

# Analytical Model of Heterogeneous Atomic Recombination on Silicalike Surfaces

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**Abstract**—An analytic model to describe the heterogeneous recombination of a single atomic species on silicalike surfaces is developed. The theoretical investigation herein presented provides ready-to-use expressions for the surface atomic recombination probability  $\gamma$  obtained as a function of surface characteristics such as the densities of adsorption sites and the activation energies for the different elementary surface processes. The model takes into account physisorption, chemisorption, thermal desorption, surface diffusion, and both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) recombination mechanisms. The results are applied to the cases of nitrogen and oxygen recombination on silica and to oxygen recombination on Pyrex. However, since the derivation is kept in a very general form, it allows the exploration of several distinct limit cases and provides a deeper understanding of the underlying surface kinetics. The dependence of the recombination probability with the wall temperature and with the gas pressure is studied in detail. It is found that  $\gamma$  can have a complex nonmonotonic behavior with the wall temperature, as a result of the competition between E–R and L–H recombination processes. The transition from first- to second-order recombinations (and vice-versa) with pressure is studied and debated.

**Index Terms**— Adsorption, desorption, Eley–Rideal (E–R), heterogeneous recombination, Langmuir–Hinshelwood (L–H), nitrogen, oxygen, surface diffusion, surface kinetics.

## I. INTRODUCTION

SURFACE kinetics plays a crucial role in several plasma-related systems, ranging from the gas discharges used both for fundamental and applied research to fluid dynamics and the study of reentry flows. In gas discharges, the concentration of active species in the reaction chambers is often influenced, or even controlled, by surface processes [1]–[6]. On the other hand, in reentry conditions, heterogeneous catalysis plays a crucial role to understand and design hypersonic vehicle thermal protection [7]–[10] (the references given should be taken as indicative examples only, as a huge list of works in the field could be cited).

The kinetics of surfaces has been modeled by several authors in many different ways. One popular approach is to use a mesoscopic description in terms of the average fractional coverage of adsorption sites, which is ruled by a set of differential equations describing elementary reactions occurring with defined rates. One important reference for this class of models is the paper by Kim and Boudart [11], but many other related works are available, such as [12]–[19]. One interesting variation on this

kind of models is the work presented in [20], in which the basic method is quite similar to the one in [11]; however, the set of elementary reactions is different, the system being better suited to study recombination in metallic surfaces.

Another possibility is to simulate the evolution of surfaces by using a Monte Carlo technique. The formal set of reactions can even be the same as in the previous class of models, but Monte Carlo methods have the advantage of furnishing a more microscopic picture of the surface. In particular, they allow an easy treatment of probabilities depending on the local configuration of the surface, which may lead to spatial correlations between the positions of the adsorbed species. Moreover, not only the average properties are obtained but also fluctuations are included by the very nature of the method. Information on these methods can be found, e.g., in [21]–[27].

Yet another strategy to investigate surface kinetics has been developed by Caciato and Billing [28], [29], providing different kind of information. They use molecular dynamics calculations and a semiclassical collision model to investigate at the atomic level the catalytic activity of different surfaces. In this method, the motion of gas-phase particles is treated classically while the dynamics of the quantized lattice atom vibrations is obtained from the time-dependent Schrödinger equation. Among other interesting results, they are able to calculate the fraction of the exothermic energy transferred to the internal states of the molecules formed on the wall due to recombination.

An attractive hybrid model between molecular dynamics and Monte Carlo has been proposed very recently [30], [31]. This scheme was not yet used in studying heterogeneous recombination directly, but rather to characterize the density, temperature, heat fluxes, and stress profiles for gases in micro and nanochannels. Nevertheless, it is worth referring to already, as it may provide a nice way to couple the flow properties with the gas–surface interactions.

In this paper, a different goal is attained. The basic formulation closely follows the one in [11] and its variants, for the study of recombination of a single atomic species. However, instead of numerically solving the system of equations leading to the determination of the heterogeneous atomic recombination probability, asymptotic analytical solutions are obtained here, as a function of the surface characteristics—such as the activation energies of the different elementary processes, the densities of adsorption sites, and the wall temperature—and the flow of atoms to the surface. These analytical solutions provide ready-to-use expressions for the recombination probability of atoms on the surface  $\gamma$  as well as a deep understanding of its behavior with the wall temperature and the gas pressure, for instance. The theoretical formulation is kept very general

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here, so that the full range of possibilities of the system under consideration is investigated. This is not just a question of the pure satisfaction associated with a fundamental study, with all the physical insight it brings, but mainly justified by the large uncertainties still existing nowadays in many rate coefficients and probabilities associated to surface processes. Therefore, it is advisable to predict and analyze the system in a wide range of variation of the main quantities involved. Even though, a practical concern is kept in mind and the theory is applied to the specific cases of nitrogen and oxygen recombination on silica and oxygen recombination on Pyrex. Partial results of this investigation were recently published in [32].

The structure of this paper is the following. The general formulation of the problem is presented in the next section. It includes a description of how the surface is considered, the elementary reactions taken into account and the derivation of the equations leading to a determination of the surface occupancy, and the evaluation of the heterogeneous recombination probability. Section III details how the rate coefficients of the different mechanisms are calculated, the system comprising physisorption, thermal desorption, chemisorption, diffusion of physisorbed atoms along the surface, and both Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) recombinations. The analytical solutions are obtained in Section IV, a particular attention being given to the dependence of  $\gamma$  with the wall temperature and with the gas pressure. The application of the model to realistic cases is performed in Section V, where an attempt has been made to cover several different possible behaviors of the recombination probability. Finally, Section VI summarizes the main conclusions of the present investigation and discusses possible extensions of the analysis developed here.

## II. GENERAL FORMULATION

### A. System Under Analysis

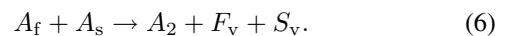
The surface is considered to be fully covered by a series of adsorption sites, which can hold atoms either reversibly or irreversibly. Adsorption in reversible sites is associated with physisorption, in which the bond between the gas atoms and the surface is due to van der Waals forces. Due to their relatively low-energy bonds, physisorbed atoms can diffuse along the surface and/or desorb back to the gas phase. Essentially, physisorption can occur at any place on the surface. On the other hand, irreversible adsorption is identified with chemisorption, where a true chemical bond exists between the adsorbed atom and the surface. It is assumed that a chemisorbed atom can only leave the surface after recombination, i.e., as part of a molecule leaving the surface into the gas phase. The limitation of not considering desorption of chemisorbed atoms, which can be important at high surface temperatures, is addressed in Section III-D.

Note that in reality, it is possible for an atom to physisorb on the top of a chemisorption site, physisorption being in this case a precursor step for chemisorption [33]. Although this is common for metallic surfaces [20], this possibility is not considered in this paper. Note that on silica chemisorption does not occur on a regular crystalline lattice, but rather as a consequence

of impurities and defects of the surface. This implies that the density of chemisorption sites is much lower than the one of physisorption sites (see Section III-A below), physisorption on the top of the chemisorption sites being, thus, negligible.

The elementary processes taken into account to describe the surface kinetics are the same as proposed in [11] and [15] to describe nitrogen or oxygen recombination on silica. Nevertheless, the theory is left very general in this paper, so that it can be directly applied to other cases.

Let  $A$  denote a gas phase atom of a generic species,  $A_f$  and  $A_s$  a physisorbed and a chemisorbed atom of the same species, respectively,  $F_v$  a vacant physisorption site, and  $S_v$  a vacant chemisorption site. Hence, the mechanisms of physisorption, thermal desorption from physisorption sites, chemisorption, E–R recombination, occupation of chemisorption sites by diffusing physisorbed atoms, and L–H recombination, can be schematically described by reactions (1)–(6), respectively:



Observe that E–R recombination involves the arrival of a gas phase atom to an occupied chemisorption site, whereas L–H recombination arises when a physisorbed atom diffuses to a filled chemisorption site. Moreover, no recombination is considered in physisorption sites. This question, which may be of importance for low surface temperatures (and consequently a large occupancy of physisorption sites), is briefly discussed in Sections III-E and G.

### B. Fractional Coverage of Adsorption Sites

In order to calculate the heterogeneous recombination probability, it is necessary to know the steady-state occupancy of both physisorption and chemisorption sites. Therefore, one has first to write down the equations ruling the occupation of these adsorption sites. In addition to providing the required steady-state conditions, these equations give the time evolution of the surface state, as well as information on the relative importance of the processes actually taking place at the surface.

Let  $[\tilde{A}]$  denote the number of atoms in the gas phase in the considered volume, which is given and assumed to be constant. In particular, the flow of  $A$  atoms to the surface is considered not to change along time. Moreover, an homogeneous gas phase system is considered for the purpose of the evaluation of the atomic flow to the surface. That being so, the surface kinetics is investigated here decoupled from the volume kinetics. A self-consistent treatment of both kinetics is certainly of importance for a complete modeling of plasma reactors, but it is irrelevant for the purpose of this paper. Note that no interaction between the gas molecules and the surface is taken into account.

Similarly, let  $[\tilde{A}_f]$  and  $[\tilde{A}_s]$  denote the number of physisorbed and chemisorbed atoms on the surface considered, respectively,

and  $[\tilde{F}_v]$  and  $[\tilde{S}_v]$  the number of vacant physisorption and chemisorption sites on the surface, respectively. Hence,  $[\tilde{F}] = [\tilde{F}_v] + [\tilde{A}_f]$  is the total number of physisorption sites, whereas  $[\tilde{S}] = [\tilde{S}_v] + [\tilde{A}_s]$  is the total number of chemisorption sites.  $[\tilde{F}]$  and  $[\tilde{S}]$  are surface characteristics and assumed to be known.

The time evolution of the number of physisorbed and chemisorbed atoms on the surface resulting from processes (1)–(6) is given by the solution to the coupled equations

$$\frac{d}{dt}[\tilde{A}_f] = [\tilde{A}][\tilde{F}_v]\tilde{k}_1 - [\tilde{A}_f]\tilde{k}_2 - [\tilde{A}_f][\tilde{S}_v]\tilde{k}_5 - [\tilde{A}_f][\tilde{A}_s]\tilde{k}_6 \quad (7)$$

and

$$\frac{d}{dt}[\tilde{A}_s] = [\tilde{A}][\tilde{S}_v]\tilde{k}_3 - [\tilde{A}][\tilde{A}_s]\tilde{k}_4 + [\tilde{A}_f][\tilde{S}_v]\tilde{k}_5 - [\tilde{A}_f][\tilde{A}_s]\tilde{k}_6. \quad (8)$$

As it should be clear,  $\tilde{k}_1$  is the adsorption rate per atom and per physisorption site,  $\tilde{k}_2$  is the desorption rate per physisorption site,  $\tilde{k}_3$  is the rate of adsorption per atom and per chemisorption site,  $\tilde{k}_4$  is the rate of E–R recombination per chemisorption site,  $\tilde{k}_5$  is the rate of occupancy of chemisorption sites due to diffusion per physisorbed atom and per chemisorption site, and  $\tilde{k}_6$  is the L–H recombination rate per physisorbed atom and per chemisorption site.

It is convenient to define  $[A_f]$ ,  $[A_s]$ ,  $[F_v]$ ,  $[S_v]$ ,  $[F]$ , and  $[S]$  per unit area, and  $[A]$  per unit volume. For instance, considering a cylindrical tube of radius  $R_t$  and length  $L$  (modification to apply the model to other geometries is immediate), one has

$$[A_f] = \frac{[\tilde{A}_f]}{(2\pi R_t L)}, \quad [A_s] = \frac{[\tilde{A}_s]}{(2\pi R_t L)} \quad (9)$$

$$[F_v] = \frac{[\tilde{F}_v]}{(2\pi R_t L)}, \quad [A_s] = \frac{[\tilde{A}_s]}{(2\pi R_t L)} \quad (10)$$

$$[A] = \frac{[\tilde{A}]}{(\pi R_t^2 L)} \quad (11)$$

and  $[F] = [F_v] + [A_f]$  and  $[S] = [S_v] + [A_s]$ . Substituting in (7) and (8), results

$$\frac{d}{dt}[A_f] = [A][F_v]k_1 - [A_f]k_2 - [A_f][S_v]k_5 - [A_f][A_s]k_6 \quad (12)$$

and

$$\frac{d}{dt}[A_s] = [A][S_v]k_3 - [A][A_s]k_4 + [A_f][S_v]k_5 - [A_f][A_s]k_6 \quad (13)$$

where the rate coefficients  $k_1 = (\pi R_t^2 L)\tilde{k}_1$ ,  $k_2 = \tilde{k}_2$ ,  $k_3 = (\pi R_t^2 L)\tilde{k}_3$ ,  $k_4 = (\pi R_t^2 L)\tilde{k}_4$ ,  $k_5 = (2\pi R_t L)\tilde{k}_5$ , and  $k_6 = (2\pi R_t L)\tilde{k}_6$  have been defined.  $k_1$ ,  $k_3$ , and  $k_4$  are given in  $\text{m}^3 \cdot \text{s}^{-1}$ ,  $k_5$ , and  $k_6$  in  $\text{m}^2 \cdot \text{s}^{-1}$ , and  $k_2$  in  $\text{s}^{-1}$ . Introducing the different reaction rates ( $\text{s}^{-1}$ ) $r_1$ – $r_6$  as

$$\begin{aligned} r_1 &= [A]k_1, & r_2 &= k_2, & r_3 &= [A]k_3 \\ r_4 &= [A]k_4, & r_5 &= [F]k_5, & r_6 &= [F]k_6 \end{aligned} \quad (14)$$

dividing (12) by  $[F]$  and (13) by  $[S]$ , and defining the fractional coverage of physisorption and chemisorption sites, respectively, by

$$\theta_f = \frac{[A_f]}{[F]} \quad \text{and} \quad \theta_s = \frac{[A_s]}{[S]} \quad (15)$$

it results

$$\frac{d\theta_f}{dt} = (1 - \theta_f)r_1 - \theta_f r_2 - \theta_f(1 - \theta_s)\frac{[S]}{[F]}r_5 - \theta_f\theta_s\frac{[S]}{[F]}r_6 \quad (16)$$

and

$$\frac{d\theta_s}{dt} = (1 - \theta_s)r_3 - \theta_s r_4 + \theta_f(1 - \theta_s)r_5 - \theta_f\theta_s r_6. \quad (17)$$

The final form of the equations to be solved is the one presented in (16) and (17). Section II-C details how to obtain the recombination probability from these equations, while the expressions for the reaction rates  $r_1$ – $r_6$  are derived in Section III.

### C. Recombination Probability

*1) Basic Derivation:* It is not difficult to obtain the value of the atomic recombination probability on the surface  $\gamma$  under the present formulation. For a surface kinetics described by the set of reactions (1)–(6), the rate of loss of  $A$  atoms from the volume due to the processes occurring at the wall is given by

$$\left( \frac{d[\tilde{A}]}{dt} \right)_{\text{wall}} = - \left( [\tilde{A}][\tilde{F}_v]\tilde{k}_1 - [\tilde{A}_f]\tilde{k}_2 + [\tilde{A}][\tilde{S}_v]\tilde{k}_3 + [\tilde{A}][\tilde{A}_s]\tilde{k}_4 \right). \quad (18)$$

Using expressions (9)–(11) and the definitions of the different coefficients  $\tilde{k}_i$ , one gets

$$\begin{aligned} \left( \frac{d[A]}{dt} \right)_{\text{wall}} &= -\frac{2}{R} ([A][F_v]k_1 - [A_f]k_2 \\ &\quad + [A][S_v]k_3 + [A][A_s]k_4) \\ &\equiv -\frac{\langle v_A \rangle \gamma}{2R_t} [A] \end{aligned} \quad (19)$$

where the factor  $(2/R_t)$  appearing in the formula is no more than the area-to-volume ratio, and

$$\langle v_A \rangle = \sqrt{\frac{8kT_g}{\pi M_A}} \quad (20)$$

with  $T_g$  and  $M_A$  denoting the gas temperature and the mass of  $A$  atoms, respectively, is the thermal speed of gas phase atoms.

Note that the apparent recombination probability  $\gamma_A$  is obtained correcting  $\gamma$  with the roughness factor  $\varepsilon \geq 1$  corresponding to the ratio of the real surface area to the geometric area  $2\pi R_t L$ ,  $\gamma_A = \varepsilon\gamma$ . For instance, in [11], a value  $\varepsilon \simeq 2.4$  is reported for nitrogen recombination in silica.

Using the flow of atoms to the surface ( $\text{m}^{-2} \cdot \text{s}^{-1}$ )

$$\phi_A = \frac{1}{4} \langle v_A \rangle [A] \quad (21)$$

and the rates (14),  $\gamma$  can be calculated from

$$\gamma = \frac{1}{\phi_A} ([F_v]r_1 - [A_f]r_2 + [S_v]r_3 + [A_s]r_4). \quad (22)$$

This last expression can be simplified by noting that, in steady state, the fractional coverages  $\theta_f$  and  $\theta_s$  have to be constant in time. Therefore, from (12) and (13)

$$[F_v]r_1 - [A_f]r_2 = [A_f][S_v]k_5 + [A_f][A_s]k_6 \quad (23)$$

and

$$[S_v]r_3 = [A_s]r_4 - [A_f][S_v]k_5 + [A_f][A_s]k_6. \quad (24)$$

Substituting in (22) and noting that  $r_6 = [F]k_6$ , it finally results

$$\begin{aligned} \gamma &= \frac{2[A_s](r_4 + \theta_f r_6)}{\phi_A} \\ &= \gamma^{\text{E-R}} + \gamma^{\text{L-H}}. \end{aligned} \quad (25)$$

$$\gamma^{\text{E-R}} = \frac{2[A_s]r_4}{\phi_A} \quad (26)$$

and

$$\gamma^{\text{L-H}} = \frac{2[A_s]\theta_f r_6}{\phi_A} \quad (27)$$

are the contributions of the E-R and L-H recombination mechanisms to the total recombination probability. Evidently, recombination proceeds essentially via an E-R process if  $r_4 \gg \theta_f r_6$ , and via an L-H one in the opposite case.

Take note that, in principle, the right-hand side of (19) and (21) can be used only for a homogenous gas phase system. In the general case, the profile of  $A$  atoms is not flat and the flow of atoms to the surface is no longer given by (21) [34], expressions (19) and (21) being only valid in the limit  $\gamma \ll 1$ . Nevertheless, for the purpose of calculating the recombination probability one can assume a homogeneous system. Evidently, if the surface kinetics is to be coupled with the volume one, then the correct expression for the atomic flow to the surface, which can be found in [34] and [35], has to be used. It subsequently leads to corrected expressions for the loss term  $(d[A]/dt)_{\text{wall}}$ . One possible correction, relying on a different assumption regarding the profile of the colliding species, is presented, for example, in [36] and [37].

2) *Alternative Deductions of (25):* It is worth to take the time to obtain the main result of this section, namely the expression for the recombination probability (25), in a slightly different way. Although in the end all derivations are equivalent, of course, the underlying philosophy of each of them is a bit different and it is enlightening and meritorious to go through them.

If the flow of atoms to the surface is  $\phi_{\text{in}} = \phi_A$ , from the very notion of recombination probability the flow of atoms coming from the surface is

$$\phi_{\text{out}} = \phi_{\text{in}} - \gamma\phi_{\text{in}}. \quad (28)$$

Thus, the probability of atomic recombination on the surface can be calculated from

$$\gamma = 1 - \frac{\phi_{\text{out}}}{\phi_{\text{in}}}. \quad (29)$$

As outlined in [38], the flow of atoms from the surface has two terms. The first one corresponds to the atoms that return to the gas phase as a result of thermal desorption from the surface. The number of atoms leaving the wall due to desorption, per second and per unit area is just  $[A_f]k_2$ . The second term describes the atoms arriving at the surface that are reflected, i.e., those which are neither adsorbed nor recombining via the E-R mechanism. Always per unit area and per second, the number of physisorbed atoms is  $[F_v][A]k_1$ , the number of chemisorbed atoms is  $[S_v][A]k_3$ , and the number of recombining atoms is  $[A][A_s]k_4$ . Accordingly, the second component of  $\phi_{\text{out}}$  is  $\phi_A - [F_v][A]k_1 - [S_v][A]k_3 - [A][A_s]k_4$ , so that

$$\gamma = \frac{-[F_v][A]k_1 + [A_f]k_2 - [S_v][A]k_3 - [A][A_s]k_4}{\phi_A}. \quad (30)$$

This equation is precisely the same as (19), subsequently leading to (25).

Yet an alternative and equivalent way of obtaining the probability  $\gamma$  is by noting that, as each molecule resulting from recombination carries two atoms

$$\phi_{\text{in}} = \phi_{\text{out}} + 2\phi_{A_2} \quad (31)$$

where  $\phi_{A_2}$  is the number of molecules coming from the surface as a result of heterogeneous recombination. Therefore, from (28) and  $\phi_{\text{in}} = \phi_A$

$$\gamma = \frac{2\phi_{A_2}}{\phi_A}. \quad (32)$$

Since

$$\phi_{A_2} = [A_s][A]k_4 + [A_s][A_f]k_6 = [A_s]r_4 + [A_s]\theta_f r_6 \quad (33)$$

(25) is recovered directly from (32) and (33).

### III. RATE COEFFICIENTS OF THE ELEMENTARY PROCESSES

The solution of (16) and (17), describing the time evolution of the occupancy of physisorption and chemisorption sites, requires the knowledge of the different rates (1)–(6). The same is true in what concerns the analysis of expression (25) for the heterogeneous recombination probability. These rates are derived below, together with a brief discussion on how the densities of adsorption sites are considered in this paper.

Nitrogen recombination on silica according to the study in [11] provides the reference case to this paper. Nevertheless, other cases are studied as well, and the full range of possibilities offered by the kinetic scheme (1)–(6) is explored along this paper.

### A. Densities of Adsorption Sites

Both physisorption and chemisorption sites are treated as having radii  $a$ . Moreover, it is assumed that the surface is fully covered with adsorption sites. In other words, the total area occupied by the adsorption sites is equal to the total area of the surface. Hence, the distance between sites is  $2a$  and the area occupied by the adsorption sites in a unit surface is equal to one

$$([F] + [S]) \pi a^2 = 1. \quad (34)$$

In principle, the chemisorption sites occupy only a small fraction of the surface. Let  $2b$  denote the distance between two chemisorption sites. The fraction of the surface covered by chemisorption sites is then

$$\varphi = \frac{[S]}{[F] + [S]} \sim \frac{a^2}{b^2}. \quad (35)$$

As typical values to serve as basis for the present investigation, we take  $a \sim 1 \text{ \AA}$ , consequently  $[F] \simeq 10^{16} \text{ cm}^{-2}$ , in accordance with [15]. We further consider  $\varphi = 2 \times 10^{-3}$  [11]. That being so,  $b \sim \varphi^{-1/2}a \sim 2 \times 10^{-7} \text{ cm}$ .

Evidently, other values are perfectly reasonable. For instance, in [39] the distance between adsorption sites  $2a$  is suggested to be of the order of  $3 \text{ \AA}$ , which leads to  $[F] \sim 1.4 \times 10^{15} \text{ cm}^{-2}$ . This value is in agreement with the densities employed in [17] and [20], of  $10^{15}$  and  $2 \times 10^{15} \text{ cm}^{-2}$ , respectively. In what concerns  $\varphi$ , the values  $\varphi = 3 \times 10^{-3}$  and  $4 \times 10^{-3}$  are considered in [15] for two independent systems of chemisorption sites, the much larger value  $\varphi = 2.5 \times 10^{-1}$  is used in [17], whereas  $6 \times 10^{-2}$  is used in [19] for Pyrex.

Currently, the dispersion in the values of  $\varphi$  is not completely understood. On the one hand, the active chemisorption sites are believed to correspond, essentially, to the presence of impurities on the surface. This makes it reasonable to admit some variation on their number depending on the precise manufacturing conditions. On the other hand, it is well known that the recombination probability is quite different under discharge and postdischarge conditions. An important change in the recombination probability of O atoms has also been observed in the afterglow if the surface was previously treated either by an oxygen or a nitrogen discharge [40], [41]. An explanation for this phenomenon is that the discharge vacates the active sites [19]. Moreover, it has been suggested that the presence of charged particles may create new active sites [15].

### B. Physisorption

Let  $k_1^{0'}$  denote the sticking probability for physisorption sites, i.e., the probability that a gas phase atom impinging on an empty physisorption site becomes adsorbed. In general, this probability can be written as

$$k_1^{0'} = k_1^0 \exp\left(-\frac{E_f}{RT_w}\right) \quad (36)$$

where  $k_1^0$  is a steric factor and  $E_f$  is the activation energy for physisorption,  $R$  is the gas constant, and  $T_w$  is the gas temperature very close to the wall, taken here as equal to the wall

temperature. Following [11], the values  $k_1^0 = 1$  and  $E_f = 0$  are chosen for the base calculations. Hence,  $k_1^{0'} = 1$ , meaning that any gas phase atom arriving from the surface at an empty physisorption site is indeed adsorbed. Note that a possible dependence of the sticking probability with the energy of the impinging atoms is not taken into account. The same applies to all the probabilities herein considered. This approximation should break down as the gas temperature becomes higher.

Since the surface does not consist solely of physisorption sites, the probability that a gas phase atom impinging on the empty surface becomes physisorbed,  $k'_1$ , is obtained from (36) upon correction by the fraction of the surface covered by physisorption sites  $1 - \varphi = [F]/([F] + [S])$

$$k'_1 = k_1^{0'}(1 - \varphi). \quad (37)$$

On the other hand, by definition,  $k'_1$  is the ratio of the number of physisorbed atoms per unit area and per second to the flow of atoms to the surface, in the case where all physisorption sites are free. Therefore

$$k'_1 = \frac{[N][F]k_1}{\phi_A}. \quad (38)$$

Finally, the rate  $r_1$  is given by

$$r_1 = [N]k_1 = \frac{k'_1\phi_A}{[F]} (\text{site})^{-1}\text{s}^{-1}. \quad (39)$$

### C. Thermal Desorption

The rate for thermal desorption from physisorption sites is readily calculated from the standard expression for  $k_2$

$$r_2 = k_2 = \tau_d^{-1} = \nu_d \exp\left(-\frac{E_d}{RT_w}\right). \quad (40)$$

In this equation,  $\nu_d$  is the frequency factor for vibration of physisorbed atoms in the direction perpendicular to the surface, typically  $\nu_d \simeq 10^{15} \text{ s}^{-1}$ , and  $E_d$  is the activation energy for desorption,  $E_d = 51 \text{ kJ} \cdot \text{mol}^{-1}$  [11] for the reference case of this paper. A value of  $E_d = 33.3 \text{ kJ} \cdot \text{mol}^{-1}$  is used in studying oxygen recombination on silica in [15].

A crude classical estimate of  $\nu_d$  is the number of attempted escapes per second from the adsorption well,  $\nu_d \sim h\nu/2$ , where  $\nu$  is the frequency of atom oscillations in the well. However,  $\nu_d$  cannot be accurately estimated in this way [42], because for physisorption the ratio of the statistical weights for escaping and trapping molecules is usually large [39], [42]. Typical values for  $\nu_d$  are in the range  $10^{14} - 10^{16} \text{ s}^{-1}$ . The very large value  $10^{20} \text{ s}^{-1}$  was suggested in [19] for oxygen recombination on Pyrex, a value that looks rather difficult to justify at present on physical grounds.

### D. Chemisorption

The evaluation of the rate of chemisorption  $r_3$  is similar to the one of physisorption  $r_1$ .

Following the development in Section III-B, let  $k'_3$  represent the probability that an atom arriving from the gas phase to an

empty surface becomes chemisorbed, and let  $k_3^{0'}$  denote the sticking probability for chemisorption sites

$$k_3^{0'} = k_3^0 \exp\left(-\frac{E_s}{RT_w}\right) \quad (41)$$

$E_s$  being the activation energy for chemisorption. Following [11], the reference model assumes  $k_3^0 = 1$ ,  $E_s = 0$  and, therefore,  $k_3^{0'} = 1$ , the same as  $k_1^{0'}$ .

Since  $k_3'$  is the ratio of the number of chemisorbed atoms per unit area and per second to the flow of atoms to the surface, in the case where all the chemisorption sites are free

$$k_3' = \frac{[N][S]k_3}{\phi_A} \quad (42)$$

Moreover, as the probability for an atom arriving from the gas phase to impinge on a chemisorption site is just the fraction of the surface covered by chemisorption sites,  $\varphi$

$$k_3' = k_3^{0'}\varphi. \quad (43)$$

Finally

$$r_3 = [N]k_3 = \frac{k_3'\phi_A}{[S]} \text{ (site)}^{-1}\text{s}^{-1}. \quad (44)$$

Note that  $r_3/r_1 = k_3^{0'}/k_1^{0'}$ . That being so, if  $k_3^{0'} = k_1^{0'}$ , i.e., if the sticking probabilities are the same for both types of adsorption sites, then  $r_3 = r_1$ , as expected, since the rates are per adsorption site.

### 1) On the Thermal Desorption From Chemisorption Sites.

In the present description, it is assumed that a chemisorbed atom can only leave the surface by recombination. This approximation imposes a limit in the wall temperature for the applicability of the model. According to the study in [11] and [43], the activation energy for an exothermic process  $AB + C \rightarrow A + BC$  is  $0.055 D(A - B)$ , where  $D(A - B)$  is the dissociation energy of  $AB$ . Using an activation energy for recombination of 16 kJ/mol (see Section III-E), the binding energy between a chemisorbed atom  $A$  and the wall (\*) can be estimated to be of the order of  $D(A - *) = 16/0.055 = 290$  kJ/mol. This value is the same as given by [16] and close to the 250 kJ/mol suggested in [43]. On the other hand, a value of the order of 500 kJ/mol for the O–Si bond is given in [13], but the desorption energy from chemisorption sites is considered to be half of the bond  $\simeq 250$  kJ/mol. If it turns out to be of importance, desorption from chemisorption sites can be taken into account using an expression similar to (40), with an exponential in  $D(A - *)/RT_w$ . Take note that for the higher values of  $T_w$  considered in this paper ( $T_w = 2000$  K), desorption from chemisorption sites can already be possible.

### E. E–R Recombination

The E–R recombination rate is readily calculated from  $r_3$ . As a matter of fact, let  $k_4'$  denote the probability for an atom arriving at an occupied chemisorption site to recombine. Then, the E–R recombination rate per occupied chemisorption site and

per second is no more than the rate of adsorption in chemisorption sites (which is assumed to be the same as if the site were vacant) multiplied by the recombination probability  $k_4'$

$$r_4 = [A]k_4 = r_3k_4'. \quad (45)$$

On the other hand

$$k_4' = k_4^0 \exp\left(-\frac{E_r}{RT_w}\right) \quad (46)$$

where  $k_4^0$  is a steric factor and  $E_r$  is the activation energy for recombination. In the base case,  $k_4^0 = 1$  and  $E_r = 14$  kJ/mol, as proposed in [11] for nitrogen and oxygen recombination on silica. Other values from the literature include  $E_r = 20$  kJ/mol [13], [15],  $E_r = 15$  kJ/mol [43],  $E_r \simeq 24$  kJ/mol [14].

Note still that no E–R recombination is considered to occur on physisorption sites. However, the bond between physisorbed atoms and the surface is relatively weak, so that recombination involving a physisorbed atom can be relatively easy (in particular for the case of L–H recombination). On the other hand, physisorbed atoms may be removed from the surface by the impingement of gas phase atoms, without recombining, particularly if the kinetic energy of the atoms arriving to the surface is relatively big. None of these processes are taken into account here, and atoms arriving from the gas phase to an occupied physisorption site are assumed simply to be reflected, as in the standard treatment of the adsorption–desorption equilibrium.

### F. Surface Diffusion

A physisorbed atom may be lost by thermal desorption, diffusion to a chemisorption site or L–H recombination. The first mechanism takes place with a rate  $k_2$  per second and per physisorbed atom; the second one occurs with rate  $[\tilde{S}_v]\tilde{k}_5 = [S_v]k_5$  per second and per physisorbed atom; the rate of the third process is  $k_6[A_s]$  per second and per physisorbed atom. Therefore, the probability that a physisorbed atom reaches a vacant chemisorption site as a consequence of diffusion and becomes chemisorbed  $k_5'$  is

$$k_5' = \frac{k_5[S_v]}{k_2 + k_5[S_v] + k_6[A_s]} = k_5[S_v]\tau_A \quad (47)$$

where

$$\tau_A = (k_2 + k_5[S_v] + k_6[A_s])^{-1} \quad (48)$$

is the lifetime of a physisorbed atom on the surface. Evidently,  $k_5'$  does depend on the state of the wall. For instance, if all chemisorption sites are occupied,  $[S_v] = 0$  and  $k_5' = 0$ . In the opposite case,  $[A_s] = 0$ , if there is no thermal desorption ( $k_2 = 0$ ), then  $k_5' = 1$ , meaning that a physisorbed atom will always be able to reach a chemisorption site. Typically, for  $T_w \geq 300$  K the average time spent by a physisorbed atom on the surface is controlled by thermal desorption  $\tau_A \simeq k_2$ .

At this point, an expression for  $k_5'$  is required. Let  $\tau_D$  designate the mean time between “hops” from one physisorbed site

to a neighboring one due to diffusion. The diffusion coefficient  $D_s$  is easily obtained [39] and is given by

$$D_s = \frac{l^2}{4\tau_D} \quad (49)$$

where  $l = 2a$  is the distance between two physisorbed sites (cf., Section III-A). Now, if in a certain time interval  $t$ , a physisorbed atom hops  $N$  times due to diffusion, its total displacement is

$$\Delta \vec{r} = \vec{r}(t) - \vec{r}(0) = \sum_{i=1}^N \vec{r}_i. \quad (50)$$

Therefore, since in each jump a physisorbed atom moves a distance  $l$ , the average distance traveled during the time interval  $t$ ,  $\Lambda_D$ , is

$$\Lambda_D^2 = \langle |\Delta \vec{r}|^2 \rangle = \sum_{i=1}^N \langle r_i^2 \rangle = N r_i^2 = \frac{t}{\tau_D} r_i^2 = \frac{t}{\tau_D} l^2. \quad (51)$$

Hence,  $\Lambda_D^2 = (t/\tau_D)l^2 = 4D_s t$ , and

$$\Lambda_D = (4D_s t)^{1/2}. \quad (52)$$

The average time between hops is given by an expression similar to (40) [11]

$$\tau_D = \nu_D^{-1} \exp\left(\frac{E_D}{RT_w}\right) \quad (53)$$

where  $\nu_D$  is the frequency of vibration of a physisorbed atom in the direction parallel to the surface,  $\nu_D \sim 10^{12} - 10^{13} \text{ s}^{-1}$  and  $E_D$  is the energy barrier for diffusion. Expression (53) simply means that for each vibration there is a probability of tunneling through the barrier  $E_D$ . For the reference case, it is assumed  $E_D/E_d = 0.5$  [11].

In summary, the average distance that a physisorbed atom travels on the surface, considering only thermal desorption, is

$$\Lambda_D = (4D_s \tau_d)^{1/2} \quad (54)$$

with

$$D_s = a^2 \nu_D \exp\left(-\frac{E_D}{RT_w}\right) \text{ m}^2 \cdot \text{s}^{-1} \quad (55)$$

and  $\tau_d$  given by (40).

Note that everything happens as if there were collection zones of radius  $\Lambda_D$  around each active (chemisorption) site, as shown in Fig. 1. Only atoms impinging the surface and becoming physisorbed within the collection zones may arrive at a chemisorption site. The probability that physisorption occurs within a collection zone is

$$k' = \begin{cases} 1, & \text{if } \Lambda_D > b \\ \frac{\Lambda_D^2 - a^2}{b^2 - a^2}, & \text{if } a \leq \Lambda_D \leq b \\ 0, & \text{if } \Lambda_D < a \end{cases} \quad (56)$$

where  $b$  was defined in Section III-A.  $\pi(\Lambda_D^2 - a^2)$  is the physisorption area of the collection zone,  $\pi(b^2 - a^2)$  is the total

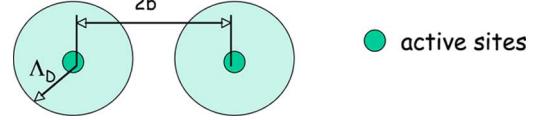


Fig. 1. Schematic representation of the surface, with scattered chemisorption sites and their respective collection zones.

physisorption area. However, for  $\Lambda_D \leq b$ , only 1/4 of the atoms arriving to the collection zone reach the chemisorption site, the remaining 3/4 traveling in a “wrong” direction and migrating to farther distances. Thus, the probability  $k'_D$  that a physisorbed atom arrives at a chemisorption site (vacant or occupied) by diffusion is, for  $a \leq \Lambda_D \leq b$

$$k'_D = \frac{1}{4} k' = \frac{1}{4} \frac{\Lambda_D^2 - a^2}{b^2 - a^2}. \quad (57)$$

Substituting  $\Lambda_D$ ,  $D_s$ , and  $\tau_d$ , and noting that  $a^2/(b^2 - a^2) = [S]/[F]$

$$k'_D = \frac{[S]}{[F]} \left[ \frac{\nu_D}{\nu_d} \exp\left(\frac{E_d - E_D}{RT_w}\right) - \frac{1}{4} \right]. \quad (58)$$

Next, the probability that a physisorbed atom arrives at a vacant chemisorption site as a result of diffusion is

$$k'_5 = k'_D \frac{[S_v]}{[S]} \quad (59)$$

with

$$k'_D = \begin{cases} 1, & \text{if } \Lambda_D > b \\ \frac{[S]}{[F]} \left[ \frac{\nu_D}{\nu_d} \exp\left(\frac{E_d - E_D}{RT_w}\right) - \frac{1}{4} \right], & \text{if } a \leq \Lambda_D \leq b \\ 0, & \text{if } \Lambda_D < a \end{cases}. \quad (60)$$

From (47), it finally results

$$k_5 = \frac{k'_5}{[S_v] \tau_A} = \frac{k'_D}{\tau_A [S]} \quad (61)$$

and

$$r_5 = [F] k_5 = \frac{k'_D}{\tau_A} \frac{[F]}{[S]} \quad (62)$$

with  $k'_D$  given by (60).

#### G. L-H Recombination

By the same procedure leading to (47), the probability that a physisorbed atom reaches an occupied chemisorption site and recombines there is

$$k'_6 = \frac{k_6 [A_s]}{k_2 + k_5 [S_v] + k_6 [A_s]} = k_6 [A_s] \tau_A. \quad (63)$$

Clearly, in the case where all chemisorption sites are occupied,  $[S_v] = 0$ , and if there is no desorption,  $k_2 = 0$ , it comes  $k'_6 = 1$ , i.e., a physisorbed atom always finishes to reach an occupied chemisorption site and to recombine. Moreover, if there is no desorption,  $k_2 = 0$ ,  $k'_5 + k'_6 = (k_5 [S_v] + k_6 [A_s]) \tau_A = 1$ ,

which means that a physisorbed atom finishes to either occupy a free chemisorption site or to recombine via the L–H process.

The probability  $k'_6$  is readily obtained following the derivation of  $k'_5$ . As a matter of fact, the probability that an atom reaches an occupied chemisorption site due to diffusion is

$$k'_s = k'_D \frac{[A_s]}{[S]}. \quad (64)$$

Thus, the probability that a diffusing physisorbed atom arrives at an occupied chemisorption site and recombines there is then

$$k'_6 = k'_s k'_4 \quad (65)$$

where it was assumed that the probability for recombination is the same for the L–H and the E–R mechanisms,  $k'_4$ . In other words, when two atoms meet at the surface, recombination depends only on the binding energy of the chemisorbed atom and it does not matter if the second atom arrives at the occupied chemisorption site from the gas phase or as a consequence of diffusion along the surface.

Thus, the last rate needed to solve (16), (17), and (25) is

$$r_6 = [F]k_6 = [F] \frac{k'_6}{[A_s]\tau_A} = \frac{k'_D k'_4}{\tau_A} \frac{[F]}{[S]} = k'_4 r_5. \quad (66)$$

As for the case of the E–R mechanism, no L–H recombination is considered between two physisorbed atoms. Nevertheless, two physisorption atoms meeting at a physisorption site are indeed likely to recombine and form a molecule desorbing to the gas phase. Hence, this process may affect the results of this paper in the limit of high fractional coverage of physisorption sites, as pointed out in Section III-E. From the analysis in [27], it can be inferred that, for the base system herein under analysis, the interactions between physisorbed atoms may start to affect the coverage of physisorption sites at about  $\theta_f \simeq 10^{-2}$ .

Take note that it is possible to eliminate  $\tau_A$  from the expressions for  $r_5$  and  $r_6$

$$\frac{1}{\tau_A} = k_2 + k_5[S_v] + k_6[A_s] = k_2 + \frac{k'_D}{\tau_A} \frac{[S_v]}{[S]} + \frac{k'_D k'_4}{\tau_A} \frac{[A_s]}{[S]} \quad (67)$$

so that

$$\tau_A = \frac{1 - k'_D(1 - \theta_s) - k'_D k'_4 \theta_s}{k_2}. \quad (68)$$

Since  $k'_4 < 1$ ,  $\tau_A$  is maximum for  $\theta_s = 1$ ,  $\tau_A(\max) = (1 - k'_D k'_4)/k_2$ , and minimum for  $\theta_s = 0$ ,  $\tau_A(\min) = (1 - k'_D)/k_2$ . Typically,  $\tau_A \sim k_2^{-1}$ .

It is still worth referring that it is desirable to define  $r_5$  and  $r_6$  as  $[F]k_5$  and  $[F]k_6$ , respectively, and not as  $[S]k_5$  and  $[S]k_6$ , since the former scheme corresponds to higher rates and, consequently, smaller characteristic times for the processes involved. This helps in the choice of the time-step used in the numeric solution to (16) and (17).

## IV. ANALYTICAL SOLUTIONS

### A. E–R Recombination

It is interesting to start with a system that does not exhibit surface diffusion nor, consequently, L–H recombination. In the present formulation, these constraints are equivalent to the condition  $r_5 = r_6 = 0$ . In this case, (16) and (17) are decoupled and the systems of physisorption and chemisorption sites are independent. Moreover, they have immediate analytical solutions

$$\theta_f(t) = \frac{r_1}{r_1 + r_2} + \left( \theta_{f0} - \frac{r_1}{r_1 + r_2} \right) e^{-(r_1 + r_2)t} \quad (69)$$

$$\theta_s(t) = \frac{r_3}{r_3 + r_4} + \left( \theta_{s0} - \frac{r_3}{r_3 + r_4} \right) e^{-(r_3 + r_4)t} \quad (70)$$

where  $\theta_{f0}$  and  $\theta_{s0}$  are, respectively, the fractional coverages of physisorption and chemisorption sites at  $t = 0$ . These expressions simply describe the evolution to physisorption–desorption and chemisorption–recombination equilibria.

The steady-state occupancies of adsorption sites are given by

$$\theta_f = \frac{r_1}{r_1 + r_2} \quad (71)$$

$$\theta_s = \frac{r_3}{r_3 + r_4}. \quad (72)$$

The recombination probability is given by (26). Using (72) and expressions (43)–(46)

$$\gamma^{\text{E–R}} = \frac{2\varphi k_3^0 k_4^0 \exp\left(-\frac{E_r}{RT_w}\right)}{1 + k_4^0 \exp\left(-\frac{E_r}{RT_w}\right)}. \quad (73)$$

Note that the E–R recombination probability is independent of the pressure (independent of  $[A]$ ) and follows an exponential behavior with  $T_w^{-1}$

$$\gamma^{\text{E–R}} \sim \exp\left(-\frac{E_r}{RT_w}\right) \quad (74)$$

except for the case of very high values for the wall temperature  $T_w$ , when the condition  $\exp(-E_r/RT_w) \ll 1$  is no longer valid and  $\gamma^{\text{E–R}}$  starts to saturate close to 1.

### B. L–H Recombination

Consider now all processes (1)–(6) and assume that the wall temperature is not extremely high, in particular, that the condition  $k'_4 = k_4^0 \exp(-E_r/RT_w) \ll 1$  holds. It is not difficult to obtain the steady-state values for the fractional coverages  $\theta_f$  and  $\theta_s$ .

As a matter of fact, from (17), in steady state

$$\theta_s = \frac{r_3 + \theta_f r_5}{r_3 + r_4 + \theta_f r_5 + \theta_f r_6}. \quad (75)$$

Since  $r_6 = k'_4 r_5$  and  $r_4 = k'_4 r_3$

$$\theta_f(r_5 + r_6) = \theta_f r_5 (1 + k'_4) \simeq \theta_f r_5 \quad (76)$$

$$r_3 + r_4 = r_3(1 + k'_4) \simeq r_3. \quad (77)$$

Therefore

$$\theta_s \simeq \frac{r_3 + \theta_f r_5}{r_3 + \theta_f r_5} = 1 \quad (78)$$

i.e., nearly all chemisorption sites are occupied.

In what concerns the occupation of physisorption sites, its steady-state value is obtained from (16) with the left-hand side equal to zero. Noting that

$$\theta_f \theta_s \frac{[S]}{[F]} r_5 - \theta_f \theta_s \frac{[S]}{[F]} r_6 = \theta_f \theta_s \frac{[S]}{[F]} r_5 (1 - k'_4) \simeq \theta_f \theta_s \frac{[S]}{[F]} r_5 \quad (79)$$

expression (16) can be rewritten as

$$0 \simeq (1 - \theta_f) r_1 - \theta_f r_2 - \theta_f (1 - \theta_s) \frac{[S]}{[F]} r_5. \quad (80)$$

Substituting

$$r_5 = \frac{k'_D}{\tau_A} \frac{[F]}{[S]} \simeq k'_D r_2 \frac{[F]}{[S]} \quad (81)$$

it comes

$$\begin{aligned} 0 &\simeq (1 - \theta_f) r_1 - \theta_f r_2 - \theta_f k'_D r_2 (1 - \theta_s) \\ &= (1 - \theta_f) r_1 - \theta_f r_2 [1 + k'_D (1 - \theta_s)] \\ &\simeq (1 - \theta_f) r_1 - \theta_f r_2 \end{aligned} \quad (82)$$

where the condition  $\theta_s \simeq 1$  has been used. That being so, the fractional coverage of physisorption sites can be evaluated from

$$\theta_f \simeq \frac{r_1}{r_1 + r_2} \quad (83)$$

precisely the same value given by (71), corresponding to the case of no diffusion studied in Section IV-A.

Using (83), (66), and  $\tau_A \simeq r_2^{-1}$ , the L–H recombination probability (27) can be approximated by

$$\gamma^{L-H} \simeq \frac{2}{\phi_A} \frac{r_1}{r_1 + r_2} r_2 k'_D k'_4 [F] \quad (84)$$

and, substituting (39)

$$\gamma^{L-H} \simeq 2k'_1 \frac{r_2}{r_1 + r_2} k'_D k'_4. \quad (85)$$

This is the final expression for the L–H recombination probability, which provides an immediate result for  $\gamma^{L-H}$  if the activation energies and the steric factors of the different elementary processes (1)–(6) are known.

Unfortunately, at present many surface characteristics and parameters are poorly known for real systems. It is therefore interesting to look in detail to (85) and explore its different limiting cases. In particular, it is useful to understand how  $\gamma^{L-H}$  can vary with temperature and pressure.

1) *L–H Recombination at High  $T_w$* : At high values of the wall temperature thermal desorption is very efficient and the collection zones do not overlap, i.e.,  $k'_D < 1$ . This also

corresponds to a low fractional coverage of physisorption sites  $\theta_f$  so that

$$\theta_f \simeq r_1 / (r_1 + r_2) \simeq r_1 / r_2 \quad (86)$$

since  $\theta_f \ll 1$  just means  $r_2 \gg r_1$ .

Thus, from (85)

$$\gamma^{L-H} \simeq 2k'_1 k'_D k'_4 = 2k_1^{0'} (1 - \varphi) k'_D k'_4. \quad (87)$$

Replacing  $\varphi$  from (35) and  $k'_D$  from (60), one finally obtains

$$\gamma^{L-H} \simeq 2k_1^{0'} \varphi \frac{\nu_D}{\nu_d} k_4^0 \exp \left( \frac{E_d - E_D - E_r}{RT_w} \right). \quad (88)$$

As the collection zones start to expand as  $T_w$  decreases, it could be expected that L–H recombination would become more effective when  $T_w$  goes down. This is indeed what occurs when  $E_d - E_D - E_r > 0$ . However, if recombination is too difficult and  $E_r$  is large, the numerator of the exponential is negative,  $E_d - E_D - E_r < 0$ ; as a consequence,  $\gamma^{L-H}$  decreases with  $(T_w)^{-1}$ , in spite of the enlargement of the collection zones. In this case, the latter effect is not enough to compensate for the decrease of the recombination probability  $k'_4$  when two atoms meet at a chemisorption site.

The relative importance of E–R and L–H recombination mechanisms is readily obtained to be

$$\frac{\gamma^{L-H}}{\gamma^{E-R}} \simeq \frac{k_1^{0'}}{k_3^{0'}} \frac{1 - \varphi}{\varphi} \frac{\nu_D}{\nu_d} \exp \left( \frac{E_d - E_D}{RT_w} \right) \quad (89)$$

where (26) has been approximated by

$$\gamma^{E-R} \simeq \frac{2[S] r_4}{\phi_N} = 2k'_4 \varphi k_3^{0'}. \quad (90)$$

That being so, the E–R mechanisms gains importance as  $T_w$  increases, as expected.

We can still define  $\gamma_0^{E-R}$  as the E–R recombination probability in the case where all adsorption sites are chemisorption sites. Similarly,  $\gamma_0^{L-H}$  corresponds to an ideal L–H recombination probability where all the surface is covered with physisorption sites (hence some of them on the top of the chemisorption sites, where L–H recombination takes place) and  $k'_D = 1$ , so that all physisorbed atoms arrive at a chemisorption site. In the present situation of high temperatures

$$\gamma_0^{E-R} \simeq 2k'_4 k_3^{0'} \quad (91)$$

and

$$\gamma_0^{L-H} \simeq 2k_1^{0'} k'_4. \quad (92)$$

Clearly

$$\gamma = k'_D (1 - \varphi) \gamma_0^{L-H} + \varphi \gamma_0^{E-R} \quad (93)$$

an expression with a straightforward physical meaning, recalling that  $(1 - \varphi)$  and  $\varphi$  are the fractions of the surface covered by physisorption and chemisorption sites, respectively. The

L–H mechanism becomes dominant over the E–R one when  $k'_D(1 - \varphi) = \varphi$ .

2) *L–H Recombination at Intermediate  $T_w$* : The region of intermediate temperatures is characterized by large enough collection zones, so that  $k'_D = 1$ , but the fractional coverage of physisorption sites remains relatively low, so that  $\theta_f \simeq r_1/r_2$ , as in the previous case.  $\gamma^{L-H}$  is then given by (87), with  $k'_D = 1$ , whereas  $\gamma^{E-R}$  can still be obtained from (90).

A few properties are interesting to note. First, the relative importance of both mechanisms is expressed by

$$\frac{\gamma^{L-H}}{\gamma^{E-R}} \simeq \frac{1 - \varphi}{\varphi} \frac{k_1^{0'}}{k_3^{0'}}. \quad (94)$$

In the case where the sticking probabilities for physisorption and chemisorption sites are the same  $k_1^{0'} = k_3^{0'}$ , this ratio reduces to the fraction of the surface covered by physisorption sites over the fraction of the surface covered by adsorption sites. This is an immediate result, as, in this case, where  $k'_D = 1$ , all physisorbed atoms arrive at occupied chemisorption sites. Since the activation energy for recombination has been assumed to be the same for both processes,  $\gamma^{L-H}/\gamma^{E-R}$  is just the probability that an atom impinges the surface on a physisorption site over the probability it does so on a chemisorption site.

Second, note that

$$\gamma \simeq (1 - \varphi)\gamma_0^{L-H} + \varphi\gamma_0^{E-R} = (1 - \varphi)2k_1^{0'}k'_4 + \varphi 2k_3^{0'}k'_4. \quad (95)$$

Again, if  $k_1^{0'} = k_3^{0'}$ , it simply results

$$\gamma \simeq 2k_1^{0'}k'_4. \quad (96)$$

Recall that this expression is only valid if  $k'_4 \ll 1$  [cf., the denominator in (26)]; otherwise, the probability  $\gamma$  given above could have values larger than one.

Finally, and very interesting but not surprising, in this situation of intermediate temperatures

$$\gamma \propto k'_4 \propto \exp\left(-\frac{E_r}{RT_w}\right). \quad (97)$$

That being so, the dependence of the recombination probability with the wall temperature is the same as for the pure E–R mechanism. In this case, it makes no difference if an atom is adsorbed in a physisorption or a chemisorption site, since all physisorbed atoms diffuse to chemisorption sites.

3) *L–H Recombination at Low  $T_w$* : Looking at expression (84), when  $k'_D = 1$

$$\gamma^{L-H} \simeq \frac{2}{\phi_A} \frac{r_1}{r_1 + r_2} r_2 k'_4 [F]. \quad (98)$$

The domain of low temperatures corresponds to  $k'_D = 1$  and

$$\theta_f \simeq \frac{r_1}{r_1 + r_2} \rightarrow 1. \quad (99)$$

Therefore

$$\gamma^{L-H} \simeq \frac{2}{\phi_A} r_2 k'_4 [F] = \frac{2}{\phi_A} [F] k_4^0 \nu_a \exp\left(-\frac{E_d + E_r}{RT_w}\right). \quad (100)$$

Thus, the dependence of  $\gamma^{L-H}$  with the wall temperature is given by

$$\gamma^{L-H} \propto \exp\left(-\frac{E_d + E_r}{RT_w}\right). \quad (101)$$

It can be concluded that  $\gamma^{L-H}$  decreases with  $T_w^{-1}$  faster than  $\gamma^{E-R}$ . As a consequence, at very low temperatures only the E–R recombination mechanism is efficient (like at very high temperatures!). What happens, in this case, is that, since  $\theta_f \simeq 1$ , almost none of the atoms arriving at the surface becomes physisorbed (the atoms arriving from the gas phase at physisorption sites are indeed reflected), and consequently, the L–H mechanism stops to work.

However, take note that in this limit, the interaction between physisorbed atoms may play an important role, as well as the removal of physisorption atoms due to the impingement of gas phase ones. These mechanisms are not taken into account in the present formulation, as emphasized in Sections III-E and G. Consequently, it would be no surprise if the results corresponding to this low-temperature case, which, from (99), can be defined, approximately, by the condition

$$r_1 \geq r_2 \quad (102)$$

would not describe accurately the surface kinetics in some real systems. Note that some authors do not consider this region of low  $T_w$ , using always an expression close to (95) if  $k'_D = 1$  [11], [19]. It is possible that such approach may give more realistic results in some cases. Nonetheless, this is not completely clear (cf., Fig. 8 and its discussion), and formally, it cannot be justified under the present simplified formulation, as (implicitly) it requires the removal of physisorbed atoms in recombination with gas phase ones and/or a multilayer physisorption description.

### C. Pressure Dependence

In the present section, asymptotic analytical solutions for the E–R and the L–H recombination probabilities have been obtained. A particular attention was given to their dependencies with the wall temperature  $T_w$  in Sections IV-A and B. The analysis of the dependence of these probabilities with pressure is now straightforward.

The recombination probability for the E–R process is given by (73). It is immediate to verify that its value is independent of the flow of  $[A]$  atoms to the surface. Accordingly,  $\gamma^{E-R}$  is independent of pressure, and consequently, the loss term in (19) is just proportional to the gas phase density  $[A]$ , i.e., E–R recombination is always a first-order process.

In what concerns the recombination probability due to the L–H mechanism, it can exhibit either a first-order or a second-order behavior with pressure. As a matter of fact, using (85), and noting that  $\phi_A \propto [A]$ ,  $r_1 \propto \phi_A$  and that  $r_2$ ,  $k'_D$ , and  $k'_4$  are

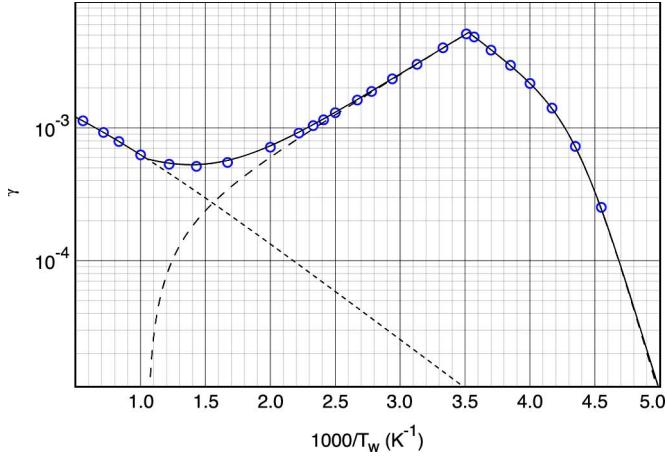


Fig. 2. Nitrogen recombination on silica according to the study in [11]. Asymptotic analytical solutions for (---)  $\gamma^{E-R}$ , (—)  $\gamma^{L-H}$ , and (—)  $\gamma^{E-R} + \gamma^{L-H}$ ; ○ numerical solution.

independent of  $[A]$ , it follows that the pressure dependence of  $\gamma^{L-H}$  is contained in the expression

$$\gamma^{L-H} \propto \frac{2}{\phi_A} \frac{r_1}{r_1 + r_2}. \quad (103)$$

As a consequence,  $\gamma^{L-H}$  is first or second order ( $\gamma^{L-H}[A] = \text{cte}$ ) if  $\theta_f \simeq r_1/(r_1 + r_2) \simeq r_1/r_2$  or  $\simeq 1$ , respectively. The former case corresponds to the situations of high and intermediate temperatures discussed above, whereas the latter one represents the low-temperature limit. As a simple estimation, the transition from a first-order to a second-order process occurs at

$$r_1 = r_2. \quad (104)$$

## V. APPLICATION AND DISCUSSION

The general formulation herein presented can now be exploited and applied to the analysis of heterogeneous recombination of real systems.

The starting point of this investigation is the recombination of atomic nitrogen in silica, according to the study in [11]. The different surface parameters required to the application of the analytical expressions of this paper were given along the text, and are repeated here:  $[F] = 10^{16} \text{ cm}^{-2}$ ,  $\varphi = 2 \times 10^{-3}$ ,  $E_d = 51 \text{ kJ/mol}$ ,  $E_r = 14 \text{ kJ/mol}$ ,  $E_D = 0.5E_d$ ,  $\nu_d = 10^{15} \text{ s}^{-1}$ ,  $\nu_D = 10^{13} \text{ s}^{-1}$ , and  $k_1^{0\prime} = k_3^{0\prime} = k_4^{0\prime} = 1$ . The recombination probability is shown in Fig. 2. The calculations from the model were made assuming a nitrogen gas density  $[N] = 10^{15} \text{ cm}^{-3}$ . The short dashes (---) represent  $\gamma^{E-R}$  as given by (73), the long dashes (—) depict  $\gamma^{L-H}$  calculated from (85), the full curve corresponds to the total recombination probability,  $\gamma^{E-R} + \gamma^{L-H}$ . The open circles ○ give the total recombination probability, obtained from (25) after the numerical solution of (16) and (17). The validity of the proposed analytical asymptotic solutions is immediately confirmed from the excellent agreement they exhibit with the exact numerical solutions. All domains of temperature are clearly identified. At very high temperatures, there is a region dominated by E-R recombination.

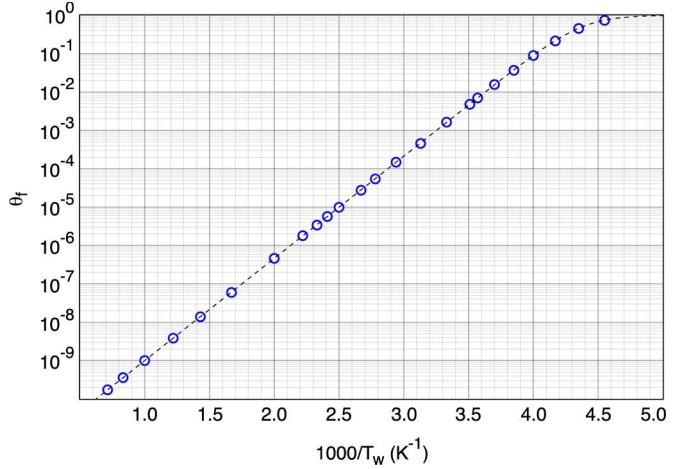


Fig. 3. Fractional coverage of physisorption sites, for the same conditions as in Fig. 2: (—) asymptotic analytical solution; ○ numerical solution.

Then, as temperature starts to decrease L-H recombination becomes increasingly important, as a consequence of the expansion of the collection zones; since  $E_d - E_D - E_r > 0$ , the total recombination probability increases when  $T_w$  decreases, when L-H becomes dominant. At about  $T_w \simeq 280 \text{ K}$  ( $1000/T_w \simeq 3.6$ ) the collection zones completely overlap, so that  $k'_D$  becomes 1 and the region of intermediate temperatures is reached. This point is clearly seen in the figure. The transition to the region of low temperatures, with a steepest decrease of  $\gamma$  with  $T_w^{-1}$  is also evident in the figure. This example shows well how a relatively simple surface kinetic scheme, described by reactions (1)–(6), can manifest a very complex nonmonotonic behavior for the recombination probability with the temperature.

Fig. 3 presents the steady-state occupancy of physisorption sites  $\theta_f$ , given by the approximate solution (83) (dashed curves) and by the numerical solution to the coupled (16) and (17), for the same conditions as in Fig. 2. Once more, the agreement between the analytical solutions derived in this paper and the exact solutions is extremely good.

The dependence of  $\gamma$  with pressure is shown in Figs. 4 and 5, corresponding to  $T_w = 220$  and  $330 \text{ K}$ , respectively, with the same notation as in Fig. 2. As debated previously,  $\gamma^{E-R}$  is independent of pressure, whereas  $\gamma^{L-H}$  has a transition from first order ( $\gamma^{L-H}$  constant with  $[N]$ ) to second order ( $\gamma^{L-H}$  is a straight line in  $\log \times \log$  scale) at about  $r_1 = r_2$ . For the situation represented in Fig. 4,  $r_2 \simeq 7.8 \times 10^{-2} \text{ s}^{-1}$  and  $r_1 \simeq 1.4 \times 10^{-12} [N] \text{ s}^{-1}$ , with  $[N]$  in  $\text{cm}^{-3}$ . Condition (104) coincides then with  $[N] \simeq 5.4 \times 10^{14} \text{ cm}^{-3}$ . Inspection of the figure confirms the position of the transition from a first to a second-order process. Moreover, the correctness of the analytical solutions is once more confirmed. Finally, note that at atomic densities above  $\sim 10^{18} \text{ cm}^{-3}$  the total recombination probability is again first order, in spite of the increase in pressure, because for those densities the first-order E-R mechanism becomes dominant. That being so, the total recombination probability has a first-order behavior both at very high and very low pressures, due to the E-R and L-H processes, respectively.

The higher temperature case depicted in Fig. 5 is quite similar to the previous one. However, as the temperature is

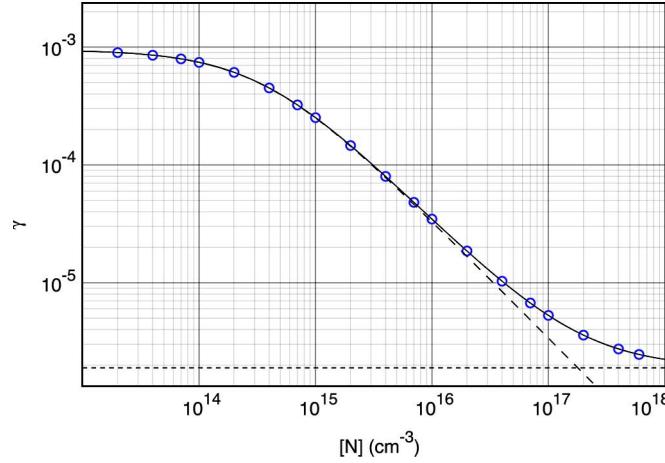


Fig. 4. Nitrogen recombination on silica according to the study in [11]. Asymptotic analytical solutions for (---)  $\gamma^{\text{E-R}}$ , (- -)  $\gamma^{\text{L-H}}$ , and (—)  $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$ ; ○ numerical solution.

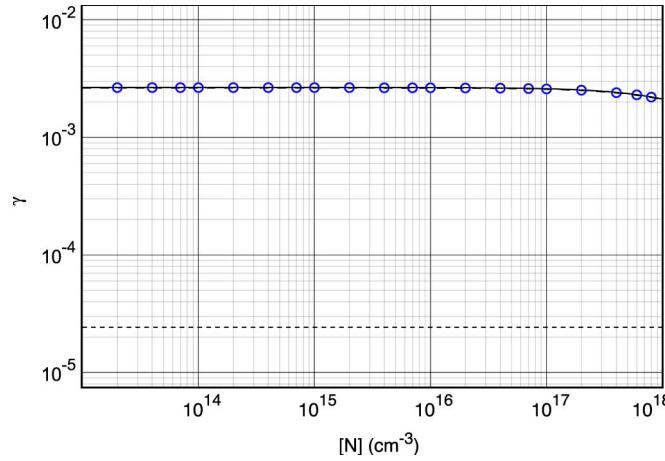


Fig. 5. Nitrogen recombination on silica according to the study in [11]. Asymptotic analytical solutions for (---)  $\gamma^{\text{E-R}}$ , (- -)  $\gamma^{\text{L-H}}$ , and (—)  $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$ ; ○ numerical solution.

higher now,  $r_1/(r_1 + r_2) \simeq r_1/r_2$  for the default conditions of the analysis. Accordingly,  $\gamma$  presents a first-order dependence practically over the all range of gas phase atomic densities considered. The transition to a second-order mechanism corresponding to  $r_1 = r_2$  takes place only at  $[N] \simeq 4 \times 10^{18} \text{ cm}^{-3}$ .

The next system studied is again nitrogen recombination on silica, but now as specified in [15]. The surface characteristics are the same as in Fig. 2, with the exception of the activation energy for recombination, which is set to  $E_r = 20 \text{ kJ/mol}$ . The results are shown in Fig. 6. The theoretical results in [15] are also plotted in the figure (x) for comparison. Note that the theoretical results in [15] are compared well with the experimental data in [11], [44]–[48], not reproduced here (cf., in [15, Fig. 6]). The general trend is very similar to the one in Fig. 2, the main difference being the magnitude of the calculated recombination probability.

Fig. 7 shows a completely different case. It describes oxygen recombination in silica according to the study in [15]. In this reference, not all surface characteristics are specified, as in some cases, only the product of two quantities is

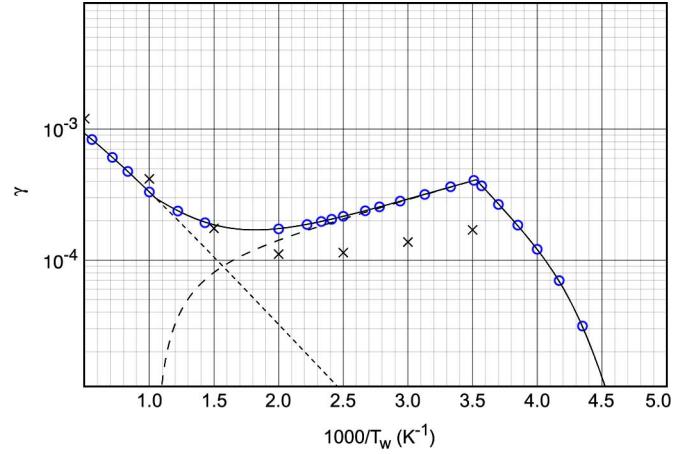


Fig. 6. Nitrogen recombination on silica according to the study in [15]. Asymptotic analytical solutions for (---)  $\gamma^{\text{E-R}}$ , (- -)  $\gamma^{\text{L-H}}$ , and (—)  $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$ ; ○ numerical solution; (x) theoretical results in [15].

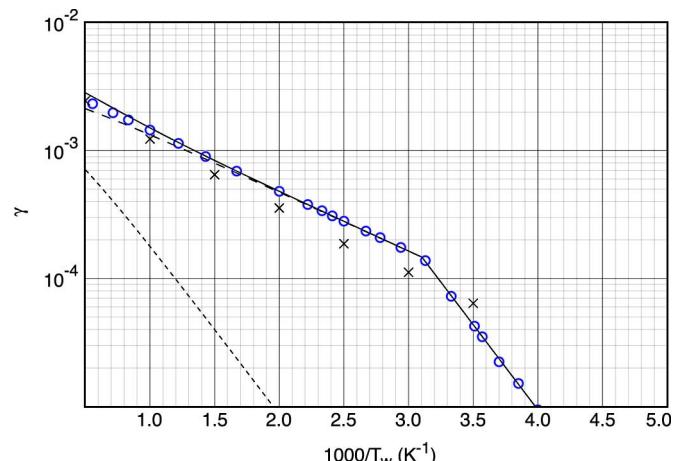


Fig. 7. Oxygen recombination on silica according to the study in [15]. Asymptotic analytical solutions for (---)  $\gamma^{\text{E-R}}$ , (- -)  $\gamma^{\text{L-H}}$ , and (—)  $\gamma^{\text{E-R}} + \gamma^{\text{L-H}}$ ; ○ numerical solution; (x) theoretical results in [15].

given. One possible solution corresponds to  $E_d = 33.3 \text{ kJ/mol}$ ,  $E_D = 0.5E_d$ ,  $E_r = 25.5 \text{ kJ/mol}$ , and  $\nu_D = \nu_d = 10^{15} \text{ s}^{-1}$ . The remaining properties remain as in Fig. 2. This system reveals a very efficient diffusion of physisorbed atoms on the surface, as  $E_D$  is lower and  $\nu_D$  is higher than before. As stated in [39], one should not be surprised by examples which exhibit “anomalous” values of  $\nu_D$ , which differ substantially from the typical  $10^{13} \text{ s}^{-1}$ ; nevertheless, the new value of  $\nu_D$ , when compared to the case of nitrogen, seems somewhat difficult to justify in physical terms. Since  $E_d - E_D - E_r < 0$ , in the high-temperature region  $\gamma^{\text{L-H}}$  decreases with  $T_w$  in spite of the enlargement of the collection zones, as explained in Section IV-B1. In any case, even with this decrease, the L-H mechanism is dominant in the domain of temperatures considered. The agreement with the theoretical calculations in [15] is quite good, and the validity of the asymptotic analytical solutions is again corroborated. It is worth noting that the theoretical results in [15] are in good agreement with the experimental data reported in [11], [49], and [50], for example (see [15, Fig. 5]).

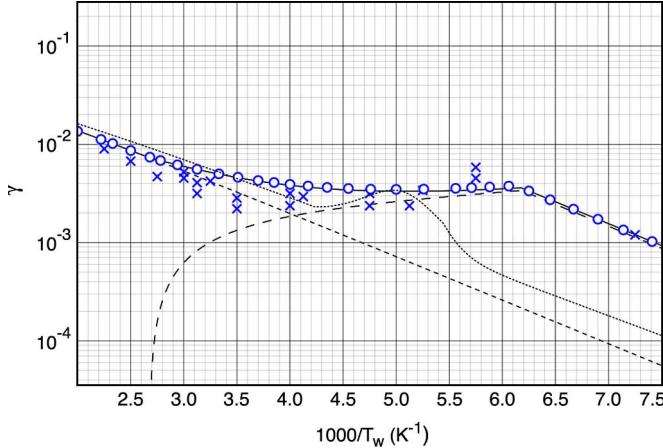


Fig. 8. Oxygen recombination on Pyrex. Asymptotic analytical solutions for (---)  $\gamma^{E-R}$ , (--)  $\gamma^{L-H}$ , and (—)  $\gamma^{E-R} + \gamma^{L-H}$ ; ○ numerical solution; (×) experimental results in [19]; (···) model results using the surface data proposed in [19].

Oxygen recombination on Pyrex was investigated in [19], both experimentally and using the model in [11]. The surface parameters used in [19] to explain the experimental results are  $\varphi = 6 \times 10^{-2}$ ,  $E_d = 57.9$  kJ/mol,  $E_r = 7.72$  kJ/mol,  $E_D = 0.5E_d$ ,  $\nu_d = 10^{20}$  s $^{-1}$ , and  $\nu_D = 10^{13}$  s $^{-1}$ , for a postdischarge at  $T_g = 300$  K and  $p = 1$  torr. These values were obtained essentially from the fitting of the model results to the experimental data. The very high value obtained for  $\nu_d$  is particularly striking and quite difficult to justify. In this paper, this case was studied first by keeping the frequency factor for desorption to the its default value  $\nu_d = 10^{15}$  s $^{-1}$ . On the other hand, the activation energies were chosen as  $E_r = 8.5$  kJ/mol and  $E_d = 20$  kJ/mol, whereas the value proposed in [19] for the fraction of the surface covered with chemisorption sites was used. The results are shown in Fig. 8. Once more, a non-monotonic behavior of  $\gamma$  with the wall temperature is found, due to the competition between the L-H and E-R recombination mechanisms. As in all the previous cases studied, the analytical asymptotic solutions are very accurate and reproduce the numerical ones. Moreover, the theoretical results are very close to the experimental data.

The theoretical results from the present model using the surface parameters proposed in [19] are also shown in the figure (dotted line) for comparison. They manifest one unusual particularity worth referring to. Although L-H recombination is always given by expression (85), in this situation, it does not exhibit a region of “intermediate” temperatures as defined in Section IV-B2. This is a consequence of the extremely high value of  $\nu_d$ , leading to the fulfillment of condition (104) for higher values of  $T_w$  than required to have  $k'_D = 1$ . It can be seen immediately that the experimental results are not adequately described for  $T_w < 200$  K. This discrepancy does not show up in the calculations in [19], because the low-temperature region is treated in a different way there, by simply using an exponential dependence as given by (95).

Two remarks have to be made at this point. The first one is that the present model, despite its possible limitations regarding the description of the low-temperature region discussed in

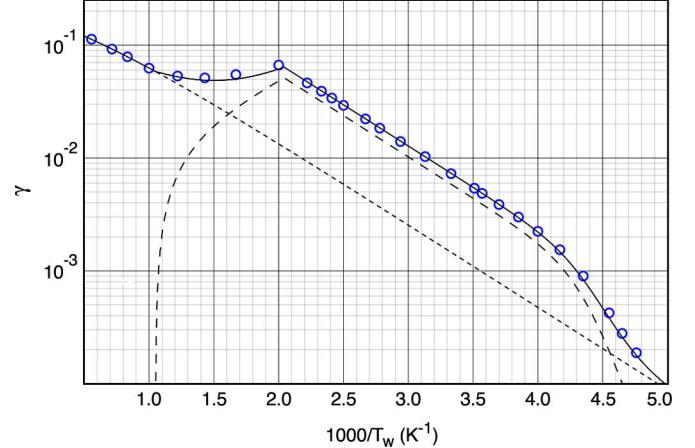


Fig. 9. Same as in Fig. 2, but with  $\varphi = 2 \times 10^{-1}$ . (---)  $\gamma^{E-R}$ , (--)  $\gamma^{L-H}$ , and (—)  $\gamma^{E-R} + \gamma^{L-H}$ ; ○ numerical solution.

Sections III-E, G and IV-B3, leads to a good comparison with the experimental data and to values for the surface characteristics that seem more realistic than those proposed in [19]. The second one is that, at present, due to the unknowns in the elementary data required for modeling, a large number of experimental data in different temperature and pressure conditions are required in order to determine accurately the surface characteristics from modeling; likewise, any fitting procedure has to be made with care, as not to make it arbitrary and incorrect. This latter observation shows by itself the relevance of more fundamental studies such as the one developed in this paper.

Finally, Fig. 9 illustrates a more academic case, where the density of chemisorption sites is increased in respect to the conditions of Fig. 2,  $\varphi = 2 \times 10^{-1}$ , a value close to the one used in [17] for the study of oxygen recombination in silica. All other surface characteristics and conditions remain the same as in Fig. 2. The main interest of this figure is the extended and well-defined region of intermediate temperatures, where (97) holds and, thus,  $\gamma$ ,  $\gamma^{L-H}$ , and  $\gamma^{E-R}$  have the same exponential dependence with  $T_w$ .

## VI. CONCLUSION AND FUTURE WORK

In this investigation, analytical approximate solutions for the heterogeneous recombination probability of a single atomic species on silicalike surfaces were obtained [expressions (73) and (85)]. The surface was assumed to be covered with physisorption and chemisorption sites, recombination taking place on the latter. Physisorbed atoms can diffuse along the surface, and both E-R and L-H mechanisms have been taken into account. The analytical solutions provide ready-to-use expressions for the recombination probability, as a function of the surface (activation energies, densities of sites, wall temperature, ...) and gas (flow of atoms to the surface) characteristics. The validity of the asymptotic analytical solutions was firmly established, form their comparison with the exact numerical solution of the system of equations describing the surface kinetics of the system, in several very different conditions.

It was shown that the recombination probability  $\gamma$  can have a rather complex behavior with the wall temperature  $T_w$  as a

result of the competition between the E–R and L–H recombination mechanisms. E–R recombination decreases exponentially when  $T_w$  decreases. It is dominant at high temperatures, as the physisorbed atoms quickly desorb back to the gas phase and cannot reach the active chemisorption sites. As the temperature decreases, the collection zones—i.e., regions around the chemisorption sites where a physisorbed atom stays long enough to be able to reach the active site by diffusion before it desorbs—start to increase and the L–H recombination probability may [or may not (see Section IV-B1)] increase. When the collection zones start to overlap, the L–H mechanism can no longer improve its efficiency, and the L–H recombination probability goes down quickly, until the E–R process becomes again dominant.

Regarding the pressure dependence, the E–R mechanism is always first order, whereas the L–H one has a transition from first to second order when the pressure increases. Therefore,  $\gamma$  is first order at low pressures. In the model investigated,  $\gamma$  is first order as well at very high pressures, since L–H recombination stops to work then and, consequently, the E–R process becomes dominant.

This paper brings physical insight into the elementary processes ruling surface kinetics in a relatively simple system. Evidently, several improvements can be made, allowing the development of similar models applicable for processes on a surface of real plasma-chemical reactors. One refinement relates to the treatment of physisorbed atoms, with a direct impact on the low-temperature results. First, recombination attempts in several chemisorption sites can be considered when the distance they travel on the surface is large enough (see the Appendix). Next, the removal of physisorbed atoms from the surface due to the impingement of gas phase atoms and recombination between two physisorbed atoms can be included. Another research path to continue this study is to abandon the monolayer description. For instance, the surface can be considered to be fully covered with chemisorption sites with physisorption sites on the top of them. This specification is particularly appropriate to study recombination in metallic surfaces. Finally, the model can be easily extended to study heterogeneous recombination in gas mixtures.

## APPENDIX

### IMPROVED TREATMENT OF L–H RECOMBINATION

The treatment of L–H recombination in this paper is not fully consistent, in particular because nothing is said about what happens to a physisorbed atom that arrives at an occupied chemisorption site and does not recombine, even if it may reach a second chemisorption site.

The inconsistency can be verified as follows. As discussed below (63), for a system with no desorption one should have  $k'_5 + k'_6 = 1$ . In this case of no desorption, and assuming diffusion continues to be possible,  $\Lambda_D = +\infty$  and so  $k'_D = 1$ . However, from (59) and (65), with  $k'_D = 1$

$$k'_5 + k'_6 = \left( \frac{[S_v]}{[S]} + \frac{[A_s]}{[S]} \right) k'_4 \neq 1. \quad (105)$$

This issue, with no importance in practice, can be easily corrected to achieve a more satisfactory formal formulation. Suppose a physisorbed atom reaches a chemisorption site as a result of diffusion. It will recombine with a probability  $k'_4$  and fail recombination with probability  $(1 - k'_4)$ . However, if this atom can travel a distance large enough to reach a second chemisorption site, it can attempt recombination a second time. In this case,  $k'_6$  should be corrected as

$$k'_6 = \frac{[A_s]}{[S]} k'_4 + \frac{[A_s]}{[S]} (1 - k'_4) \frac{[A_s]}{[S]} k'_4. \quad (106)$$

Of course  $k'_5$  should also be corrected in this case, to

$$k'_5 = \frac{[S_v]}{[S]} + \frac{[A_s]}{[S]} (1 - k'_4) \frac{[S_v]}{[S]}. \quad (107)$$

Similarly, if the distance the atoms travels is large enough to permit it attempts recombination in three chemisorption sites, one should still correct  $k'_6$  with an additional factor of

$$\frac{[A_s]}{[S]} (1 - k'_4) \frac{[A_s]}{[S]} (1 - k'_4) \frac{[A_s]}{[S]} k'_4$$

whereas for  $k'_5$  this additional term should be

$$\frac{[A_s]}{[S]} (1 - k'_4) \frac{[A_s]}{[S]} (1 - k'_4) \frac{[S_v]}{[S]}.$$

For  $\Lambda_D = +\infty$ , we should in fact write

$$k'_5 = (1 - \theta_s) \sum_{n=0}^{+\infty} [\theta_s (1 - k'_4)]^n = \frac{1 - \theta_s}{1 - \theta_s (1 - k'_4)} \quad (108)$$

and

$$k'_6 = \theta_s k'_4 \sum_{n=0}^{+\infty} [\theta_s (1 - k'_4)]^n = \frac{\theta_s k'_4}{1 - \theta_s (1 - k'_4)}. \quad (109)$$

Now, the equations are formally correct, as  $k'_5 + k'_6$  is indeed 1 in the case of no desorption. In conclusion, the formulas for  $k'_5$  and  $k'_6$  should be corrected as  $\Lambda_D$  increases beyond  $2b$ ,  $4b$ , etc., and the physisorbed atoms start to be able to meet more than one chemisorption site during their diffusion along the surface.

Another simple way to solve this problem is with the truncation on the first site suggested in [27], by assuming that when a physisorbed atom arrives to a chemisorption site and fails recombination, it desorbs back to the gas phase. This process can be schematically written as  $N_f + N_s \rightarrow N_s + F_v + N$ . The probability for a physisorbed atom to arrive at an occupied chemisorption site and failing recombination is

$$k'_7 = \frac{[A_s]}{[S]} (1 - k'_4) k'_D. \quad (110)$$

Using this truncation,  $k'_5 + k'_6 + k'_7 = k'_D$  always, so that the problem does not exist.

## ACKNOWLEDGMENT

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