrm{T_e^{0.5}} \exp(-17/\mathrm{T_e}) \qquad \mathrm{m^3/s}$$

given by Lieberman and Lichtenberg (1994).

2.4 Electron impact dissociation of the oxygen molecule

The lowest threshold energy for dissociation of the oxygen molecule is 4.5 eV. There is some uncertainty and controversy regarding the absolute values of the electron impact excitation and dissociation cross sections (Eliasson and Kogelshatz, 1986b; Cosby, 1993). There are several compilations of electron impact excitation cross sections in molecular oxygen (Eliasson and Kogelshatz, 1986a; Phelps, 2004; Itikawa et al., 1989). Here we use a dissociation cross sections that is inferred from the excitation cross sections. The electron impact dissociation of the oxygen molecule can follow three paths (Eliasson and Kogelshatz, 1986a,b; Cosby, 1993). Excitation from ground state favors a process leading to dissociation via electronic transition to the Herzberg states

$$e + \mathrm{O_2} \longrightarrow \mathrm{O_2}(\mathrm{A}^3\Sigma_u^+, \mathrm{A'}^3\Delta_u, c^1\Sigma_u^-) \longrightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P}) + e$$

which has a threshold of 6.0 V and rate coefficient of

$$6.86 \times 10^{-15} \exp(-6.29/\mathrm{T_e}) \qquad \mathrm{m^3/s},$$

and a process leading to dissociation via electronic transition to the Schuman-Runge states

$$e + \mathrm{O_2} \longrightarrow \mathrm{O_2}(\mathrm{B}^3\Sigma_u^-, \mathrm{B'}^3\Sigma_u^-, 2^3\Pi_u) \longrightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^1\mathrm{D}) + e$$

which has a threshold of 8.4 V and rate coefficient of

$$3.49 \times 10^{-14} \exp(-5.92/\mathrm{T_e}) \qquad \mathrm{m^3/s}.$$

The process

$$e + \mathrm{O}_2 \longrightarrow \mathrm{O}(^1\mathrm{D}) + \mathrm{O}(^1\mathrm{D}) + e$$

which has a threshold of 9.97 V and rate coefficient of

$$1.44 \times 10^{-16} \exp(-17.25/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}$$

is of less importance. The rate coefficients are calculated from the cross sectional data compiled by (Phelps, 2004) and fitted in the range 1 – 7 V (Gudmundsson, 2002).

The rate coefficient for dissociation of the meatstable oxygen molecule $\mathrm{O}_2(a^1\Delta_g)$ by electron impact

$$e + \mathrm{O}_2(a^1\Delta_g) \longrightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P}) + e$$

is found by applying threshold reduction to give

$$6.86 \times 10^{-15} \exp(-5.31/\mathrm{T_e})$$

and similarly for

$$e + \mathrm{O}_2(a^1\Delta_g) \longrightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^1\mathrm{D}) + e$$

the rate coefficient is

$$3.49 \times 10^{-14} \exp(-4.94/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}.$$

2.5 Electron impact ionization of the oxygen atom

The ionization potential of the oxygen atom is $\mathcal{E}_{\mathrm{iz}} = 13.61$ eV. The rate coefficient for the electron impact ionization of the oxygen atom

$$e + \mathrm{O}(^3\mathrm{P}) \longrightarrow \mathrm{O}^+ + 2e$$

was estimated to be

$$9.0 \times 10^{-15} \mathrm{T_e}^{0.7} \exp(-13.6/\mathrm{T_e})$$

by Lee et al. (1994). They list the report by Eliasson and Kogelshatz (1986a) as the source.

2.6 Dissociative electron attachment to the oxygen molecule

The maximum of the cross section for dissociative electron attachment to the metastable oxygen molecule $O_2(a^1\Delta_g)$ is roughly 3.5 times higher than starting from the ground state and was first measured by Burrow (1973). The cross sections for the dissociative electron attachment to the oxygen molecule have been more recently measured by Jaffke et al. (1992). The rate coefficients are calculated from these recent cross sections data. Dissociative electron attachment to the ground state oxygen molecule

$$e + O_2(^3\Sigma_g^-) \longrightarrow O_2^{*-}(^2\Pi_u) \longrightarrow O^- + O(^3P) \tag{7}$$

has a rate coefficient

$$1.07 \times 10^{-15} T_e^{-1.391} \exp(-6.26/T_e) \qquad m^3/s$$

compared to the earlier commonly used value of $8.8 \times 10^{-17} \exp(-4.4/T_e)$ m^3/s (Lieberman and Lichtenberg, 1994) which was based on data from Eliasson and Kogelshatz (1986a). This is close to the rate coefficient of $9.76 \times 10^{-16} T_e^{-1.358} \exp(-6.07/T_e)$ m^3/s found by by fitting the data given by Slinker and Ali (1982). It is known that the dissociative electron attachment to O_2 via the $O_2^{*-}(^2\Pi_u)$ resonance is strongly dependent on the neutral gas temperature (Henderson et al., 1969). The threshold energy shifts from ~ 4 eV at 300 K to ~ 1.2 eV at 1930 K. Furthermore, the magnitude of the cross section and the resonance width are increased with increased temperature.

Dissociative electron attachment to the singlet delta state oxygen molecule

$$e + O_2(a^1\Delta_g) \longrightarrow O_2^{*-}(^2\Pi_u) \longrightarrow O^- + O(^3P) \tag{8}$$

has a rate coefficient

$$4.19 \times 10^{-15} T_e^{-1.376} \exp(-5.19/T_e) \qquad m^3/s$$

compared to the earlier value of $2.28 \times 10^{-16} \exp(-2.29/T_e) m^3/s$ (Gudmundsson et al., 2001) which was based on the measured cross section by Burrow (1973) and fitted in the range 1 - 4.5 V. For dissociative attachment to the metastable oxygen molecule to create a metastable oxygen atom

$$e + O_2(a^1\Delta_g) \longrightarrow O_2^{*-}(^2\Sigma_u^+) \longrightarrow O^- + O(^1D)$$

the rate coefficient is

$$9.93 \times 10^{-16} \mathrm{T_e}^{-1.437} \exp(-7.44/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}.$$

For the dissociative electron attachment to metastable oxygen molecule $\mathrm{O}_2(b^1\Sigma_g^+)$

$$e + \mathrm{O}_2(b^1\Sigma_g^+) \longrightarrow \mathrm{O}^- + \mathrm{O}(^3\mathrm{P}) \tag{9}$$

we assume the same process as for reaction (8) with a reduced threshold energy and the rate coefficient is

$$4.19 \times 10^{-15} \mathrm{T_e}^{-1.376} \exp(-4.54/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}$$

Dissociative electron attachment to metastable oxygen molecules in the Herzberg states $\mathrm{O}_2(\mathrm{A}^3\Sigma_u^+, \mathrm{A}'^3\Delta_u, c^1\Sigma_u^-)$

$$e + \mathrm{O}_2(\mathrm{A}^3\Sigma_u^+, \mathrm{A}'^3\Delta_u, c^1\Sigma_u^-) \longrightarrow \mathrm{O}^- + \mathrm{O}(^3\mathrm{P}) \tag{10}$$

was investigated by (Hayashi and Kadota, 1999) who assembled the cross section for the process. A fit to the rate coefficient calculated from their cross section is

$$7.32 \times 10^{-16} \mathrm{T_e}^{-1.072} \exp(-0.468/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}.$$

2.7 Excitation and deexcitation of metastable oxygen molecules $\mathrm{O}_2(a^1\Delta_g)$ and $\mathrm{O}_2(b^1\Sigma_g^+)$ by electron impact

The excitation to the metastable oxygen molecule $\mathrm{O}_2(a^1\Delta_g)$ from the ground state

$$e + \mathrm{O}_2(X^3\Sigma_g^-) \longrightarrow \mathrm{O}_2(a^1\Delta_g) + e$$

has a rate coefficient of

$$1.37 \times 10^{-15} \exp(-2.14/\mathrm{T_e}) \qquad \mathrm{m}^3/\mathrm{s}$$

which is calculated from the cross section data compiled by Phelps (2004). The deexcitation of metastable oxygen molecule $\mathrm{O}_2(a^1\Delta_g)$ by electron impact

$$e + \mathrm{O}_2(a^1\Delta_g) \longrightarrow \mathrm{O}_2(X^3\Sigma_g^-) + e$$

has been assigned a rate coefficient $5.6 \times 10^{-15} \exp(-2.2/\mathrm{T_e})$ $\mathrm{m^3/s}$ (Lieberman and Lichtenberg, 1994). This rate coefficient is based on a fit to the data given by Eliasson and Kogelshatz (1986a) and Masek et al. (1978). Here we propose a rate coefficient using the principle of detailed balancing. The ground state of molecular oxygen is ${}^3\Sigma_g^-$ and has $3 \times 1 = 3$ degenerate states and the $a^1\Delta_g$ state has $1 \times 2 = 2$ degenerate states. The threshold energy for the reverse process is 0.977 eV. Thus $(3/2) \times 1.37 \times 10^{-15} \exp(-2.14/\mathrm{T_e}) \exp(0.977/\mathrm{T_e})$ gives a rate coefficient of

$$2.06 \times 10^{-15} \exp(-1.163/\mathrm{T_e}) \quad \mathrm{m^3/s}.$$

This is supported by the measurements of Hall and Trajmar (1975) which demonstrated that neglecting the different rotational levels of the two states can be justified when applying the principle of detailed balancing for the $X^3\Sigma_g^- \rightleftharpoons a^1\Delta_g$ transition.

The excitation to the metastable oxygen molecule $\mathrm{O_2}(b^1\Sigma_g^+)$ from the ground state

$$e + \mathrm{O_2}(X^3\Sigma_g^-) \longrightarrow \mathrm{O_2}(b^1\Sigma_g^+) + e$$

has a rate coefficient of

$$3.24 \times 10^{-16} \exp(-2.218/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

which is calculated from the cross section data compiled by Phelps (2004). The deexcitation of metastable oxygen molecule $\mathrm{O_2}(b^1\Sigma_g^+)$ by electron impact

$$e + \mathrm{O_2}(b^1\Sigma_g^+) \longrightarrow \mathrm{O_2}(X^3\Sigma_g^-) + e$$

is similarly estimated applying the principle of detailed balancing. The $b^1\Sigma_g^+$ state has $1 \times 1 = 3$ degenerate states and the threshold for the reverse process is 1.627 eV. Thus $(3/1) \times 3.24 \times 10^{-16} \exp(-2.218/\mathrm{T_e}) \exp(1.627/\mathrm{T_e})$ gives a rate coefficient of

$$9.72 \times 10^{-16} \exp(-0.591/\mathrm{T_e}) \quad \mathrm{m^3/s}.$$

The cross section for the $a^1\Delta_g \longrightarrow b^1\Sigma_g^+$ transition has been measured to be more than one order of magnitude larger at 4.5 eV than the excitation of the $b^1\Sigma_g^+$ from the ground state (Hall and Trajmar, 1975).

2.8 Excitation and deexcitation of metastable oxygen atom O(^{1}D) by electron impact

The rate coefficient for the excitation to the metastable oxygen atom O(^{1}D) by electron impact

$$e + \mathrm{O}(^3\mathrm{P}) \longrightarrow \mathrm{O}(^1\mathrm{D}) + e$$

is calculated using the excitation cross section given in the review by Laher and Gilmore (1990) as

$$4.54 \times 10^{-15} \exp(-2.36/\mathrm{T_e}) \quad \mathrm{m^3/s}.$$

The rate coefficient for the deexcitation of the metastable oxygen atom O(^{1}D) by electron impact

$$e + \mathrm{O}(^1\mathrm{D}) \longrightarrow \mathrm{O}(^3\mathrm{P}) + e$$

is estimated by applying the principle of detailed balancing. The ground state of the oxygen atom is ^{3}P and which has 9 degenerate states and the ^{1}D state has 5 degenerate states. The threshold energy for the reverse process is 1.96 eV. Thus $(9/5) \times 4.54 \times 10^{-15} \exp(-2.36/\mathrm{T_e}) \exp(1.96/\mathrm{T_e})$ gives a rate coefficient of

$$8.17 \times 10^{-15} \exp(-0.4/\mathrm{T_e}) \quad \mathrm{m^3/s}.$$

2.9 Electron impact detachment from O$^-$

The cross section for the electron impact detachment from O$^-$

$$e + \mathrm{O}^- \longrightarrow \mathrm{O} + 2e$$

was measured by Vejby-Christensen et al. (1996). Their measurements were carried out down to the low energy range of importance here and lower than the early measurements by Peart et al. (1979). From the cross section measured by Vejby-Christensen et al. (1996) the rate coefficient is found by assuming Maxwellian electron energy distribution and fit over an electron temperature range 1 – 7 V to give

$$5.47 \times 10^{-14} \mathrm{T_e}^{0.324} \exp(-2.98/\mathrm{T_e}) \qquad \mathrm{m^3/s}.$$

2.10 Charge transfer

The rate coefficient for the charge transfer

$$O^+ + O_2 \longrightarrow O(^3P) + O_2^+$$

is given by Eliasson and Kogelshatz (1986a) as

$$2 \times 10^{-17}(300/T_g)^{1/2} \qquad m^3/s.$$

2.11 Mutual neutralization of oxygen ions

Recent measurements of the mutual neutralization cross sections in oxygen have suggested that the rate coefficients commonly used are significantly overestimated (Hayton and Peart, 1993; Padgett and Peart, 1998; Gudmundsson and Lieberman, 2004). This claim is further supported by a measurement of the rate coefficient for $O^- + O^+$ (Ishikawa et al., 1998). The commonly used rate coefficients for mutual neutralization of O^+ by O^-

$$O^- + O^+ \longrightarrow O + O \tag{11}$$

are $2.7 \times 10^{-13}(300/T_i)^{1/2}$ m^3/s (Eliasson and Kogelshatz, 1986a; Lee et al., 1994) and $2.0 \times 10^{-13}(300/T_i)^{1/2}$ m^3/s (Kossyi et al., 1992; Eliasson and Kogelshatz, 1986a; Gordiets et al., 1995; Niles, 1970) were T_i is the ion temperature in Kelvins. These rate coefficients are consistent with the measurements of Olson et al. (1970) that give an experimental value of 2.8×10^{-13} m^3/s and a theoretical value of 1.1×10^{-13} m^3/s at 300 K. Later Olson (1972) used the Landau-Zener method to calculate the upper limit reaction rate and the energy dependence of the total cross section for the ion-ion recombination reaction of $O^- + O^+$ and $O^- + O_2^+$ in the energy range 0.03 – 100 eV. This theoretical work predicts equal cross sections (to within ± 10 %) for both $O^- + O^+$ and $O^- + O_2^+$ mutual neutralization and agreed very well with the early measurements. More recent measurements of the cross section by Hayton and Peart (1993) are a factor of 6 – 10 times lower. Their measurement is supported by a new theoretical calculation of the cross section by Zhou and Dickinson (1997) which is in excellent agreement with the cross section measured. Unfortunately, the measured and calculated data do not go below 1 eV.

We propose a new estimate of the recombination rate coefficient by assuming the low energy scaling seen by Olson (1972), is qualitatively correct for energies below 1 eV.

This scaling is consistent with the classical Coulomb focusing expected at low energies. Thus, we use the cross section calculated by Olson (1972) and scale it down by a factor of 6.4 to fit the measured data of Hayton and Peart (1993). We then extrapolated the cross section down to 0.001 eV. Using this cross section we calculate a rate coefficient by assuming Maxwellian energy distribution of the ions in the range 300 K $\leq T_{\rm i} \leq$ 1200 K. The rate coefficient for the mutual neutralization of $O^- + O^+$ is thus found to be

$$4.0 \times 10^{-14} \left(\frac{300}{T_{\rm i}}\right)^{0.43} \qquad {\rm m}^3/{\rm s}.$$

The rate coefficients commonly used for mutual neutralization of O_2^+ by O^-

$$O^- + O_2^+ \longrightarrow O + O_2 \tag{12}$$

and

$$O^- + O_2^+ \longrightarrow 3O \tag{13}$$

are $2.0 \times 10^{-13}(300/T_{\rm i})^{1/2}$ m^3/s (Kossyi et al., 1992; Eliasson and Kogelshatz, 1986a; Gordiets et al., 1995; Niles, 1970) or 0.96×10^{-13} m^3/s (Eliasson and Kogelshatz, 1986a) for the former reaction and 1.0×10^{-13} m^3/s (Kossyi et al., 1992; Eliasson and Kogelshatz, 1986a; Gordiets et al., 1995) for the latter. These values are consistent with the early measurements of Moseley et al. (1972), which reported a value of 1.0×10^{-13} m^3/s at 300 K. Recent measurements by Padgett and Peart (1998) suggest that the cross section is a factor of five lower than the earlier measurements. Their measurements indicate that reactions (12) and (13) each contribute roughly 50 % at 120 eV. Since their measurements are made for energies above 6 eV we use the cross section calculated by Olson (1972) and scale it down by a factor of 5.0 to fit the measured data of Padgett and Peart (1998). We then extrapolated the cross section down to 0.001 eV. Using this cross section we calculate a rate coefficient by assuming Maxwellian energy distribution of the ions. The rate coefficient for the mutual neutralization of $O^- + O_2^+$ is thus

$$5.2 \times 10^{-14} \left(\frac{300}{T_{\rm i}}\right)^{0.44} \qquad {\rm m}^3/{\rm s}$$

and is valid in the range 300 K $\leq T_{\rm i} \leq$ 1200 K. The data of Eliasson and Kogelshatz (1986a) indicates a 50 – 70 % range as the ratio of reactions (12) and (13). Based on this and the Padgett and Peart (1998) data, we assume that each reaction contributes 50 %

to the reaction rate, we propose a rate coefficient of $2.6 \times 10^{-14}(300/T_{\rm i})^{0.44}$ for each of the reactions (12) and (13).

The ion-ion mutual neutralization cross section for $O_2^+ + O_2^-$ was measured by Peterson et al. (1971). They measured the rate coefficient to be $(4.2 \pm 13) \times 10^{-13}$ m^3/s. The commonly used rate coefficient for the reactions

$$O_2^- + O_2^+ \longrightarrow O_2 + O_2 \tag{14}$$

and

$$O_2^- + O^+ \longrightarrow O + O_2 \tag{15}$$

are $2.7 \times 10^{-13}(300/T_{\rm i})^{1/2}$ m^3/s (Kossyi et al., 1992; Lieberman and Lichtenberg, 1994) and 2.01×10^{-13} m^3/s at 300 K for reaction (14) (Eliasson and Kogelshatz, 1986a). For

$$O_2^- + O_2^+ \longrightarrow O_2 + 2O \tag{16}$$

the rate coefficients are 1.01×10^{-13} m^3/s and 2.01×10^{-12} m^3/s (Eliasson and Kogelshatz, 1986a). Based on the above discussion on mutual neutralization involving the O^- ion these values are probably an overestimate.

2.12 Dissociative recombination of O_2^+-ions with electrons

The rate coefficient for the recombination of O_2^+-ions with electrons

$$e + O_2^+ \longrightarrow O + O \tag{17}$$

has been measured by Mehr and Biondi (1969) over the entire range $300 \leq T_{\rm e} \leq 5000$ K. They find the rate coefficient to vary as $T_{\rm e}^{-0.56}$ in the range $1200 \leq T_{\rm e} \leq 5000$ K and as $T_{\rm e}^{-0.7}$ in the range $300 \leq T_{\rm e} \leq 1200$ K, where the electron temperature is given in Kelvins. For $T_{\rm e} = 300$ K they report a value of $(1.95 \pm 0.2) \times 10^{-13}$ m^3/s. This value has been confirmed by more recent measurements (Gougousi et al., 1997; Church and Smith, 1978) and is commonly accepted (Eliasson and Kogelshatz, 1986a). Mul and McGowan (1979) measured the cross section for the recombination of O_2^+-ions with electrons and calculate a rate coefficient that shows a $T_{\rm e}^{-0.5}$ dependence and is in good agreement with the early measurements of Mehr et al. (Kasner and Mehr, 1968; Mehr and Biondi, 1969). The rate coefficient of $2 \times 10^{-13}(300/T_{\rm e})$ m^3/s is valid in the range $205 \leq T_{\rm e} \leq 690$ K (Kasner

and Mehr, 1968; Kossyi et al., 1992; Kozlov et al., 1988), the conditions expected in the upper atmosphere where $T_e \approx T_i$. These values are also consistent with a theoretical calculation by Guberman (1988) that gives $2.21 \times 10^{-13} \times (T_e/300)^{-0.46}$ m^3/s for the reaction $e + O_2^+ \longrightarrow O(^3P) + O(^1D)$ in the range $100 \leq T_e \leq 3000$ K. The rate coefficient for $O(^1S)$ creation by the dissociative recombination of O_2^+-ions with electrons has much lower yield (Guberman and Giusti-Suzor, 1991).

For low pressure discharges with $T_e \gg 1000$ K the rate coefficient of $2 \times 10^{-13}(300/T_e)$ m^3/s is not appropriate. We assume a rate coefficient $k = k_0 T_e^{-0.5}$ consistent with Mul and McGowan (1979) and determine k_0 by fitting to the data measured by Mehr and Biondi (1969) from 1700 K to 5000 K. We propose a rate coefficient of

$$2.2 \times 10^{-14} \times T_e^{-0.5} \qquad \text{m}^3/\text{s}$$

for the reaction

$$e + O_2^+ \longrightarrow O(^3P) + O(^1D)$$

where T_e is given in electron volts, for the conditions $1 < T_e < 7$ V expected in processing discharges.

2.13 Associative detachment by oxygen atom

The rate coefficient for associative detachment by oxygen atom

$$O^- + O(^3P) \longrightarrow O_2 + e$$

was measured by Belostotsky et al. (2004) as

$$(1.6 \pm 0.3) \times 10^{-16} \qquad \text{m}^3/\text{s}$$

and by Fehsenfeld et al. (1967) as 1.9×10^{-16} m^3/s, Phelps (1969) lists a value of 1.4×10^{-16} m^3/s, Sommerer and Kushner (1992) a value of 3.0×10^{-16} m^3/s, and Kossyi et al. (1992) a value of 5×10^{-16} m^3/s.

2.14 Detachment by molecular oxygen in ground state $O_2(X^3\Sigma_g^-)$

The cross section for the electron detachment by molecular oxygen in ground state $O_2(X^3\Sigma_g^-)$

$$O^- + O_2 \longrightarrow O + O_2 + e$$

was measured by Roche and Goodyear (1969) in the range 3 – 100 eV. The threshold for the process is 1.46 eV which is consistent with the accepted value of the electron affinity of the oxygen atom. It is pointed out by Vahedi and Surendra (1995) that if the negative ion temperature is of the order of the gas temperature the negative ions are not likely to get over the threshold energy for detachment.

2.15 Detachment by the metastable molecular oxygen $O_2(a^1\Delta_g)$

The rate coefficient for the detachment by collision of oxygen ion O^- with metastable oxygen molecules $O_2(a^1\Delta_g)$ or the reaction

$$O^- + O_2(a^1\Delta_g) \longrightarrow \text{products}$$

was recently measured by Belostotsky et al. (2004) as $1.3 \pm 0.3 \times 10^{-16}$ m^3/s. This value is somewhat lower than the earlier measurements of Fehsenfeld et al. (1969) which reported a value of 3×10^{-16} m^3/s. These early measurements were accompanied by a factor of ten uncertainty. Another recent measurement by Upschulte et al. (1994) gives a value of 3.3×10^{-17} m^3/s. They assign this rate coefficient for the reaction $O^- + O_2(a^1\Delta_g) \longrightarrow O_3 + e$. This recent measurement is considered to have an uncertainty of $+100\%/-50\%$ and is about a factor of ten lower than the other two measurements. Thus we can assign for the reaction

$$O^- + O_2(a^1\Delta_g) \longrightarrow O_2^- + O \tag{18}$$

a rate coefficient of

$$1.0 \times 10^{-16} \qquad \text{m}^3/\text{s}$$

and for the reaction

$$O^- + O_2(a^1\Delta_g) \longrightarrow O_3 + e \tag{19}$$

a rate coefficient of

$$3.3 \times 10^{-17} \qquad \text{m}^3/\text{s}.$$

For the reaction

$$O_2^- + O_2(a^1\Delta_g) \longrightarrow 2O_2 + e$$

a rate coefficient of

$$2.0 \times 10^{-16} \qquad \text{m}^3/\text{s}$$

was measured by Fehsenfeld et al. (1969) compared to a more recent value of 2.7×10^{-17} m^3/s measured by Upschulte et al. (1994).

2.16 Detachment by the metastable molecular oxygen $O_2(b^1\Sigma_g^+)$

The reaction rate coefficient for detachment by the metastable molecular oxygen $O_2(b^1\Sigma_g^+)$

$$O^- + O_2(b^1\Sigma_g^+) \longrightarrow O + O_2 + e$$

was estimated by Aleksandrov (1978) to be

$$6.9 \times 10^{-16} \qquad \text{m}^3/\text{s}.$$

2.17 Pooling of the metastable molecular oxygen $O_2(a^1\Delta_g)$

The pooling reaction of two singlet oxygen molecules to form the metastable $O_2(b^1\Sigma_g^+)$

$$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \longrightarrow O_2(b^1\Sigma_g^+) + O_2(X^3\Sigma_g^-) \tag{20}$$

was investigated by Derwent and Thrush (1971) which give a rate coefficient of 2×10^{-17} m^3/s at 300 K. Based on a number of measurements at various temperatures Cohen and Westberg (1983) recommend a rate coefficient of

$$1.8 \times 10^{-24} \, (T_\text{g}/300)^{3.8} \exp(700/T_\text{g}) \quad \text{m}^3/\text{s}$$

Two singlet oxygen molecules can also undergo simultaneous transition to the ground state giving up their energy as a single quantum of radiation

$$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \longrightarrow O_2(X^3\Sigma_g^-) + O_2(X^3\Sigma_g^-) + h\nu \tag{21}$$

which produces photons of wavelength 0.634 μm (Gray and Ogryzlo, 1969; Derwent and Thrush, 1971; Fisk and Hays, 1981; Borrell and Rich, 1983). Based on the early measurements Borrell and Rich (1983) recommend a rate coefficient of

$$5.5 \times 10^{-29} \, (T_\text{g}/300)^{0.5} \quad \text{m}^3/\text{s}$$

in the range 300 – 1000 K.

Other reactions for the quenching of the metastable oxygen molecule $O_2(a^1\Delta_g)$ are

$$O_2(a^1\Delta_g) + O(^3P) \longrightarrow O_2(^3\Sigma_g^-) + O(^3P)$$

with a rate coefficient given by Clark and Wagner (1969) as

$$1.3 \times 10^{-22} \quad \mathrm{m^3/s}$$

and 7.0×10^{-22} $\mathrm{m^3/s}$ by Kossyi et al. (1992), and the reaction

$$O_2(a^1\Delta_g) + O_2(^3\Sigma_g^-) \longrightarrow O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$$

with a rate coefficient given by Kossyi et al. (1992) as

$$2.2 \times 10^{-24}(T_g/300)^{0.8} \quad \mathrm{m^3/s}$$

an as 2.4×10^{-24} $\mathrm{m^3/s}$ by Clark and Wagner (1969).

2.18 Dissociative electron attachment to ozone

For dissociative electron attachment to ozone

$$e + O_3 \longrightarrow O^- + O_2 \tag{22}$$

we use the cross section measured by Senn et al. (1999) and find a rate coefficient

$$2.12 \times 10^{-15} T_e^{-1.058} \exp(-0.93/T_e) \qquad \mathrm{m^3/s}$$

and for the reaction

$$e + O_3 \longrightarrow O_2^- + O \tag{23}$$

we use the cross section measured by Rangwala et al. (1999) and find a rate coefficient

$$9.75 \times 10^{-14} T_e^{-1.309} \exp(-1.007/T_e) \qquad \mathrm{m^3/s}$$

The cross section measured by Senn et al. (1999) for this process is in good agreement with the cross section measured by Rangwala et al. (1999). The electron attchment rate coefficient was measured by Van Doren et al. (2003) assuming that reaction (22) is the dominating process. They report a value of 9×10^{-18} $\mathrm{m^3/s}$ at 300 K and 51×10^{-18} $\mathrm{m^3/s}$ at 550 K. These values dissagree strongly with the measurements by Senn et al. (1999). Cicman et al. (2003) evaluated the rate coefficients for the dissociative electron attachment to ozone in the range 0.001 – 10 eV. They report a value of 2×10^{-16} $\mathrm{m^3/s}$ at 300 K and 1×10^{-15} $\mathrm{m^3/s}$ at 3 eV for reaction (22). In an early measurement Fehsenfeld et al. (1967) estimated the rate coefficient to be 4×10^{-17} $\mathrm{m^3/s}$ at 300K.

3 The oxygen reaction set

The basic reaction set for the oxygen discharge is listed in table 1. The rate coefficients for electron impact collisions were calculated assuming Maxwellian electron energy distribution and fit over an electron temperature range 1 – 7 eV.

The lowest threshold energy for dissociation of the oxygen molecule is 4.5 eV. However, the lowest lying metastable state of the oxygen molecule $O_2(a^1\Delta_g)$ has a threshold energy of 0.98 eV above the ground state and has lifetime of $\sim$ 4400 s (Newman et al., 2000). Another metastable state $O_2(b^1\Sigma_g^+)$ is located 1.627 eV above the ground state and has lifetime of 7.1 s. The metastable oxygen molecule $O_2(a^1\Delta_g)$ is known to be an important specie in the oxygen discharge. Our earlier modelling work indicates that the $O_2(a^1\Delta_g)$ density is of the order of 10 % of the total molecular oxygen density (Gudmundsson et al., 2000b). The reactions involving the metastable oxygen molecule $O_2(a^1\Delta_g)$ are listed in table 2.

The oxygen discharge is known to be weakly electronegative and the dominant negative ion is O^-. The reactions involving the negative oxygen ion O^- are listed in table 3. The most important reactions for creation of O^- are dissociative attachment from the ground state and the singlet delta state of the oxygen molecule, reactions (7) and (8), respectively (Gudmundsson et al., 2001). The negative ion is mainly lost through detachment with electrons at low pressures and oxygen atoms at higher pressures, but ion-ion recombination plays an important role in particular at low pressure (Gudmundsson, 2004). The density of the negative ion O_2^- is much smaller than the density of the negative ion O^- in low pressure processing discharge. The reactions involving the negative oxygen ion O_2^- are listed in table 4.

The metastable oxygen atom $O(^1D)$ is long lived, with radiative lifetime of 148 s. The reactions involving the metastable oxygen atom $O(^1D)$ are listed in table 5. The reactions involving the creation and destruction of ozone and O_3^- are listed in table 6. Ozone is almost entirely created through detachment by collision of O^- with the metastable oxygen molecule $O_2(a^1\Delta_g)$ (reaction (19)). The creation of O_2^- is mainly through dissociative attachment of ozone O_3. The creation of O_2^- is thus greatly influenced by this detachment process and neglecting the detachment has a significant influence on the density of O_2^- ions (Gudmundsson et al., 2000b, 2001).

Table 7 lists selected three body reactions. We do not expect these reactions to be of

great importance at low pressures, however.

The rate coefficients involving the metastable molecular oxygen $O_2(b^1\Sigma_g^+)$ and the highly excited Herzberg states $O_2(A^3\Sigma_u^+, A'^3\Delta_u, c^1\Sigma_u^-)$ (or O_2^H) are listed in table 8. The $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ states lie 0.98 eV and 1.63 eV above the ground state $O_2(^3\Sigma_g^-)$, respectively. The Herzberg states lie 4.05 – 4.34 eV above the ground state. Unfortunately there appear to be no cross sections for dissociation and ionization from the $O_2(b^1\Sigma_g^+)$ and the Herzberg states. The rate coefficients for quenching og the $O_2(A^3\Sigma_u^+)$ state by O, O_2 and Ar were determined by Kenner and Ogryzlo (1980). Reaction rate coefficients for dissociation and ionization from the metastables are estimated using the ground-state rate coefficient with the threshold shifted by the metastable excitation energy. The ground state reactions used in calculating the threshold shifted reaction rate coefficient are listed as reactions I – VI in table 8.

The rate coefficients for the excitation of the oxygen atom are listed in table 9 and the rate coefficients for the excitation of the oxygen molecule are listed in table 10 are taken from Gudmundsson (2002).

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Table 1: The basic reaction set for the oxygen discharge.

Reaction	Rate coefficient [m^3/s]	Ref.
$e+O_2 \longrightarrow O_2^+ + 2e$	$2.34 \times 10^{-15} T_e^{1.03} \exp(-12.29/T_e)$	(Krishnakumar and Srivastava, 1992)
$e+O_2 \longrightarrow O(^3P)+O^-$	$1.07 \times 10^{-15} T_e^{-1.39} \exp(-6.26/T_e)$	(Jaffke et al., 1992)
$e+O(^3P) \longrightarrow O^+ + 2e$	$9.0 \times 10^{-15} T_e^{0.7} \exp(-13.6/T_e)$	(Lee et al., 1994)
$e+O_2 \longrightarrow O(^3P)+O(^3P)+e$	$6.86 \times 10^{-15} \exp(-6.29/T_e)$	(Phelps, 2004)
$e+O_2 \longrightarrow O(^3P)+O^+ + 2e$	$1.88 \times 10^{-16} T_e^{1.699} \exp(-16.81/T_e)$	(Krishnakumar and Srivastava, 1992)
$O^+ + O_2 \longrightarrow O(^3P) + O_2^+$	$2 \times 10^{-17} (300/T_g)^{1/2}$	(Eliasson and Kogelshatz, 1986a)

T_g [K]
T_e [eV]

Table 2: The reactions involving the metastable oxygen molecule $O_2(a^1\Delta_g)$.

Reaction	Rate coefficient [m^3/s]	Ref.
$e+ O_2 \longrightarrow O_2(a^1\Delta_g) + e$	$1.37 \times 10^{-15} \exp(-2.14/T_e)$	(Phelps, 2004)
$e+O_2(a^1\Delta_g) \longrightarrow O_2^+ + 2e$	$2.34 \times 10^{-15} T_e^{1.03} \exp(-11.31/T_e)$	(Krishnakumar and Srivastava, 1992)
$e+O_2(a^1\Delta_g) \longrightarrow O(^3P)+O^+ + 2e$	$1.88 \times 10^{-16} T_e^{1.699} \exp(-15.83/T_e)$	Threshold reduced
$e+ O_2(a^1\Delta_g) \longrightarrow O^-+O(^3P)$	$4.19 \times 10^{-15} T_e^{-1.376} \exp(-5.19/T_e)$	(Jaffke et al., 1992)
$e+ O_2(a^1\Delta_g) \longrightarrow O^-+O(^1D)$	$9.93 \times 10^{-16} T_e^{-1.437} \exp(-7.44/T_e)$	(Jaffke et al., 1992)
$e+ O_2(a^1\Delta_g) \longrightarrow O_2(^3\Sigma_g^-) + e$	$2.06 \times 10^{-15} \exp(-1.163/T_e)$	Detailed balancing
$e + O_2(a^1\Delta_g) \longrightarrow O(^3P) + O(^3P) + e$	$6.96 \times 10^{-15} \exp(-5.31/T_e)$	Threshold reduced
$e + O_2(a^1\Delta_g) \longrightarrow O(^3P) + O(^1D) + e$	$3.49 \times 10^{-14} \exp(-4.94/T_e)$	Threshold reduced
$O^-+ O_2(a^1\Delta_g) \longrightarrow O_2^-+O(^3P)$	1.0×10^{-16}	(Belostotsky et al., 2004)
$O_2(a^1\Delta_g) + O(^3P) \longrightarrow O_2 + O(^3P)$	1.3×10^{-22}	(Clark and Wagner, 1969)
$O_2(a^1\Delta_g) + O_2(^3\Sigma_g^-) \longrightarrow 2\ O_2(^3\Sigma_g^-)$	$2.2 \times 10^{-24} (T_g/300)^{0.8}$	(Kossyi et al., 1992)
$2\ O_2(a^1\Delta_g) \longrightarrow O_2(b^1\Sigma_g^+)+O_2(^3\Sigma_g^-)$	$1.8 \times 10^{-24} (T_g/300)^{3.8} \exp(700/T_g)$	(Cohen and Westberg, 1983)
$2\ O_2(a^1\Delta_g) \longrightarrow 2\ O_2(^3\Sigma_g^-)$	$5.5 \times 10^{-29} (T_g/300)^{0.5}$	(Borrell and Rich, 1983)

T_g [K]
T_e [eV]

Table 3: The reactions involving the negative oxygen ion O^-.

Reaction	Rate coefficient [m^3/s]	Ref.
$O^-+O_2^+ \longrightarrow O(^3P)+O_2$	$2.6 \times 10^{-14} (300/T_g)^{0.44}$	(Gudmundsson and Lieberman, 2004)
$O^-+O_2^+ \longrightarrow 3\ O(^3P)$	$2.6 \times 10^{-14} (300/T_g)^{0.44}$	(Gudmundsson and Lieberman, 2004)
$O^-+O^+ \longrightarrow O(^3P)+O(^3P)$	$4.0 \times 10^{-14} (300/T_g)^{0.43}$	(Gudmundsson and Lieberman, 2004)
$e+O^- \longrightarrow O(^3P)+2e$	$5.47 \times 10^{-14} T_e^{0.324} \exp(-2.98/T_e)$	(Vejby-Christensen et al., 1996)
$O(^3P) +O^- \longrightarrow O_2(^3\Sigma_g^-) + e$	1.6×10^{-16}	(Belostotsky et al., 2004)
$e+O_2 \longrightarrow O^-+O^+ + e$	$7.1 \times 10^{-17} T_e^{0.5} \exp(-17/T_e)$	(Lieberman and Lichtenberg, 1994)
$O^-+O_2(a^1\Delta_g) \longrightarrow O_3 + e$	3.3×10^{-17}	(Upschulte et al., 1994)

T_g [K]
T_e [eV]

Table 4: The reactions involving the negative oxygen ion O_2^-.

Reaction	Rate coefficient [m^3/s]	Ref.
$O_2^- + O_2(a^1\Delta_g) \longrightarrow 2O_2 + e$	2.0×10^{-16}	(Fehsenfeld et al., 1969)
$O_2^- + O(^3P) \longrightarrow O^- + O_2$	3.31×10^{-16}	(Eliasson and Kogelshatz, 1986a)
$O_2^- + O_2^+ \longrightarrow O_2 + O_2$	$2.01 \times 10^{-13}(300/T_g)^{1/2}$	(Eliasson and Kogelshatz, 1986a)
$O_2^- + O^+ \longrightarrow O_2 + O(^3P)$	$2.7 \times 10^{-13}(300/T_g)^{1/2}$	(Kossyi et al., 1992)
$O_2^- + O_2^+ \longrightarrow O_2 + 2O(^3P)$	$1.01 \times 10^{-13}(300/T_g)^{1/2}$	(Eliasson and Kogelshatz, 1986a)
T_g [K]		
T_e [eV]		

Table 5: The reactions involving the metastable oxygen atom $O(^1D)$.

Reaction	Rate coefficient [m^3/s]	Ref.
$e + O_2 \longrightarrow O(^3P) + O(^1D) + e$	$3.49 \times 10^{-14} \exp(-5.92/T_e)$	(Phelps, 2004)
$e + O_2 \longrightarrow O(^1D) + O(^1D) + e$	$1.44 \times 10^{-16} \exp(-17.25/T_e)$	(Phelps, 2004)
$O_2 + O(^1D) \longrightarrow O_2(a^1\Delta_g) + O(^3P)$	1.0×10^{-18}	(Eliasson and Kogelshatz, 1986a)
$e + O_2^+ \longrightarrow O(^3P) + O(^1D)$	$2.2 \times 10^{-14} T_e^{-0.5}$	(Gudmundsson and Lieberman, 2004)
$e + O(^3P) \longrightarrow O(^1D) + e$	$4.54 \times 10^{-15} \exp(-2.36/T_e)$	(Gudmundsson, 2002)
$O(^1D) + O_2 \longrightarrow O(^3P) + O_2$	$2.56 \times 10^{-17} \exp(67/T_g)$	(Eliasson and Kogelshatz, 1986a)
$O(^1D) + O(^3P) \longrightarrow 2O(^3P)$	8.0×10^{-18}	(Eliasson and Kogelshatz, 1986a)
$e + O(^1D) \longrightarrow O^+ + 2e$	$9 \times 10^{-15} T_e^{0.7} \exp(-11.6/T_e)$	(Lee et al., 1994)
$e + O(^1D) \longrightarrow e + O(^3P)$	$8.17 \times 10^{-15} \exp(-0.4/T_e)$	Detailed balancing
T_g [K]		
T_e [eV]		

Table 6: The reactions involving the creation and destruction of ozone and O_3^-.

Reaction	Rate coefficient [m^3/s]	Ref.
$e+O_3 \longrightarrow O^- + O_2$	$2.12 \times 10^{-15} T_e^{-1.06} \exp(-0.93/T_e)$	(Senn et al., 1999)
$e+O_3 \longrightarrow O + O_2^-$	$9.758 \times 10^{-14} T_e^{-1.309} \exp(-1.007/T_e)$	(Rangwala et al., 1999)
$O^- + O_2 \longrightarrow O_3 + e$	5.0×10^{-21}	(Kossyi et al., 1992)
$O^+ + O_3 \longrightarrow O_2^+ + O_2$	1.0×10^{-16}	(Kossyi et al., 1992)
$O + O_3 \longrightarrow 2O_2$	$1.81 \times 10^{-17} \exp(-2300/T_g)$	(Eliasson and Kogelshatz, 1986a)
$O^- + O_3 \longrightarrow O_3^- + O$	5.3×10^{-16}	(Eliasson and Kogelshatz, 1986a)
$O_3^- + O(^3P) \longrightarrow O_2^- + O_2$	1.0×10^{-16}	(Eliasson and Kogelshatz, 1986a)
$O_3^- + O\ (^3P) \longrightarrow 2O_2 + e$	3.0×10^{-16}	(Eliasson and Kogelshatz, 1986a)
$O_3^- + O_2^+ \longrightarrow O_2 + O_3$	$2 \times 10^{-13} (300/T_g)^{1/2}$	(Eliasson and Kogelshatz, 1986a)
$O_3^- + O_2^+ \longrightarrow 2O + O_3$	$1.01 \times 10^{-13} (300/T_g)^{1/2}$	(Eliasson and Kogelshatz, 1986a)
$O_2^- + O_3 \longrightarrow O_2 + O_3^-$	4×10^{-16}	(Eliasson and Kogelshatz, 1986a)
$O_2^- + O(^3P) \longrightarrow O_3 + e$	3.3×10^{-16}	(Fehsenfeld et al., 1967)
$O_3 + O_2 \longrightarrow O_2 + O_2 + O$	$7.26 \times 10^{-16} \exp(-11400/T_g)$	(Eliasson and Kogelshatz, 1986a)
$e + O_3 \longrightarrow O_2 + O(^3P) + e$	1.0×10^{-14}	(Eliasson and Kogelshatz, 1986a)
$O_2(a^1\Delta_g) + O_3 \longrightarrow 2\ O_2 + O(^3P)$	$6.01 \times 10^{-17} \exp(-2853/T_g)$	(Jeong et al., 2000)
T_g [K]		
T_e [eV]		

Table 7: Selected three body reactions.

Reaction	Rate coefficient [m^6/s]	Ref.
$e + O(^3P) + O_2 \longrightarrow O_2^- + O(^3P)$	1×10^{-43}	(Eliasson and Kogelshatz, 1986a)
$e+O_2+O_2 \longrightarrow O_2^- + O_2$	$2.26 \times 10^{-42} (300/T_g)^{1/2}$	(Shimamori and Fessenden, 1981)
$e + e + O^+ \longrightarrow e + O(^3P)$	$7.9 \times 10^{-39}/T_e^{4.5}$	(Eliasson and Kogelshatz, 1986a)
$e+O_2 + O^+ \longrightarrow O(^3P) + O_2$	1×10^{-38}	(Eliasson and Kogelshatz, 1986a)
$O^- + O_2 + O_2 \longrightarrow O_3^- + O_2$	$1.11 \times 10^{-42} (300/T_g)$	(Eliasson and Kogelshatz, 1986a)
$O^- + O^+ + O_2 \longrightarrow O_2 + O_2$	$2.1 \times 10^{-37} (300/T_g)^{2.5}$	(Eliasson and Kogelshatz, 1986a)
$O + O_2 + O_2 \longrightarrow O_3 + O_2$	$6.9 \times 10^{-46} (300/T_g)^{1.25}$	(Eliasson and Kogelshatz, 1986a)
$e + O(^3P) + O_2 \longrightarrow O^- + O_2$	1×10^{-43}	(Eliasson and Kogelshatz, 1986a)
$2O_2 + O(^3P) \longrightarrow O_3 + O_2$	$6.9 \times 10^{-40} (300/T_g)^{-1.25}$	(Eliasson and Kogelshatz, 1986a)
$O_2^- + 2O(^3P) \longrightarrow O_3 + O(^3P)$	3.82×10^{-40}	(Eliasson and Kogelshatz, 1986a)
$O^- + O_2^+ + O_2 \longrightarrow O_2 + O_3$	$2.01 \times 10^{-37} (300/T_g)^{2.5}$	(Eliasson and Kogelshatz, 1986a)
$O + O + O_2 \longrightarrow O_2^H + O_2$	1.2×10^{-46}	(Kenner and Ogryzlo, 1980)
$O_2(a^1\Delta_g) + O(^3P) + O_2 \longrightarrow 2\ O_2 + O(^3P)$	1×10^{-44}	(Vasiljeva et al., 2004)
$O + O + O \longrightarrow O_2(a^1\Delta_g) + O$	$1.93 \times 10^{-47} (300/T_g)^{0.63}$	(Gordiets et al., 1995)
$O + O + O_2 \longrightarrow O_2(a^1\Delta_g) + O_2$	$6.93 \times 10^{-47} (300/T_g)^{0.63}$	(Gordiets et al., 1995)
T_g [K]		
T_e [eV]		

Table 8: The reaction set involving the metastable $O_2(b^1\Sigma_g^+)$ and the Herzberg states $O_2(A^3\Sigma_u^+, A'^3\Delta_u, c^1\Sigma_u^-)$.

no.	Reaction	Rate coefficient [m^3/s]	Ref.
	$O_2(^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$		
I	$e+O_2(^3\Sigma_g^-) \longrightarrow O_2^+ + 2e$	$2.34 \times 10^{-15} T_e^{1.03} \exp(-12.29/T_e)$	(Krishnakumar and Srivastava, 1992)
II	$e+O_2(^3\Sigma_g^-) \longrightarrow O(^3P) + O(^3P)+e$	$6.86 \times 10^{-15} \exp(-6.29/T_e)$	(Gudmundsson, 2002)
III	$e+O_2(^3\Sigma_g^-) \longrightarrow O(^3P)+O(^1D) + e$	$3.49 \times 10^{-14} \exp(-5.92/T_e)$	(Gudmundsson, 2002)
IV	$e+O_2(^3\Sigma_g^-) \longrightarrow O(^3P)+O^+ + 2e$	$1.88 \times 10^{-16} T_e^{1.699} \exp(-16.81/T_e)$	(Krishnakumar and Srivastava, 1992)
V	$e+O_2(a^1\Delta_g) \longrightarrow O_2 + e$	$2.06 \times 10^{-15} \exp(-1.163/T_e)$	Detailed balancing
VI	$e+O_2(a^1\Delta_g) \longrightarrow O(^3P) + O^-$	$4.19 \times 10^{-15} T_e^{-1.376} \exp(-5.19/T_e)$	(Jaffke et al., 1992)
	Metastable $O_2(b^1\Sigma_g^+)$		
101	$e+O_2 \longrightarrow O_2(b^1\Sigma_g^+) + e$	$3.24 \times 10^{-16} \exp(-2.218/T_e)$	(Gudmundsson, 2002)
102	$e+O_2(a^1\Delta_g) \longrightarrow O_2(b^1\Sigma_g^+) + e$	reaction 101 threshold reduced	
103	$e+O_2(b^1\Sigma_g^+) \longrightarrow O(^3P)+O(^3P)+e$	reaction II threshold reduced	
104	$e+O_2(b^1\Sigma_g^+) \longrightarrow O(^3P)+O(^1D)+e$	reaction III threshold reduced	
105	$e+O_2(b^1\Sigma_g^+) \longrightarrow O_2^+ + 2e$	reaction I threshold reduced	
106	$e+O_2(b^1\Sigma_g^+) \longrightarrow O+O^+ + 2e$	reaction IV threshold reduced	
107	$O^-+O_2(b^1\Sigma_g^+) \longrightarrow O+O_2 + e$	6.9×10^{-16}	(Aleksandrov, 1978)
108	$O+O_2(b^1\Sigma_g^+) \longrightarrow O_2(a^1\Delta_g)+O$	8.1×10^{-20}	(Gordiets et al., 1995)
109	$e+O_2(b^1\Sigma_g^+) \longrightarrow O_2 + e$	$9.72 \times 10^{-16} \exp(-0.591/T_e)$	Detailed balancing
110	$O_2+O_2(b^1\Sigma_g^+) \longrightarrow O_2(a^1\Delta_g)+O_2$	$4.3 \times 10^{-28} T_g^{2.4} \exp(-281/T_g)$	(Gordiets et al., 1995)
111	$e+O_2(b^1\Sigma_g^+) \longrightarrow O+O^-$	reaction VI threshold reduced	
112	$O_2(b^1\Sigma_g^+)+ O_3 \longrightarrow 2\ O_2(^3\Sigma_g^-) + O(^3P)$	1.5×10^{-17}	(Jeong et al., 2000)
113	$2\ O_2(b^1\Sigma_g^+) \longrightarrow 2\ O_2(a^1\Delta_g) + O_2(^3\Sigma_g^-)$	$3.6 \times 10^{-23} (T_g/300)^{1/2}$	(Stafford and Kushner, 2004)
	Herzberg states $O_2(A^3\Sigma_u^+, A'^3\Delta_u, c^1\Sigma_u^-)$		
114	$e+O_2 \longrightarrow O_2^R + e$	$1.13 \times 10^{-15} \exp(-3.94/T_e)$	(Gudmundsson, 2002)
115	$e+O_2(a^1\Delta_g) \longrightarrow O_2^H + e$	reaction 113 threshold reduced	
116	$e+O_2(b^1\Sigma_g^+) \longrightarrow O_2^H + e$	reaction 113 threshold reduced	
117	$e+O_2^H \longrightarrow O+O^-$	$7.32 \times 10^{-16} T_e^{-1.07} \exp(-0.47/T_e)$	(Hayashi and Kadota, 1999)
118	$e+O_2^H \longrightarrow O+O+e$	reaction II threshold reduced	
119	$e+O_2^H \longrightarrow O+O(^1D) + e$	reaction III threshold reduced	
120	$O(^3P)+O_2^H \longrightarrow O_2(^3\Sigma_g^-) + O(^3P)$	4.95×10^{-18}	(Vasiljeva et al., 2004)
121	$O(^3P)+O_2^H \longrightarrow O_2(a^1\Delta_g) + O(^1D)$	2.7×10^{-18}	(Vasiljeva et al., 2004)
122	$O(^3P)+O_2^H \longrightarrow O_2(b^1\Sigma_g^+) + O(^1D)$	1.35×10^{-18}	(Vasiljeva et al., 2004)
123	$O_2(^3\Sigma_g^-) + O_2^H \longrightarrow 2\ O_2(b^1\Sigma_g^+)$	2.9×10^{-19}	(Kenner and Ogryzlo, 1980)
124	$O_2^H \longrightarrow O_2(^3\Sigma_g^-) + h\nu$	$6.25\ s^{-1}$	(Kenner and Ogryzlo, 1983)
	T_g [K]		
	T_e [eV]		

Table 9: Rate coefficients, excited states of atomic oxygen.

Reaction	Thresh. [V]	Rate coefficient [m^3/s]
Non-Rydberg States		
$e+O(^3P) \longrightarrow O(^1D) + e$	1.96	$k_{^1D} = 4.54 \times 10^{-15} \exp(-2.36/T_e)$
$e+O(^3P) \longrightarrow O(^1S) + e$	4.18	$k_{^1S} = 7.86 \times 10^{-16} \exp(-4.489/T_e)$
$e+O(^3P) \longrightarrow O(^3P^o) + e$	15.65	$k_{^3P^o} = 2.53 \times 10^{-15} \exp(-17.34/T_e)$
Rydberg States		
$e+O(^3P) \longrightarrow O(^5S^o) + e$	9.14	$k_{^5S} = 9.67 \times 10^{-16} \exp(-9.97/T_e)$
$e+O(^3P) \longrightarrow O(^3S^o) + e$	9.51	$k_{^3S} = 3.89 \times 10^{-15} \exp(-9.75/T_e)$
$e+O(^3P) \longrightarrow O^{h*} + e$	12.0	$k_{h*} = 4.31 \times 10^{-14} \exp(-18.59/T_e)$

Table 10: Rate coefficients for excitation of the oxygen molecule.

Reaction	Threshold [V]	Rate coefficient [m^3/s]
$e+O_2(r=0) \longrightarrow O_2(r>0) + e$	0.02	$k_{rot} = 1.87 \times 10^{-17} \exp(-2.9055/T_e)$
$e+O_2(v=0) \longrightarrow O_2(v=1) + e$	0.19	$k_{v=1} = 2.8 \times 10^{-15} \exp(-3.72/T_e)$
$e+O_2(v=0) \longrightarrow O_2(v=2) + e$	0.38	$k_{v=2} = 1.28 \times 10^{-15} \exp(-3.67/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(a^1\Delta_g) + e$	0.977	$k_{a^1\Delta_g} = 1.37 \times 10^{-15} \exp(-2.14/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(b^1\Sigma_g^+) + e$	1.627	$k_{b^1\Sigma_g^+} = 3.24 \times 10^{-16} \exp(-2.218/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(ex1) + e$	4.5	$k_{ex1} = 1.13 \times 10^{-15} \exp(-3.94/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(1dis) + e$	6.0	$k_{1dis} = 6.86 \times 10^{-15} \exp(-6.29/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(2dis) + e$	8.4	$k_{2dis} = 3.49 \times 10^{-14} \exp(-5.92/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(3dis) + e$	9.97	$k_{3dis} = 1.44 \times 10^{-16} \exp(-17.25/T_e)$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(ex2) + e$	14.7	$k_{ex2} = 1.13 \times 10^{-15} \exp(-18.35/T_e)$