Material-Dependent Catalytic Recombination Modeling for Hypersonic Flows

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A new model to predict catalytic recombination rates of O and N atoms over silica re-entry thermal protection system is reported. The model follows the general approach of Halpern and Rosner, but adds estimates of some key physical mechanism parameters based on realistic surface potentials. This novel feature can therefore produce rate expressions for any surface for which structure is known. Testing the model for N over W, and N and O over SiO₂ produces recombination probabilities in good agreement with published measurements at high surface temperature. In the case of N and O over SiO₂, the model accounts for surface NO production due to O and N cross recombination.

Nomenclature

$A, B, \ldots$	=	chemical species
(a)	=	adsorbed atom, adatom
D_i	=	Fick's diffusion coefficient of species i
D_{ij}	=	bond energy between i and j atoms
E_{ai}	=	adsorption activation energy of species i
E_{mi}	=	migration energy of species i
E_{OH}	=	activation energy for OH desorption
E–R	=	Eley–Rideal recombination
(g)	=	gas atom or molecule
h	=	Planck constant
k	=	Boltzmann constant
L–H	=	Langmuir–Hinshelwood recombination
m_i	=	mass of species i
n	=	site density, number of sites per unit area
n_{cij}	=	number of collisions between i and j adatoms per unit area and time
n'_i	=	"hopping" i adatoms per unit area
P_{erij}	=	steric factor of E–R recombination of i adatoms and j gas atoms
P_i	=	adsorption steric factor of species i
p_i	=	partial pressure of species i
Q_{ai}	=	i atom-surface bond energy
Q_{erij}	=	activation energy of E–R recombination of i adatoms and j gas atoms
Q_{lhij}	=	activation energy of L–H recombination of i and j adatoms
s_i	=	sticking coefficient of species i
T	=	temperature
T_w	=	wall temperature
w_i	=	mass flux of species i
Y_i	=	mass fraction of species i
Z_{adi}	=	total flux of adsorbing i atoms
Z_{ai}	=	flux of adsorbing i gas atoms
Z_{dei}	=	total flux of desorbing i atoms
Z_{erij}	=	flux of E–R recombining i adatoms and j gas atoms
Z_i	=	impinging flux of species i
Z_{lhij}	=	flux of L–H recombining i and j adatoms
Z_{tdi}	=	flux of thermally desorbing i adatoms
γ_{ij}	=	recombination probability of gas atom i in ij molecule
γ^*_{ij}	=	E–R recombination probability of gas atom i in ij molecule
Δ	=	mean distance between sites
η	=	coordinate normal to the wall
θ_i	=	percentage of surface sites occupied by species i
θ_f	=	percentage of free surface sites
ν_i	=	hopping frequency of species i
ρ	=	density

Introduction

THE purpose of this article is to present a new model of catalytic recombination of O and N atoms over SiO₂ [a material representative of thermal protection system (TPS) coatings] derived directly from surface properties. Current models in hypersonics computational fluid dynamics (CFD) often use either the noncatalytic or the fully catalytic assumptions as two limiting conditions that should bracket actual material behavior. Discarding the former as unrealistic, the latter largely overpredicted wall heat transfer on the U.S. Orbiter.[1]

Hypersonic (air-breathing) space planes require accurate heat transfer (HT) predictions in some key regions such as the cowl lip, where recirculation may entail "long" residence times.[2] Finite rate catalytic recombination may be crucial in such regions.

The model presented here is an attempt to simulate O and N recombination over SiO₂, following the manner used for atom recombination on metals,[3] including the effect of surface structure on recombination via an approximate analysis of key surface processes.

Literature Review

Catalytic recombination effects in CFD are usually accounted for by introducing the recombination probability γ_{ij} $(0 \leq \gamma_{ij} \leq 1)$. This variable is defined as the ratio of the number of atoms impinging on the surface that recombine to molecules, to the overall number of atoms impinging on the surface, and is obtained either by fitting experimental data[3-5] or by some physical model; in both cases, typically only one chemical species is dissociated.[3,6-10]

Data fits from experiments are usually written in terms of an Arrhenius dependence. For instance, for single species O and N recombination on the silica-based shuttle high-temperature reusable surface insulation (HRSI) material, Scott[4] obtained

$$\gamma_{OO} = 16e^{-10,721/T_w} \qquad (1)$$

$$\gamma_{NN} = 0.0714e^{-2219/T_w} \qquad (2)$$

On the other hand, a physical model of the recombination process of one dissociated species on metal surfaces was proposed by Halpern and Rosner.[3] They modeled recombination describing each surface step, i.e., 1) adsorption of atoms, 2) adsorption of molecules, 3) recombination between gas atoms and adsorbed atoms (adatoms) in gas molecules $(E-R)$, 4) recombination between adatoms in gas molecules $(L-H)$, and 5) thermal desorption. Each of these phenomena is described by the flux of particles involved, i.e., the number of particles per area and time unit. These fluxes are obtained as functions of the flowfield (T and p_i), of the surface structure, and of the surface coverage θ_i (i.e., the fraction of adsorption sites occupied by i adatoms, $0 \leq \theta_i \leq 1$).

By assuming steady-state conditions, the mass balance at the gas–surface interface can be written in terms of atomic and molecular fluxes arriving at and leaving the surface. This balance gives the unknown value of the surface coverage, from which the recombination probability can be computed.

Other models have been proposed[6-10] based on similar ideas, but with more details about the determination of parameters related to the surface structure and to the chemical bonds structure and energy.

Single-Species Model

Modeling recombination of a single dissociated species is described first. In this case, the gas phase is a mixture of molecules A_2 and atoms A. The molecular species of interest are N_2, NO, and O_2; we neglect physisorption, which is important at very low (condensation) temperatures.

Chemisorption, reaction, and desorption are patterned after the Halpern and Rosner approach[3]; however, a great deal of information concerning the interaction between gas and surface structure is added that plays a significant new role. The assumption is made that, after reaction, recombined molecules desorb in local internal equilibrium at the catalyst surface temperature (thermal accommodation factor equals unity). An important consequence is that the recombination energy is immediately released at the reaction site.

The recombination probability is computed by analyzing what each atom or molecule probably does when striking the surface. This analysis is based on the kinetic theory of gases, on the atomic structure of the surface, and on the energies involved in the chemical bonds between atoms and molecules of the gas and the surface atoms. From the kinetic theory of gases

$$Z_i = (p_i/\sqrt{2\pi m_i kT}) \qquad (i = A, A_2) \qquad (3)$$

Only a portion of these atoms and molecules is adsorbed on the surface, while a certain number of adatoms leaves the

surface according to three processes: $E-R$, $L-H$, and thermal desorption. Then the steady-state mass balance is

$$Z_{aA} + Z_{aA2} = Z_{erA} + Z_{lhA} + Z_{tdA} \qquad (4)$$

An atom can be adsorbed only if the corresponding adsorption site is free. Z_{aA} is then proportional to $\theta_f = 1 - \theta_A$. A correction coefficient, the sticking coefficient s_A, accounts for uncertainty in the direction and the energy of the collision that may influence the adsorption process, and therefore,

$$Z_{aA} = s_A \theta_f Z_A \qquad (0 \leq s_A \leq 1) \qquad (5)$$

Clusters of free sites are necessary for the adsorption of a molecule as a couple of adatoms. Z_{aA2} is then proportional to the square of the fraction of free sites. Obviously each adsorbed molecule gives two adatoms, thus Z_{aA2} is a fraction of $2Z_{A2}$. The sticking coefficient s_{A2} is less than s_A, because a chemical bond must be broken. Therefore, an activation energy E_{aA2} is introduced in the s_{A2} expression, since only molecules with enough energy will break the chemical A—A bond. The steric factor P_{A2}, accounts for directional effects that cannot be adequately described otherwise. With this

$$Z_{aA2} = 2s_{A2}\theta_f^2 Z_{A2} \qquad (0 \leq s_{A2} \leq 1) \qquad (6)$$

$$s_{A2} = P_{A2} \exp[-(E_{aA2}/kT)] \qquad (0 \leq P_{A2} \leq 1) \qquad (7)$$

In the Eley–Rideal recombination an atom of gas reacts with an adatom forming a molecule of gas. The number of adatoms that leave the surface by this process is equal to the number of atoms of gas that react in this way, and whose flux is Z_{erAA}. This is a fraction of Z_A proportional to the number of occupied sites via the $E-R$ probability γ_{AA}^*. As is often done for chemical reactions, an activation energy Q_{erAA} is considered together with a steric factor P_{erAA} that corrects the formulas from errors due to directional or other unknown phenomena. The activation energy can be related to the fact that the chemical bond between the adatom and the surface has to be broken:

$$Z_{erAA} = \gamma_{AA}^* \theta_A Z_A \qquad (0 \leq \gamma_{AA}^* \leq 1) \qquad (8)$$

$$\gamma_{AA}^* = P_{erAA} \exp[-(Q_{erAA}/kT)] \qquad (0 \leq P_{erAA} \leq 1) \qquad (9)$$

In the Langmuir–Hinshelwood recombination process, two adatoms moving on the catalyst surface collide and, if there is enough energy, react forming a molecule A_2, which immediately desorbs releasing the recombination energy on the surface. The surface adatom density is $n\theta_A$, but only the fraction

$$n_A' = n\theta_A \exp[-(E_{mA}/kT)] \qquad (10)$$

can move ("hop") along the surface, i.e., can move from a site to another. The migration energy[11] E_{mA} is the energy jump between the potential well corresponding to a site and the potential peak between the sites.

The characteristic hopping frequency ν_A is the number of different sites that an adatom can occupy per unit time if it does not collide with other adatoms. The number of collisions per unit of area and time is the number of sites occupied by the "moving" adatoms $\nu_A n_A'$ (it can be greater than n because each adatom occupies many sites in the unit time) times the probability to find another adatom θ_A. This is also the number of collisions n_{cAA}, only if few adatoms move, so that most collisions occur between a moving and a "still" adatom. This is the case of the gas–surface interactions analyzed: N over W, N over SiO_2, and O over SiO_2 (see the following sections). Therefore,

$$n_{cAA} = \nu_A \theta_A n_A' \qquad (11)$$

For each collision with enough energy two adatoms leave the surface. The adatom flux is then

$$Z_{lhAA} = 2\nu_A n\theta_A^2 \exp[-(Q_{lhAA}/kT)] \qquad (12)$$

where Q_{lhAA} is the greatest between E_{mA} and the activation energy for this recombination process, given[3] by $2Q_{aA} - D_{AA}$. The characteristic frequency ν_A can be obtained as

$$\nu_A = (c_A/\Delta)\sqrt{\pi kT/2m_A} \qquad (13)$$

where the square root term is the mean velocity of the adatoms assuming a two-dimensional gas in the kinetic theory and c_A is a constant factor.

According to transition state theory[12] for reaction rates, the thermal desorption process is described by

$$Z_{tdA} = n\theta_A(kT/h)\exp[-(Q_{aA}/kT)] \qquad (14)$$

where the assumption has been made that the adatom and the gas atom have the same partition function (it corresponds to assuming zero activation entropy). The density of occupied sites $n\theta_A$ represents the reactants concentration.

The balance equation (4) can be solved for θ_A for assigned T, p_A, and p_{A2} by inserting the formulas obtained previously for the fluxes.

The recombination probability can now be expressed knowing which atoms recombine: 1) the atoms that are adsorbed, but that do not desorb as atoms $Z_{aA} - Z_{tdA}$ and 2) the atoms that strike an adatom recombining with the E-R process Z_{erAA}. Therefore,

$$\gamma_{AA} = \frac{Z_{aA} - Z_{tdA} + Z_{erAA}}{Z_A} \qquad (15)$$

In summary, θ_A and then γ_{AA} can be obtained as functions of T, p_A, and p_{A2}, if the values of the parameters s_A, P_{A2}, E_{aA}, P_{erAA}, Q_{erAA}, n, Δ, E_{mA}, Q_{aA}, and D_{AA} are known for the gas species A and the surface material considered. In the following we will deal with how the previous parameters can be determined.

Surface Representation

Some of the parameters introduced earlier can be theoretically predicted if a realistic model of the surface atomic structure and of the forces between gas and surface atoms is developed. A metal lattice (W) interacting with N atoms was studied first. The potential energy of an N atom on a W surface is calculated by summing the contributions due to each isolated N-W pair. The pair interaction is modeled by Morse potentials,[13] and only the nearest W atoms are considered because of the strongly decreasing dependence of chemical force on distance. Surface sites are the potential wells for N on W, and their density is $n = 9.92 \times 10^{18}$ m^{-2}, corresponding to $\Delta = 3.17$ Å. $E_{mN} = 236.2$ kJ/mol is the minimum potential barrier to overcome to go from site-to-site. Consequently, gas kinetics predict that only 2% of the adatoms can move along the surface and Eq. (12) can be applied. The dissociative adsorption of the N$_2$ molecules is possible, in fact, the distance between sites Δ is comparable with N$_2$ dimensions (~ 2.57 Å).

The same method was applied to silica crystalline surfaces. Due to the strong Si-O and Si-N bonds, O and N sites coincide with Si atoms location. Site density was obtained in this way for β quartz, β tridimite, and β crystobalite. The result was $n \simeq 4.5 \times 10^{18}$ m^{-2} and $\Delta \simeq 5$ Å for any kind of silica (amorphous silica properties were also examined). A mean value was taken for n as 4.5×10^{18} m^{-2}. Based on Si-O or Si-N isolated pairs, the potential energy of N and O atoms on SiO$_2$ surface is calculated by means of Morse potentials. The surface consists only of Si atoms and the action of internal

O and Si atoms is neglected. This model yields $E_{mO} = 159.1$ kJ/mol and $E_{mN} = 82.2$ kJ/mol and a corresponding adatom mobility of 0.007 and 0.7%, respectively, which means that Eq. (12) can be applied.

Note that the dissociative chemisorption of N$_2$, O$_2$, and NO on silica can be neglected: in fact, Δ is large if compared with typical dimensions of these molecules, which range from 2.57 to 2.69 Å. This means that only one of the two atoms of the molecule can be close to an adsorption site. In this case, chemisorption would be possible only if the gas molecule was dissociated in an adatom and an atom of gas. The last result is very improbable because the combined energy of an adatom/gas-atom pair is higher than that of the gas molecule, and therefore, the high activation energy of the process yields an activation temperature of at least 5000 K (silica melting temperature is 1983 K).

Surface description also includes effects due to H$_2$O adsorption. Water molecules easily penetrate glass pores and tend to be chemisorbed to Si atoms, forming Si-OH bonds where possible (i.e., mostly on the surface), and reducing sites available to O and N atoms. Because of bond strength, water (OH) tends to remain on the surface even at $T \sim 1700$ K.[14-17] At room temperature the measured adsorbed OH density for silica[14] is 4.610^{18} m^{-2}, i.e., nearly the same as Si atoms, implying $\theta_{OH} \simeq 1$. Therefore,

$$\theta_{OH} = A\{1 - \exp[-(E_{OH}/kT)]\} \qquad (16)$$

was assumed. E_{OH} and A were varied from 0 to 15 kJ/mol and from 0 to 1, respectively, to check their effect on γ. While the choice of A has minor effects, the influence of E_{OH} is not negligible; $E_{OH} = 2.5$ kJ/mol was chosen since it predicts reasonable γ values (see Figs. 1 and 2).
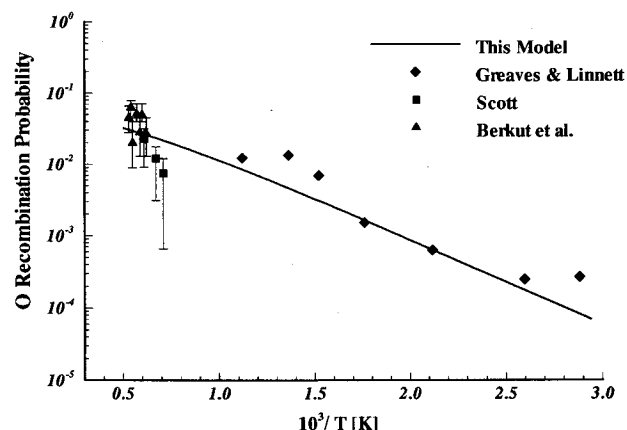

Fig. 1 Oxygen recombination probability γ_{OO} over silica vs inverse temperature.
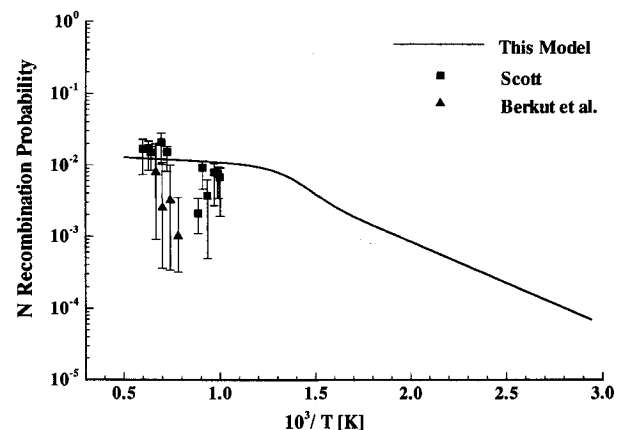

Fig. 2 Nitrogen recombination probability γ_{NN} over silica vs inverse temperature.

Two-Species Model

Based on the single-species model, an extension to a simultaneous recombination of N and O in N_2, O_2, and NO on silica surface has been performed. The dissociative chemisorption of N_2, O_2, and NO molecules on silica surfaces can be neglected, as stated previously.
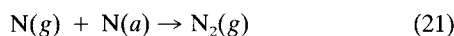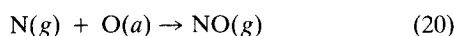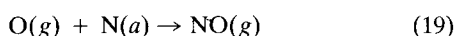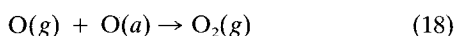
The two-species recombination can be described by the four recombination probabilities γ_{OO}, γ_{NN}, γ_{ON}, and γ_{NO}. Due to the competition between O and N, the corresponding γ_{ij} will not be independent of each other; this is instead the case for experimental fits of γ_{ij} obtained from single-species measurements [Eqs. (1) and (2)]. In other words, single-species experimental measurements of γ_{NN} and γ_{OO} will tend to overpredict N and O recombination when both species are present.

The surface coverages θ_O and θ_N can be defined as fractions of the overall n, because O and N atoms are adsorbed on the same sites. Moreover, the sites available for O and N adsorption are reduced by Si-OH surface bonds.

The free-sites fraction θ_f is therefore,

$$\theta_f = 1 - \theta_O - \theta_N - \theta_{OH} \qquad (0 \le \theta_f \le 1) \qquad (17)$$

and the impinging atom fluxes are given by Eq. (3). The adsorption fluxes Z_{aO} and Z_{aN} are from Eq. (5). Four different E-R recombination processes can now take place:

$$O(g) + O(a) \rightarrow O_2(g) \qquad (18)$$

$$O(g) + N(a) \rightarrow NO(g) \qquad (19)$$

$$N(g) + O(a) \rightarrow NO(g) \qquad (20)$$

$$N(g) + N(a) \rightarrow N_2(g) \qquad (21)$$

The corresponding fluxes are from Eqs. (8) and (9). Due to its importance at high T, modeling the L-H process in which O and N adatoms migrate (hop) over silica is crucial. The moving O and N adatoms densities n'_O and n'_N are obtained by Eq. (10) and the characteristic hopping frequencies ν_O, ν_N by Eq. (13). The number of collisions between adatoms is now given as in Eq. (11) by

$$n_{cOO} = \theta_O \nu_O n'_O \qquad (22)$$

$$n_{cNO} = \theta_O \nu_N n'_N \qquad (23)$$

$$n_{cON} = \theta_N \nu_O n'_O \qquad (24)$$

$$n_{cNN} = \theta_N \nu_N n'_N \qquad (25)$$

Because of these collisions, the adatoms can leave the surface as O_2, NO, or N_2 molecules with fluxes

$$Z_{lhOO} = 2\nu_O n \theta_O^2 \exp[-(Q_{lhOO}/kT)] \qquad (26)$$

$$Z_{lhNN} = 2\nu_N n \theta_N^2 \exp[-(Q_{lhNN}/kT)] \qquad (27)$$

$$Z_{lhNO} = (\nu_N + \nu_O) n \theta_O \theta_N \exp[-(Q_{lhNO}/kT)] \qquad (28)$$

where the activation energies have the same meaning as that in Eq. (12). In particular, $Q_{lhOO} = 2Q_{aO} - D_{OO}$, $Q_{lhNN} = 2Q_{aN} - D_{NN}$, and $Q_{lhNO} = Q_{aO} + Q_{aN} - D_{NO}$, because these values are greater than the corresponding migration energies. The thermal desorption process is the same as the single-species model, and then the thermal desorption fluxes are given by Eq. (14).

Based on the previous formulas the recombination probabilities can now be computed as functions of the variables p_O, p_N, T, θ_O, and θ_N, once all the parameters in the formulas have been assigned.

In fact, the number of the impinging O atoms that desorb as O_2 molecules is given by L-H recombining adatoms Z_{lhOO} + E-R recombining adatoms Z_{erOO} + E-R recombining gas atoms Z_{erOO}. Reasoning in the same way for the other species yields

$$\gamma_{OO} = (Z_{lhOO} + 2Z_{erOO})/Z_O \qquad (29)$$

$$\gamma_{NN} = (Z_{lhNN} + 2Z_{erNN})/Z_N \qquad (30)$$

$$\gamma_{ON} = (Z_{lhNO} + Z_{erNO} + Z_{erON})/Z_O \qquad (31)$$

$$\gamma_{NO} = (Z_{lhNO} + Z_{erNO} + Z_{erON})/Z_N \qquad (32)$$

To obtain the recombination probabilities as functions of p_O, p_N, and T, both θ_O and θ_N must be now used as being unknown. Imposing steady-state flux balance for O and N (as in the single-species model) yields

$$Z_{aO} = Z_{erNO} + Z_{erOO} + Z_{lhNO} + Z_{lhOO} + Z_{dtO} \qquad (33)$$

$$Z_{aN} = Z_{erON} + Z_{erNN} + Z_{lhNO} + Z_{lhNN} + Z_{dtN} \qquad (34)$$

i.e., a system of two quadratic equations for θ_O and θ_N, easily solved by a Newton–Raphson routine.

Boundary conditions for the Navier–Stokes species conservation equations are usually given in terms of species mass fluxes at the wall w_i (positive from gas to the wall), as

$$\rho D_i \frac{\partial Y_i}{\partial \eta} = w_i \qquad (i = O, N, O_2, NO, N_2) \qquad (35)$$

This is a simplified form of the more general species boundary condition, obtained assuming short adsorption times, steady state, and Fick's diffusion.[18,19] The w_i depend on γ_{ij} and Z_i:

$$w_O = m_O(\gamma_{OO} + \gamma_{ON})Z_O \qquad (36)$$

$$w_N = m_N(\gamma_{NN} + \gamma_{NO})Z_N \qquad (37)$$

$$w_{O_2} = -m_O \gamma_{OO} Z_O \qquad (38)$$

$$w_{NO} = -(m_O \gamma_{ON} Z_O + m_N \gamma_{NO} Z_N) \qquad (39)$$

$$w_{N_2} = -m_N \gamma_{NN} Z_N \qquad (40)$$

Care must be used to numerically implement Eq. (35) inside CFD codes.[20,21]

Results

To apply either the single- or the double-species model some physical parameters must be known. They can be classified as 1) predicted from literature data, 2) obtained from the surface model, 3) semiempirically predicted, and 4) obtained by fitting γ_{ij} experimental data. In group 1 are chemical bond energies, as D_{ij} and in group 2 Q_{ai}, n, Δ, and E_{mi}. There are semiempirical models to obtain the activation energies E_{ai} and Q_{erij} in group 3, but no theoretical results exist to date for steric factors P_{erij}, P_i, and sticking coefficients s_i in group 4.

The model was first tested to reproduce experimental data available for single-species recombination on metals, in this case N on W. Testing the model on metal surfaces is very important because of the high (and reliable) recombination probability. In fact, the ultimate aim is to apply the model to "noncatalytic" surfaces like silica, where recombination probabilities are small and their measurement less accurate and more difficult. Experimental data for γ_{NN} are available for the case of nitrogen recombination on tungsten.[3] Literature

values[3] for the chemical bond energies are D_{NN} = 941.8 kJ/mol and Q_{aN} = 638.4 kJ/mol. Concerning activation energies, Q_{erNN} was assumed zero since N_2 has a low energy compared to the N(a) and N(g) pair. A best fit with experimental γ_{NN} data gives E_{aN_2} = 43 kJ/mol, c_A = 3.5, s_N = 0.75, P_{N_2} = 0.5, and P_{erNN} = 0.1. The comparison between model predictions and experimental results for γ is shown in Fig. 3. This indicates transition from E–R to L–H recombination starting at ≈1500 K and ending near 2500 K. Note that nothing can be said about reaction order from such a figure. Reaction order is instead discussed in the following test cases.

The two-species model for silica surface can be used to compare our prediction with single-species recombination measurements and to obtain reasonable values of unknown parameters. For pure oxygen recombination ($p_O \gg p_N$) D_{OO} = 498 kJ/mol from literature,[22] Q_{aO} = 499.8 kJ/mol as computed from isolated Si-O pair bond energy[23] (D_{SiO} = 451.9 kJ/mol) and this surface model, and s_O = 0.05, P_{erOO} = 0.1, and Q_{erOO} = 20 kJ/mol from comparison with experiments by Scott[4] and Berkut et al.[5] These parameters produce the results reported in Fig. 1. These show that the present model predicts reasonably well high-temperature (i.e., >1300 K) data. Notice that error bars in Scott's results[4] refer to conditions for Ni surface experiments. No sharp E–R to L–H transition can be detected, the recombination being controlled by the former. It is important to note the large spread of experimental data[9] and that the reaction is first-order, as the γ_{OO} vs pressure plot shows (Fig. 4).

In the case of pure nitrogen single-species recombination ($p_N \gg p_O$), the data are[22] D_{NN} = 941.3 kJ/mol and (Ref. 23) D_{SiN} = 435.1 kJ/mol. The latter, together with this surface model gives Q_{aN} = 530.8 kJ/mol. Similarly, to the O recom-

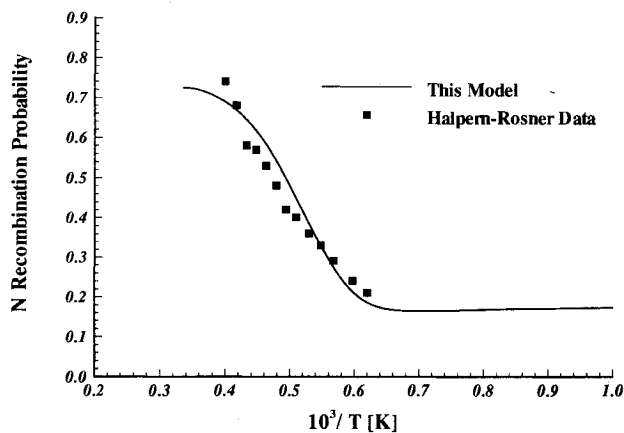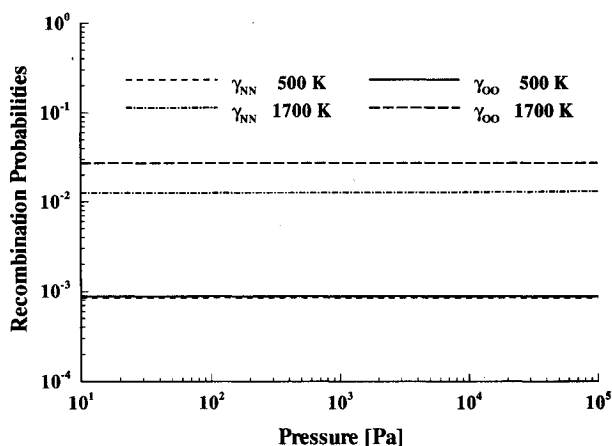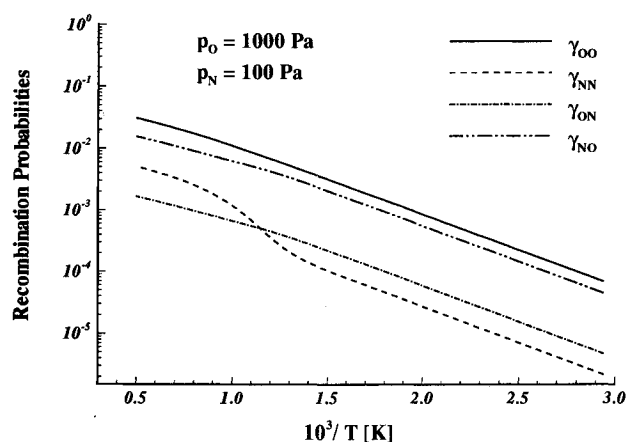Fig. 5   Recombination probability γ_{ij} over silica vs inverse temperature.

bination model, the remaining unknown parameters were obtained by comparing the results with the experimental data[4,5]: s_N = 0.015, P_{erNN} = 0.1, and Q_{erNN} = 20 kJ/mol. The results for γ_{NN} are shown in Fig. 2. These indicate a transition to L–H recombination starting at low temperature and completed around 1000 K. Pressure independence, except in the transition range, indicates first-order recombination even when L–H recombination is activated (Fig. 4).

The results obtained for single-species O and N recombination separately, can be used to model the simultaneous O and N case, where no experimental values are available to date. Unknown parameters were taken from the single-species recombination model. In fact, no further analysis of the silica structure was needed, since O and N have the same adsorption sites. Two of the four steric factors and activation energies are known: P_{erOO} = 0.1, Q_{erOO} = 20 kJ/mol, P_{erNN} = 0.1, and Q_{erNN} = 20 kJ/mol. The remaining two are taken from the following reasoning. In the recombination of O(g) and N(a) the adsorbed N chemical bond must be broken, as in the N(g) and N(a) recombination. Therefore, it is plausible to take Q_{erON} = Q_{erNN} = 20 kJ/mol. The steric factor is mainly dependent on how a gas particle sees the adatom, and on the adatom position on the surface. As the adatom is the same in both Eq. (19) and (21) recombinations, a suitable choice is P_{erON} = P_{erNN} = 0.1. In the same way for O(a) and N(g): Q_{erNO} = Q_{erOO} = 20 kJ/mol and P_{erNO} = P_{erOO} = 0.1. The other parameters are known: Q_{aO} and Q_{aN} from the single-species case, and D_{NO} = 625.1 kJ/mol from literature.[22]

The four recombination probabilities are shown in Fig. 5 for an O and N mixture with p_O = 1000 Pa and p_N = 100 Pa. From this figure it can be seen how γ_{NN} and γ_{OO} are lower than their values for the pure gas results (see also Figs. 1 and 2). This is due to a coverage competition: (the number of sites available for O atom adsorption is reduced by the N adatoms and vice versa) and to the possibility of NO formation at the surface.

Fig. 3   Nitrogen recombination probability γ_{NN} over tungsten vs inverse temperature.

Fig. 4   Recombination probability γ_{ij} over silica vs pressure.

Conclusions

The work presented here is an attempt to produce a model for recombination probabilities based on physiochemical arguments. It does reproduce recombination probabilities for N or O recombination over silica, and also can estimate those for a simultaneous N and O recombination on this material accounting for the N_2, O_2, and NO surface production. Reasonable agreement was found between model results and experimental data[4,5] for γ_{NN} and γ_{OO}. The O recombination was found to be a first-order process, driven by the E–R mechanism over the entire range of temperature explored. On the other hand, the N recombination was found driven by the E–R mechanism for $T < 1100$ K and by an L–H mechanism for higher temperatures showing a different behavior with respect
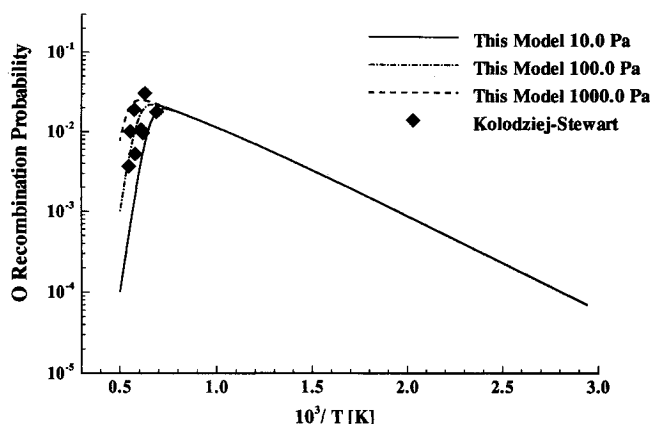
Fig. 6 Oxygen recombination probability γ_{OO} over silica vs inverse temperature.
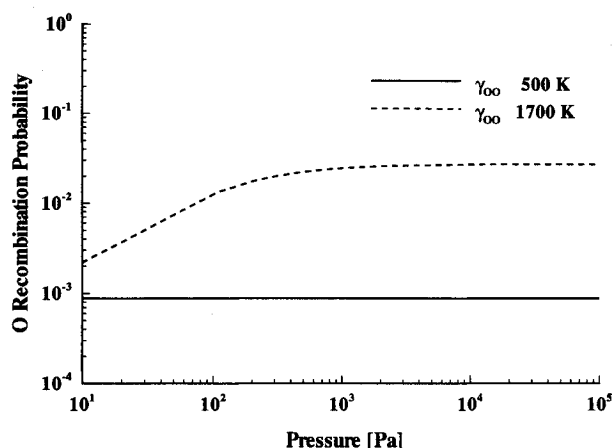

Fig. 7 Recombination probability γ_{OO} over silica vs pressure.

to what is reported in Refs. 9 and 10. Therefore, in this case, more data are necessary to verify the effective transition from $E-R$-dominant to $L-H$-dominant mechanisms.

For temperatures above 1600 K, experimental results reported in Ref. 24 show that recombination probabilities begin to decline. The model presented here, based on older data, does not show this behavior. Analyzing this problem, the major effect was found to be the thermal desorption of O. In fact, by reducing the thermal desorption energy to a value near the half-bond energy for the Si-O bond (250 kJ/mol), desorption becomes already effective at $T > 1500$ K and γ_{OO} shows a maximum, fitting the experimental data of Ref. 24 better (see Fig. 6). In this case a reaction order greater than one was found for low pressures, as shown in Fig. 7. Further work is needed to modify the model on the basis of these new data.

This model represents an attempt to better understand the physics and importance of different phenomena that are involved in heterogeneous catalysis. It represents a starting point to determine a more accurate and less empirical model. The authors belief is that this model can be a useful tool to describe the heterogeneous chemistry for wall boundary conditions in hypersonic flows computations.

Acknowledgments

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