
Recombination rate coefficients in oxygen discharges

by

Jón Tómas Gudmundsson

and

Michael A. Lieberman



RH-16-2004

Science Institute

University of Iceland

Recombination rate coefficients in oxygen discharges

J. T. Gudmundsson^{1,2,*} and M. A. Lieberman³

¹*Science Institute, University of Iceland,
Dunhaga 3, IS-107 Reykjavik, Iceland*

²*Department of Electrical and Computer Engineering,
University of Iceland, Hjardarhaga 2-6, IS-107 Reykjavik, Iceland*

³*Department of Electrical Engineering and Computer Sciences,
University of California, Berkeley, CA 94720, USA*

(Dated: 29th November 2004)

Abstract

We have evaluated the recombination rate coefficients for the mutual neutralization of $O^- + O^+$ and $O^- + O_2^+$ and dissociative recombination of O_2^+ -ions with electrons in processing discharges. We propose a rate coefficient of $4.0 \times 10^{-14} (300/T_i)^{0.43} \text{ m}^3/\text{s}$ for the reaction $O^- + O^+ \rightarrow O + O$ where T_i is the ion temperature in Kelvins. For the reaction $O^- + O_2^+ \rightarrow O + O + O$ we suggest a rate coefficient of $2.6 \times 10^{-14} (300/T_i)^{0.44} \text{ m}^3/\text{s}$ and for $O^- + O_2^+ \rightarrow O + O_2$ a rate coefficient of $2.6 \times 10^{-14} (300/T_i)^{0.44} \text{ m}^3/\text{s}$. For dissociative recombination of O_2^+ -ions with electrons we suggest a rate coefficient of $2.2 \times 10^{-14} \times T_e^{-0.5} \text{ m}^3/\text{s}$ where T_e is the electron temperature in electron volts.

PACS numbers: 52.35.Sb, 52.77.Dq

*Electronic address: tumi@hi.is

I. 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, removing polymer films and oxidation or deposition of thin film oxides. 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 [1, 2]. 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 [3–13], but many of the cross sections for binary processes among these species have not been carefully measured or calculated [14]. In a low pressure processing discharge O^- is found to be the dominant negative ion [11] and ion-ion recombination is suggested to play an important role at pressures below 10 mTorr [15]. Recent measurements of the mutual neutralization cross sections in oxygen have suggested that the rate coefficients commonly used are significantly overestimated [16, 17]. This claim is further supported by a measurement of the rate coefficient for $O^- + O^+$ [18]. The aim of this work is to evaluate the recombination rate coefficient for the mutual neutralization of $O^- + O^+$ and $O^- + O_2^+$ and dissociative recombination of O_2^+ -ions with electrons in processing discharges, $T_e \approx 1 - 7$ V and $T_i \ll T_e$, where T_e is the electron temperature and T_i is the ion temperature. Throughout the text we use the roman typeface symbol T for the voltage equivalent of the temperature.

II. MUTUAL NEUTRALIZATION OF OXYGEN IONS

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



are $2.7 \times 10^{-13}(300/T_i)^{1/2}$ m³/s [3, 7] and $2.0 \times 10^{-13}(300/T_i)^{1/2}$ m³/s [3, 4, 6, 19] where T_i is the ion temperature in Kelvins. These rate coefficients are consistent with the measurements of Olson et al. [20] that give an experimental value of 2.8×10^{-13} m³/s and a theoretical value

of $1.1 \times 10^{-13} \text{ m}^3/\text{s}$ at 300 K. Later Olson [21] 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 $\text{O}^- + \text{O}^+$ and $\text{O}^- + \text{O}_2^+$ in the energy range 0.03 – 100 eV. This theoretical work predicts equal cross sections (to within $\pm 10 \%$) for both $\text{O}^- + \text{O}^+$ and $\text{O}^- + \text{O}_2^+$ mutual neutralization and agreed very well with the early measurements. More recent measurements of the cross section by Hayton and Peart [16] are a factor of 6 – 10 times lower. Possible reasons for the disparities were discussed by Dolder and Peart [22]. The measurement of Hayton and Peart [16] is supported by a new theoretical calculation of the cross section by Zhou and Dickinson [23] which is in excellent agreement with the cross section measured. We plot the cross section measured by Hayton and Peart [16] in figure 1 (a) for the energy range 1 – 100 eV. Unfortunately, the measured data do not go below 1 eV and the theoretical calculation by Zhou and Dickinson [23] do not go below 0.8 eV.

We propose a new estimate of the recombination rate coefficient by assuming the low energy scaling seen by Olson [21], is qualitatively correct for energies below 1 eV. This scaling is consistent with the classical Coulomb focusing expected at low energies. Thus, we plot the cross section calculated by Olson [21] and scale it down by a factor of 6.4 to fit the measured data of Hayton and Peart [16]. 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 $300 \text{ K} \leq T_i \leq 1200 \text{ K}$. We assume that the ion energy distribution to be Maxwellian and that the thermal velocity of the ions dominates the drift velocity. The rate coefficient for the mutual neutralization of $\text{O}^- + \text{O}^+$ is thus found to be

$$4.0 \times 10^{-14} \left(\frac{300}{T_i} \right)^{0.43} \text{ m}^3/\text{s}.$$

Ishikawa et al. [18] have estimated the rate coefficient to be $4.1 \times 10^{-15} \text{ m}^3/\text{s}$ at $\sim 0.1 \text{ eV}$. Our value at 0.1 eV is significantly higher, $2.2 \times 10^{-14} \text{ m}^3/\text{s}$, but roughly a factor of five lower than the commonly accepted value.

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



and



are $2.0 \times 10^{-13} (300/T_i)^{1/2}$ m³/s [3, 4, 6, 19] or 0.96×10^{-13} m³/s [3] for the former reaction and 1.0×10^{-13} m³/s [3, 4, 6] for the latter. These values are consistent with the early measurements of Moseley et al. [24], which reported a value of 1.0×10^{-13} m³/s at 300 K. Recent measurements by Padgett and Peart [17] suggest that the cross section is a factor of five lower than the earlier measurements. Their measurements indicate that reactions (2) and (3) each contribute roughly 50 % at 120 eV. We plot the cross section measured by Padgett and Peart [17] in figure 1 (b) for the energy range 6 – 100 V. Since their measurements are made for energies above 6 eV we plot the cross section calculated by Olson [21] and scale it down by a factor of 5.0 to fit the measured data of Padgett and Peart [17]. 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

$$5.2 \times 10^{-14} \left(\frac{300}{T_i} \right)^{0.44} \quad \text{m}^3/\text{s}$$

and is valid in the range $300 \text{ K} \leq T_i \leq 1200 \text{ K}$. The data of Eliasson and Kogelshatz [3] indicates a 50 – 70 % range as the ratio of reactions (2) and (3). Based on this and the Padgett and Peart [17] data, we assume that each reaction contributes 50 % to the reaction rate, we propose a rate coefficient of $2.6 \times 10^{-14} (300/T_i)^{0.44}$ for each of the reactions (2) and (3).

III. DISSOCIATIVE RECOMBINATION OF O_2^+ -IONS WITH ELECTRONS

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



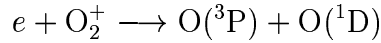
has been measured by Mehr and Biondi [25] over the entire range $300 \leq T_e \leq 5000$ K. They find the rate coefficient to vary as $T_e^{-0.56}$ in the range $1200 \leq T_e \leq 5000$ K and as $T_e^{-0.7}$ in the range $300 \leq T_e \leq 1200$ K, where the electron temperature is given in Kelvin. For $T_e = 300$ K they report a value of $(1.95 \pm 0.2) \times 10^{-13}$ m³/s. This value has been confirmed by more recent measurements [26, 27] and is commonly accepted [3]. Mul and McGowan [28] measured the cross section for the recombination of O_2^+ -ions with electrons and calculate a rate coefficient that shows a $T_e^{-0.5}$ dependence and is in good agreement with the early

measurements of Mehr et al. [25, 29]. The rate coefficient of $2 \times 10^{-13}(300/T_e)$ m³/s is valid in the range $205 \leq T_e \leq 690$ K [4, 29, 30], the conditions expected in the upper atmosphere where $T_e \approx T_i$. These values are also consistent with a theoretical calculation by Guberman [31] that gives $2.21 \times 10^{-13} \times (T_e/300)^{-0.46}$ m³/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 O₂⁺-ions with electrons has much lower yield [32].

For low pressure discharges with $T_e \gg 1000$ K the rate coefficient of $2 \times 10^{-13}(300/T_e)$ m³/s is not appropriate. We assume a rate coefficient $k = k_0 T_e^{-0.5}$ consistent with Mul and McGowman [28] and determine k_0 by fitting to the data measured by Mehr and Biondi [25] from 1700 K to 5000 K. The $T_e^{-0.5}$ temperature dependence of the direct dissociative recombination process is argued by Bates and Dalgarno if the ion wave function varies just slightly with electron energy [33]. We propose a rate coefficient of

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

for the reaction



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

IV. CONCLUSION

We have evaluated the recombination rate coefficients for the mutual neutralization of $O^- + O^+$ and $O^- + O_2^+$. The rate coefficients we suggest are up to an order of magnitude lower than that commonly used in modeling work. Furthermore, we propose a rate coefficient for dissociative recombination of O₂⁺-ions with electrons that is roughly an order of magnitude larger than commonly used.

Acknowledgments

We are grateful to Professor A. S. Dickinson for valuable comments on mutual neutralization of oxygen ions. This work was partially supported by the University of Iceland

Research Fund, the Icelandic Research Council, National Science Foundation Grant ECS-0139956, and a UC Discovery Grant from the Industry-University Cooperative Research Program (IUCRP).

- [1] A. J. Lichtenberg, V. Vahedi, M. A. Lieberman, and T. Rognlien, *Journal of Applied Physics* **75**, 2339 (1994).
- [2] T. H. Chung, *Journal of the Korean Physical Society* **34**, 24 (1999).
- [3] B. Eliasson and U. Kogelshatz, *Basic data for modeling of electrical discharges in gases: Oxygen*, Report KLR-11C, Brown Boveri Konzernforschung, CH5405, Baden (1986).
- [4] I. A. Kossyi, A. Y. Kostinsky, A. A. Matveyev, and V. P. Silakov, *Plasma Sources Science and Technology* **1**, 207 (1992).
- [5] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (John Wiley & Sons, New York, 1994).
- [6] B. F. Gordiets, C. M. Ferreira, V. L. Guerra, J. M. A. H. Loureiro, J. Nahorny, D. Pagnon, M. Touzeau, and M. Vialle, *IEEE Transactions on Plasma Science* **23**, 750 (1995).
- [7] C. Lee, D. B. Graves, M. A. Lieberman, and D. W. Hess, *Journal of the Electrochemical Society* **141**, 1546 (1994).
- [8] C. Lee and M. A. Lieberman, *Journal of Vacuum Science and Technology A* **13**, 368 (1995).
- [9] K. K. Patel, Master's thesis, University of California at Berkeley (1998).
- [10] J. T. Gudmundsson, A. M. Marakhtanov, K. K. Patel, V. P. Gopinath, and M. A. Lieberman, *Journal of Physics D: Applied Physics* **33**, 1323 (2000).
- [11] J. T. Gudmundsson, I. G. Kouznetsov, K. K. Patel, and M. A. Lieberman, *Journal of Physics D: Applied Physics* **34**, 1100 (2001).
- [12] E. Meeks, R. S. Larson, P. Ho, C. Apblett, S. M. Han, E. Edelberg, and E. S. Aydil, *Journal of Vacuum Science and Technology A* **16**, 544 (1998).
- [13] M. W. Kiehlbauch and D. B. Graves, *Journal of Vacuum Science and Technology A* **21**, 660 (2003).
- [14] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (John Wiley & Sons, New York, 1994).
- [15] J. T. Guðmundsson, *Journal of Physics D: Applied Physics* **37**, 2073 (2004).

- [16] D. A. Hayton and B. Peart, *Journal of Physics B: Atomic, Molecular and Optical Physics* **26**, 2879 (1993).
- [17] R. Padgett and B. Peart, *Journal of Physics B: Atomic, Molecular and Optical Physics* **31**, L995 (1998).
- [18] T. Ishikawa, D. Hayashi, K. Sasaki, and K. Kadota, *Applied Physics Letters* **72**, 2391 (1998).
- [19] F. E. Niles, *Journal of Chemical Physics* **52**, 408 (1970).
- [20] R. E. Olson, J. R. Peterson, and J. T. Moseley, *Journal of Chemical Physics* **53**, 3391 (1970).
- [21] R. E. Olson, *Journal of Chemical Physics* **56**, 2979 (1972).
- [22] K. Dolder and B. Peart, *Reports on Progress in Physics* **48**, 1283 (1985).
- [23] X. Zhou and A. S. Dickinson, *Nuclear Instruments and Methods in Physics Research B* **124**, 5 (1997).
- [24] J. T. Moseley, W. Aberth, and J. R. Peterson, *Journal of Geophysical Research* **77**, 255 (1972).
- [25] F. J. Mehr and M. A. Biondi, *Physical Review* **181**, 264 (1969).
- [26] T. Gougousi, M. F. Golde, and R. Johnsen, *Chemical Physics Letters* **265**, 399 (1997).
- [27] M. J. Church and D. Smith, *Journal of Physics D: Applied Physics* **11**, 2199 (1978).
- [28] P. M. Mul and J. W. McGowan, *Journal of Physics B: Atomic, Molecular and Optical Physics* **12**, 1591 (1979).
- [29] W. H. Kasner and F. J. Mehr, *Physical Review* **174**, 139 (1968).
- [30] S. I. Kozlov, V. A. Vlaskov, and N. V. Smirnova, *Cosmic Research* **26**, 635 (1988).
- [31] S. L. Guberman, *Planetary and Space Science* **36**, 47 (1988).
- [32] S. L. Guberman and A. Giusti-Suzor, *Journal of Chemical Physics* **95**, 2602 (1991).
- [33] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press, New York, 1962), pp. 245 – 271.

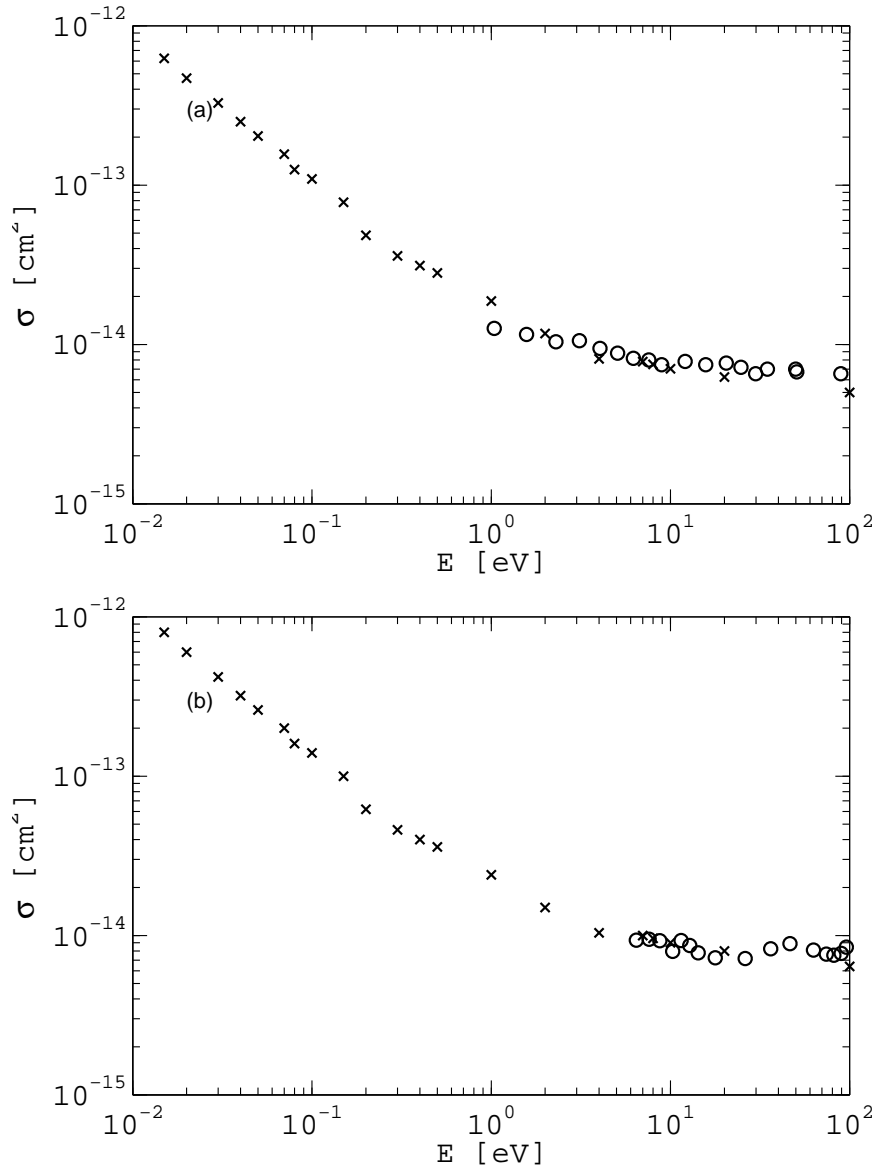


Figure 1: The proposed cross section for the mutual neutralization. (a) The cross section for $O^- + O^+$, o measured by Hayton and Peart [16] and \times theoretical calculation by Olson [21], scaled down by a factor of 6.4 to fit the measured data. (b) The cross section for $O^- + O_2^+$, o measured by Padgett and Peart [17] and \times theoretical calculation by Olson [21], scaled down by a factor of 5.0 to fit the measured data.