Theoretical Investigation of the Influence of the Wall Temperature on the Probability for Surface Atomic Recombination of a Single Species

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The probability for surface atomic recombination of a single gas is theoretically investigated, for a system that takes into account atomic adsorption in physisorption and chemisorption sites, surface desorption, surface diffusion, and both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) recombination mechanisms. Analytic asymptotic solutions are obtained for the value of the recombination probability and are validated by their comparison with numeric calculations for the system of equations describing the same sequence of elementary processes. The dependence of the recombination probability on the value of the wall temperature is analysed in detail. [DOI: 10.1143/JJAP.45.8200]

1. Introduction

The study of the surface kinetics of atomic species, such as N and O atoms, and in particular of the elementary processes leading to heterogeneous recombination, is nowadays an important subject of research in various problems of rarefied gas dynamics, such as the aerodynamics of space vehicles moving in rarefied gases. On the other hand, many of the characteristics of plasma reactors are in practice controlled by wall reactions. Therefore, there is a need to address the questions of the role of surface processes in the overall behavior of different gas discharges, as it was pointed out, e.g., in refs. 1 and 2.
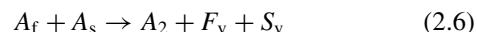
Many theoretical works have been done recently in order to investigate surface recombination of atoms. For instance, phenomenological models have been developed in refs. 3 and 4 and a dynamical Monte Carlo has been presented in ref. 5. All these models provide important physical insight into the various elementary mechanisms occurring at the surface and, particularly for the case of the Monte Carlo, allow to perform quite complete and detailed simulations. The purpose of this work is to follow a different approach, by obtaining asymptotic analytic solutions for the recombination probability. It is shown that the approximate analytic solutions describe the system with very high accuracy. Thus, for the system under analysis, the recombination probability can be readily evaluated from a simple expression, with no need for any numeric treatment. As a consequence, the dependence of the recombination probability on different surface parameters, such as the activation energies of the various processes and the wall temperature, can be fully understood.

2. Theoretical Model

The surface model was described in detail in ref. 5. It is assumed that the surface is totally covered with adsorption sites of radius a (typically ~ 1 Å). Each adsorption site can hold atoms either reversibly (physisorption) or irreversibly (chemisorption), while the average distance between chemisorption sites is $2b$. Physisorption basically corresponds to a bond between surface and gas particles due to van der Waals forces (so that, roughly, any place on the surface can hold a physisorbed atom). Due to their low bond energy, physisorbed atoms can desorb from the surface and/or diffuse along it. On the other hand, in chemisorption there is a true chemical bond between the adsorbed atom and the solid surface. The atom remains trapped in the potential well of the chemisorption site, and can be removed essentially by atomic recombination.

The system under analysis was originally designed to describe nitrogen and oxygen recombination on silica surfaces as in ref. 3, but it will be kept in a very general form. It includes adsorption and desorption of atoms at reversible sites (2.1, 2.2), chemisorption on irreversible sites (2.3), recombination of chemisorbed atoms with gas-phase atoms — Eley–Rideal (E–R) recombination (2.4), surface diffusion of physisorbed atoms (2.5), and recombination between a diffusing physisorbed atom and a chemisorbed one — Langmuir–Hinshelwood (L–H) recombination (2.6). At the present stage, recombination involving only physisorbed atoms is not considered, nor it is desorption from chemisorption sites. Take note that such approximations may influence the results for very low and very high surface temperatures, respectively. The elementary processes taken into account can be written schematically in the form

$$A + F_\mathrm{v} \rightarrow A_\mathrm{f} \tag{2.1}$$

$$A_\mathrm{f} \rightarrow A + F_\mathrm{v} \tag{2.2}$$

$$A + S_\mathrm{v} \rightarrow A_\mathrm{s} \tag{2.3}$$

$$A + A_\mathrm{s} \rightarrow A_2 + S_\mathrm{v} \tag{2.4}$$

$$A_\mathrm{f} + S_\mathrm{v} \rightarrow A_\mathrm{s} + F_\mathrm{v} \tag{2.5}$$

$$A_\mathrm{f} + A_\mathrm{s} \rightarrow A_2 + F_\mathrm{v} + S_\mathrm{v} \tag{2.6}$$

where A and A_2 denote gas phase atoms and molecules, F_v and S_v vacant physisorption and chemisorption sites, and A_f and A_s physisorbed and chemisorbed atoms, respectively. The corresponding densities are herein represented by the symbols $[\cdots]$.

The rates for the elementary processes (2.1)–(2.6), $r_1 - r_6$, are given in $(\mathrm{site})^{-1}\,\mathrm{s}^{-1}$ and their expressions can be found in ref. 5. For the surface densities of reversible and irreversible sites, $[F]$ and $[S]$, respectively, we have $[F] = [F_\mathrm{v}] + [A_\mathrm{f}]$ and $[S] = [S_\mathrm{v}] + [A_\mathrm{s}]$. Then, for a surface described by the set of processes (2.1)–(2.6), the fractional coverage of reversible and irreversible sites, θ_f and θ_s, can be calculated from expressions

$$\frac{d\theta_f}{dt} = (1 - \theta_f)r_1 - \theta_f r_2$$
$$- \theta_f(1 - \theta_s)\frac{[S]}{[F]}r_5 - \theta_f\theta_s\frac{[S]}{[F]}r_6 \qquad (2.7)$$

and

$$\frac{d\theta_s}{dt} = (1 - \theta_s)r_3 - \theta_s r_4 + \theta_f(1 - \theta_s)r_5 - \theta_f\theta_s r_6. \qquad (2.8)$$

The recombination probability γ of atoms of a certain species A can be found from the creation-loss balance of gas-phase A atoms at the wall,

$$\left(\frac{d[A]}{dt}\right)_{\text{Wall}} = -\frac{2}{R_t}([F_v][A]k_1 - [A_f]k_2 + [S_v][A]k_3$$
$$+ [A_s][A]k_4) = -\frac{\langle v_A \rangle \gamma[A]}{2R_t}. \qquad (2.9)$$

In this expression we have used the reaction rates $k_1 - k_6$ given by $r_1 = [A]k_1$, $r_2 = k_2$, $r_3 = [A]k_3$, $r_4 = [A]k_4$, $r_5 = [F]k_5$, and $r_6 = [F]k_6$, R_t is the tube radius, $\langle v_A \rangle$ is the thermal speed of gas phase atoms A, and the roughness factor, which is the ratio of the real surface area to the geometric area ($2\pi R_t L$ for a tube of radius R_t and length L), has been taken to be 1. Actually the roughness factor, ε, is bigger than one (ref. 3), but it is straightforward to include it in the expressions from this work. As a matter of fact, the corrected recombination probability is just obtained multiplying the expressions of γ given in this work by ε. Notice that the quantities $[F]$, $[S]$, $[F_v]$, $[S_v]$, $[A_f]$, and $[A_s]$ are defined per unit area (for instance $[F] = [\tilde{F}]/2\pi R_t L$, where $[\tilde{F}]$ is the number of physisorption sites in a tube of radius R_t and length L), whereas $[A]$ is defined per unit volume ($[A] = [\tilde{A}]/\pi R_t^2 L$, $[\tilde{A}]$ denoting the total number of gas phase atoms in the considered volume). Moreover, the rate coefficients k_i are given in units of $m^3 \cdot s^{-1}$ for $i = 1, 3, 4$, in s^{-1} for $i = 2$, and in $m^2 \cdot s^{-1}$ for $i = 5, 6$. The factor $(2/R_t)$ in the middle part of equation (2.9) is simply a geometric factor accounting for the definitions of volume and surface densities.

Solving for γ and using the steady-state conditions for the fractional coverage θ_f and θ_s, it results

$$\gamma = \frac{2[A_s](r_4 + \theta_f r_6)}{\Phi_A} = \gamma^{\text{E-R}} + \gamma^{\text{L-H}}. \qquad (2.10)$$

$\gamma^{\text{E-R}} = 2[A_s]r_4/\Phi_A$ and $\gamma^{\text{L-H}} = 2[A_s]\theta_f r_6/\Phi_A$ are, respectively, the contributions of E–R and L–H recombination to the total recombination probability, and Φ_A is the flow of gas-phase atoms A to the wall in $m^{-2} \cdot s^{-1}$, $\Phi_A = \langle v_A \rangle[A]/4$, being $\langle v_A \rangle$ the thermal speed of gas phase A atoms close to the wall.

3. Results and Discussion

From the solution of the equations above, and noting that for a system with no L–H recombination and at steady-state $\theta_s = r_3/(r_3 + r_4)$, it is possible to obtain the E–R recombination probability. As a matter of fact, it comes,

$$\gamma^{\text{E-R}} = \frac{2[A_s]r_4}{\Phi_A} = \frac{2\theta_s r_4}{\Phi_A}[S] = \frac{2r_3 r_4}{r_3 + r_4}\frac{[S]}{\Phi_A}. \qquad (3.1)$$

Substituting r_3 and r_4 as given in ref. 5, $r_3 = \Phi_A \varphi k_3^{0\prime}/[S]$ and $r_4 = r_3 k_4^0 \exp(-E_r/RT_w)$, where E_r is the activation energy for recombination, $\varphi = [S]/([S] + [F]) = a^2/b^2$, R is

the gas constant, and $k_3^{0\prime}$ and k_4^0 are the sticking probabilities on irreversible sites for processes (2.3) and (2.4), respectively, usually assumed to be equal to one, one finally obtains

$$\gamma^{\text{E-R}} \simeq \frac{2\varphi k_3^{0\prime} k_4^0 \exp\left(-\dfrac{E_r}{RT_w}\right)}{1 + k_4^0 \exp\left(-\dfrac{E_r}{RT_w}\right)}, \qquad (3.2)$$

That being so, $\gamma^{\text{E-R}}$ is essentially proportional to $\exp(-E_r/RT_w)$, as long as the wall temperature is not "too high" so that the inequality $\exp(-E_r/RT_w) \ll 1$ holds.

The Langmuir-Hinshelwood recombination probability exhibits a much more complex behavior with the wall temperature. Each chemisorption site is surrounded by a "collection zone", whose size depends on the surface parameters (activation energies of the different elementary processes) and wall temperature. Basically, only atoms that impinge the surface within a collection zone can reach, by diffusion, a chemisorption site (refs. 3 and 5). Let k_D' denote the probability for a physisorbed atom to reach an irreversible site (vacant or occupied).

Using a similar procedure as the one leading to expression (3.2),

$$\gamma^{\text{L-H}} = \frac{2[S]\theta_f r_6}{\Phi_A} \simeq \frac{2}{\Phi_A}\frac{r_1}{r_1 + r_2}r_6$$
$$\simeq \frac{2}{\Phi_A}\frac{r_1}{r_1 + r_2}r_2 k_D' k_4^0 \exp\left(-\frac{E_r}{RT_w}\right)[F], \qquad (3.3)$$

where it has been used $\theta_f \simeq r_1/(r_1 + r_2)$ and r_6 has been substituted according to the expressions given in ref. 5.

For $0 < k_D' < 1$ this probability is given in ref. 5 by

$$k_D' = \frac{[S]}{[F]}\left[\left(\frac{\nu_D}{\nu_d}\right)\exp\left(\frac{E_d - D_D}{RT_w}\right) - \frac{1}{4}\right], \qquad (3.4)$$

where ν_d and ν_D are the frequency factors associated with desorption and surface diffusion of physisorbed atoms, respectively, and E_d and E_D are the corresponding activation energies.

The range of high temperatures corresponds to small collection zones (desorption is very efficient) and hence $k_D' < 1$. It also corresponds to a low fractional coverage θ_f. In this case, it can be shown from the expressions above that

$$\gamma^{\text{L-H}} \propto \exp\left(\frac{E_d - E_D - E_r}{RT_w}\right). \qquad (3.5)$$

Starting from high temperatures, the collection zones start to expand as T_w decreases. One could then expect L–H recombination would become more effective. This is in fact what happens when $E_d - E_D - E_r > 0$. However, if recombination is too difficult and E_r is large, it can be seen from the previous equation that $E_d - E_D - E_r < 0$ and $\gamma^{\text{L-H}}$ always goes down with $(T_w)^{-1}$, in spite of the enlargement of the collection zones.

At "intermediate values" of T_w, the collection zones start to overlap, $k_D' = 1$, and all physisorbed atoms reach the chemisorption sites. The second condition defining this temperature range is that the inequality $r_2 \gg r_1$ still holds. Under these conditions,
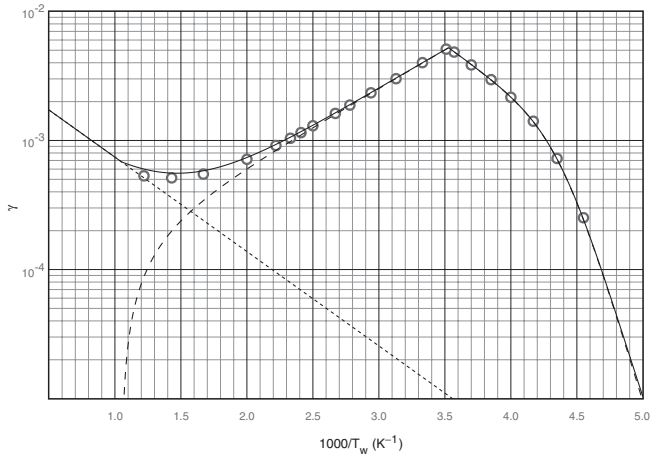
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Fig. 1. Nitrogen recombination on silica according to ref. 3. (- - -) $\gamma^{\text{E-R}}$; (- -) $\gamma^{\text{L-H}}$; (—) $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$; ○ numeric solution.

Fig. 2. Nitrogen recombination on silica according to ref. 3. (- - -) $\gamma^{\text{E-R}}$; (- -) $\gamma^{\text{L-H}}$; (—) $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$; × theoretical results from ref. 4; ○ numeric solution.

$$\gamma^{\text{L-H}} \propto \exp\left(-\frac{E_r}{RT_w}\right), \tag{3.6}$$

like $\gamma^{\text{E-R}}$. As a matter of fact, in this situation it makes no difference if an atom is adsorbed in a reversible or irreversible site, since all physisorbed atoms diffuse to chemisorption sites.

Finally, at "low temperatures", $k'_D = 1$ and thermal desorption becomes difficult. Since physisorbed atoms practically do not desorb, the physisorption sites are almost entirely occupied. The dependence of $\gamma^{\text{L-H}}$ on T_w in this case is

$$\gamma^{\text{L-H}} \propto \exp\left(-\frac{E_d + E_r}{RT_w}\right), \tag{3.7}$$

and $\gamma^{\text{L-H}}$ decreases with $(T_w)^{-1}$ faster than $\gamma^{\text{E-R}}$. Notice that, because reversible adsorption sites are occupied, almost none of the atoms arriving at the surface become physisorbed and L–H recombination stops working.

Figure 1 shows the analytic solution for the set of parameters indicated in ref. 3 as corresponding to nitrogen recombination in silica, namely $[F] = 10^{16}$ cm^{-2}, $[S]/([S] + [F]) = 2 \times 10^{-3}$, $E_d = 51$ kJ/mol, $E_r = 14$ kJ/mol, $E_D = 0.5E_d$, $\nu_d = 10^{15}$ s^{-1}, $\nu_D = 10^{13}$ s^{-1}, and $k_3^{0'} = k_1^{0'} = k_4^0 = 1$. All the calculations were performed for a gas temperature $T_g = 500$ K and a gas phase atomic density $[N] = 10^{15}$ cm^{-3}. This figure clearly shows the domination of E–R recombination at high temperatures, the increase of L–H recombination as a result of the increase of the collection zones as T_w decreases, and finally the subsequent decrease of $\gamma^{\text{L-H}}$ at low temperatures, when k'_D becomes equal to unity. Also shown in the figure with open circles are the numeric solutions of the system of eqs. (2.7) and (2.8), confirming the validity of the present analytic solutions.

Figure 2 shows again nitrogen recombination on silica, according to ref. 4. The only difference to the previous case is that now $E_r = 20$ kJ/mol. The theoretical results from ref. 4 are also shown, represented by the "×" symbols. The behavior of γ in this case is very similar to the one from previous figure, the only difference relating to its magnitude.

Figure 3 illustrates a completely different case, corresponding to oxygen recombination on silica according to
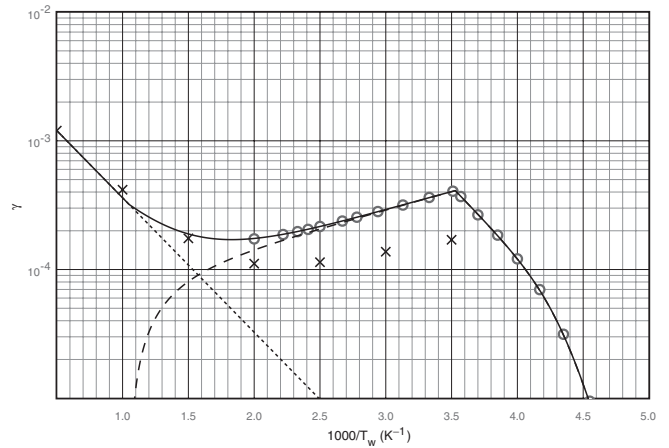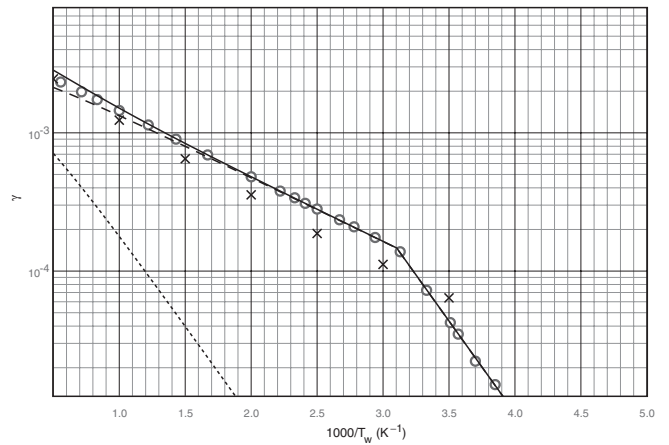

Fig. 3. Oxygen recombination on silica according to ref. 3. (- - -) $\gamma^{\text{E-R}}$; (- -) $\gamma^{\text{L-H}}$; (—) $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$; × theoretical results from ref. 4.

ref. 4. In this case, $E_d = 33.3$ kJ/mol, $E_D = 0.5E_d$, $E_r = 25.5$ kJ/mol, and $\nu_D = \nu_d = 10^{15}$ s^{-1}. With these parameters diffusion is very efficient, so that L–H recombination is dominant for a wide range of T_w. Furthermore, since $E_d - E_D - E_r < 0$, $\gamma^{\text{L-H}}$ always decreases with $(T_w)^{-1}$.

Finally, Fig. 4 shows an academic case with all parameters as in Fig. 1, with the exception of $\varphi = [S]/([S] + [F])$, which is assumed to be 2×10^{-1} instead of 2×10^{-3}. The density of chemisorption sites is much bigger than previously, resulting a higher recombination probability. However, the main interest of this case is the striking extended "intermediate zone", corresponding to a well defined region in which eq. (3.6) holds, $\gamma^{\text{L-H}}$ having the same exponential dependence as $\gamma^{\text{E-R}}$.

These figures demonstrate that even a relatively simple system for heterogeneous recombination, such as the one considered here and described by reactions (2.1)–(2.6), can exhibit very different behaviors. The advantage of the present treatment is to provide a direct and simple explanation for such richness, and to provide ready-to-use expressions allowing an immediate calculation of the recombination probability.
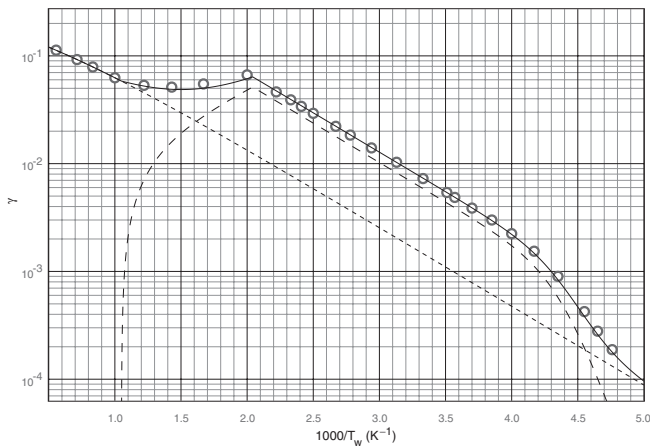
Fig. 4. The same as in Fig. 1, but with $\varphi = [S]/([S] + [F]) = 2 \times 10^{-1}$. $(\text{- - -})\ \gamma^{\text{E–R}};\ (\text{– –})\ \gamma^{\text{L–H}};\ (\text{—})\ \gamma^{\text{E–R}} + \gamma^{\text{L–H}}$.

4. Conclusions

In this work, asymptotic analytic solutions for the value of the recombination probability, γ, have been obtained in terms of the different surface parameters, such as activation energies and densities of adsorption sites. We have shown that γ can have very different dependencies with the wall temperature, T_w, which result from the competition between the Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) mechanisms of recombination. In the model assumed here, E–R recombination dominates both at "very low" and "high" values of T_w, where γ essentially follows an exponential with T_w (notice that the what is meant by a "low" temperature, for instance, is related to condition (3.7) and, in absolute numbers, can vary from case to case). However, at "intermediate" temperatures the influence of L–H recombination may originate strong deviations from this exponential behavior. The validity of the asymptotic analytic solutions has been confirmed from their comparison with the numeric solution to the system of equations.

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