Model for Oxygen Recombination on Silicon-Dioxide Surfaces

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This paper addresses the problem of modeling the catalytic recombination of oxygen on silicon dioxide, the principal material making up the Space Shuttle thermal protection tiles. A new mechanism involving the surface oxygen of the silicon-dioxide matrix itself is proposed. The detailed rate equations describing the proposed mechanism are written and solved at steady state. The predicted rates are shown to match catalytic data specifically collected for the silicon-dioxide/oxygen system.

I. Introduction

MODELING the catalytic recombination of oxygen and nitrogen on silica-based materials has received increased attention recently because of its role in affecting the heat loading on the Space Shuttle thermal protection tiles.[1,2] Because the energies of molecular oxygen and nitrogen, as examples, are less than that of two atoms of oxygen and nitrogen, respectively, when these species recombine, the excess energy must go some place. In the case of surface catalysis, this excess energy (or at least a large portion of the energy[3]) is transferred directly to the surface. This transferred energy combines additively to the usual thermal-gradient-type heat transfer, thereby increasing the surface heat load. The exposed surface of the shuttle thermal protection tiles is principally silicon dioxide.[4]

As pointed out by Stalker,[5] during a large portion of the re-entry phase of the Space Shuttle, the associated shock wave dissociates the nitrogen and oxygen of the atmosphere; this dissociated mixture remains in a nonequilibrium flow condition as it encounters and flows by the Shuttle thermal protection tiles. At Mach numbers of <14 (below 200,000 ft), the shock is sufficiently strong to dissociate the oxygen but not the nitrogen.[5] Thus, there exists a theoretical as well as a practical interest in studying the recombination of oxygen (alone) on silicon dioxide to begin to understand the detailed mechanisms and role that catalytic recombination plays in reentry heating.

II. Recombination and Surface Activity Data for Silica-Based Materials

There is a fair amount of data in the literature for recombination of both oxygen and nitrogen on silica-based materials. Although data for oxygen are of principle interest in the present study, compatibility arguments for the model that will be presented here are strengthened by those data involving nitrogen; thus, these are also reviewed. More extensive reviews of the available data are contained in Refs. 6 and 7.

We start with the canonical (i.e., most widely accepted) data set for the temperature dependence for catalytic recombination of oxygen on silicon dioxide given by Greaves and Linnett.[8] Although there is reason to question the extent to which these data are to be absolutely believed,[9] the data are considered the best to date and have even been used for calibration purposes.[10] Figure 1 shows the recombination coefficient γ as a function of reciprocal temperature.[8] The data shown are for one series of experiments, but the flattening of the fared-in curve at the elevated temperatures, indicating a maximum, is representative of many other experiments and appears to be a true representation of the data trend.[10] It is of some interest to point out in Fig. 1 that there is a clear indication that the negative (log-linear) slope of γ increases nonlinearly with decreasing inverse temperature. Greaves and Linnett[8] interpreted this slope irregularity as being due to the activation energy increasing from 1 kcal/mole at room temperature to 13 kcal/mole at 573 K. This explanation will be addressed later in this paper. The fact that such an interpretation of the nature of an activation energy is present in the literature points out that, although a very good

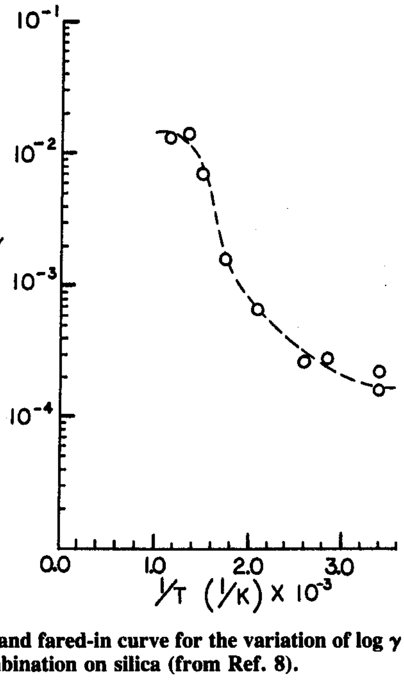

Fig. 1 Data and fared-in curve for the variation of log γ with $1/T$ for oxygen recombination on silica (from Ref. 8).

Presented as Paper 90-0054 at the AIAA 28th Aerospace Sciences Meeting, Reno, NV, Jan. 8–11, 1990; received March 26, 1990; revision received Aug. 7, 1990; accepted for publication Aug. 31, 1990. This paper is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

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data set for recombination of oxygen on silicon dioxide has existed for some time, the details of the recombination process are not yet understood. In this paper, we hope to contribute to that understanding.

In addition to the canonical data set, there are other characteristics that are known about the surface activity of silicon dioxide and silicon-dioxide-based materials. Because of its implications toward the character of the recombination process, the way that the reaction changes with pressure is important; this pressure dependence is known as order, so that first order would mean that the reaction rate goes linearly with pressure, second order would mean that it goes as pressure squared, etc. To date, the recombination of oxygen on silicon dioxide has shown itself to be first order in pressure over a temperature range from 350 to 1100 K,[8,11] representing the entire range over which order has been examined. This appears to be atypical of many simple heterogeneous recombination processes (on metal surfaces, for example) that are characteristically first order at lower temperatures and transition to second order at higher temperatures.[12] This point too will be addressed later with regard to the temperature at which second-order behavior might be expected and why these temperature data have not been taken. (See Epilogue for further comments.)

There are also some results involving nitrogen that are of interest to this study. In studies of nitrogen recombination on Pyrex, Rahman and Linnett[13] report observing BN in the products, interpreting this to mean that, since nitrogen atoms bond to boron, the active recombination sites might be the boron and silicon atoms in the glass. Evenson and Burch[14] found that the recombination coefficient for nitrogen on quartz decreased as the oxygen impurity of the nitrogen source gas increased; that is, the oxygen atoms act as a poison for nitrogen recombination. Using x-ray photoelectron spectroscopy (XPS) to analyze silica and silicon carbide samples exposed to an oxygen atom plus nitrogen atom mixture, Rosner (see Ref. 10) reported that at 1490 K the nitrogen atoms reacted with the silica to form either silicon nitride or silicon oxynitride or perhaps simply adsorbed nitrogen. When silicon carbide samples were exposed to the same mixture at temperatures up to 1620 K, a surface of only silica (i.e., silicon dioxide) was produced. Below 1620 K, oxidation is favored over nitridation, although both are formed. Finally, Rahman and Linnett[15] reported that nitrogen recombination on silicon dioxide did appear to have some second-order behavior at elevated temperatures under certain experimental conditions.

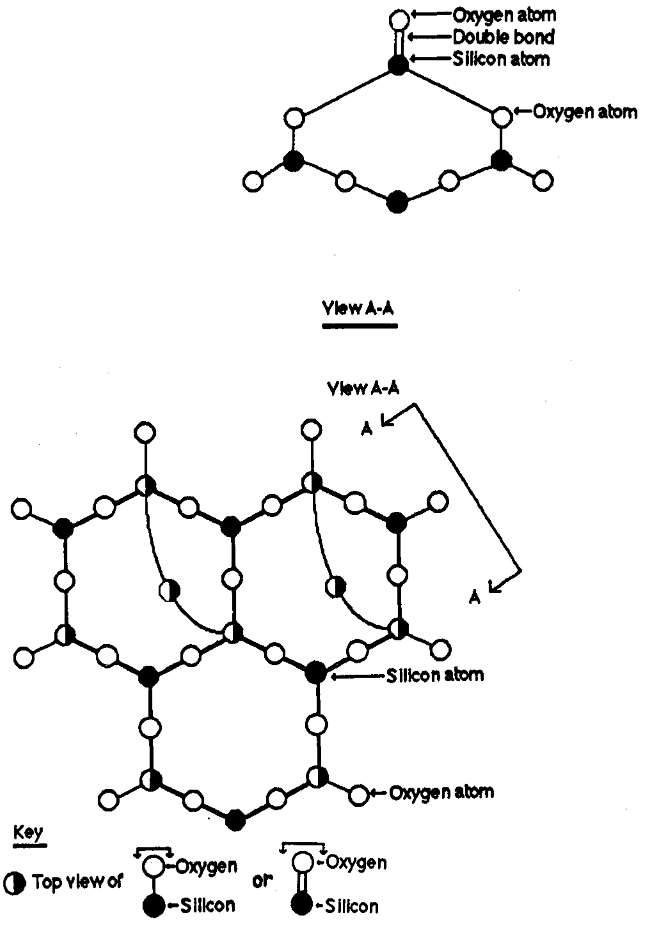

Fig. 2 Surface structure for SiO_2 on quartz substructure (from Ref. 7).

Generally, heterogeneous recombination (i.e., involving catalytic surfaces as opposed to gas-phase only, homogeneous, reactions) is modeled in two steps; the first is adsorption of the atomic species onto the surface.[16,17] This first step involves the probability that a gas-phase collision at a clean surface site will result in an adsorption and is expressed as a temperature dependent initial sticking coefficient S_o. The sticking coefficient S is then given as a function of the fractional surface coverage θ as

$$S = S_o(1 - \theta) \tag{1}$$

This form of S has been experimentally verified by Antonini[18] for CO_2 and O_2 on "fresh" silica. By "fresh," Antonini meant freshly created surfaces made by breaking glass, for example. His comment was that the required adsorption sites do not exist on glass and silica surfaces in their natural state. Using his freshly created surfaces, he was able to determine the temperature dependence for the initial sticking coefficient for oxygen on silica over the range of 300 to 800 K to be

$$S_o = 0.0375 \exp(-0.0021\ T) \tag{2}$$

III. Structure of Silicon Dioxide

In each of the various forms of silicon dioxide [cristobalite, quartz, and tridymite (alpha and beta forms)], the bulk of the material is made up of silicon atoms bonded in a covalent manner at the center of a regular oxygen tetrahedron.[19,20] The tetrahedra link together corner to corner and the different rotations (tetrahedron to tetrahedron) determine the different forms of the silicon dioxide. In the bulk, then, the structure not only satisfies the stoichiometric relationship of SiO_2, but the substructure matrix is such that each silicon atom is bonded to four oxygen atoms via half bonds: $Si[(1/2)O]_4$; that is, each oxygen atom in the substructure is shared by two silicon atoms.

The surface, on the other hand, presents a somewhat different structural problem. Surface structures have been suggested in Refs. 8 and 21, for example. The requirements are that O satisfies two bonds and Si satisfies four bonds. Newman[7] constructed numerous models and came to the conclusion that the only real possibility for the surface structure of silicon dioxide is that shown in Fig. 2, where oxygen atoms form the surface layer by double bonding with the silicon atoms below them. It should be noted that the substructure in Fig. 2 is quartz and the single bond lengths are longer than in the tetrahedra substructures. The various bond lengths and orientations of the surface bond structures are directly dependent on the substructure tetrahedra orientations and, thus, the particular form of the silicon dioxide.

Because of the dependence of the bond orientations of the surface structure on the substructure form, one would expect that surface activity involving the oxygen atoms would be temperature dependent as the temperature dependence of the bulk form. The temperature dependence and relationship between the crystalline forms of silicon dioxide are as follows[22]:

$$\begin{array}{ccccccccc} \propto \text{quartz} & \overset{573^\circ\mathrm{C}}{\rightleftharpoons} & \beta \text{ quartz} & \overset{870^\circ\mathrm{C}}{\rightleftharpoons} & \beta \text{ tridymite} & \overset{1470^\circ\mathrm{C}}{\rightleftharpoons} & \beta \text{ cristobalite} & \overset{1710^\circ\mathrm{C}}{\rightleftharpoons} & \text{liquid} \\ & & & & \Big\Updownarrow {\scriptstyle 160-120^\circ\mathrm{C}} & & \Big\Updownarrow {\scriptstyle 200-275^\circ\mathrm{C}} & & \\ & & & & \propto \text{tridymite} & & \propto \text{cristobalite} & & \end{array} \quad (3)$$

IV. Catalysis Models in General

There are several mechanisms cited in the literature as possible models for catalytic recombination. The Langmuir-Hinshelwood mechanism requires the atomic species to adhere to the surface at adjacent sites prior to recombining.[12] The adjacent site requirement dictates that the reaction rate should go as the square of the gas-phase pressure, thereby dictating a second-order reaction at all temperatures.[16] Since the reaction of interest has not demonstrated second-order performance over the temperature range for which data are available, we can rule out this model. The second mechanism is that of slow surface adsorption followed by rapid surface migration and subsequent recombination proposed by Laidler.[23] Such a model would dictate a first-order reaction characteristic at all temperatures; recall that the oxygen recombination reaction has only been observed to be first order. The idea of highly mobile surface adhered oxygen atoms at temperatures of interest to this study, however, does not seem likely.

Because of previous successes in modeling surface reactions by Jumper et al.[17] using a third reaction mechanism, the Langmuir-Rideal (L-R) mechanism, this third mechanism was given the most attention in our study. It should be noted that the L-R mechanism has been alternately termed the Rideal mechanism[16] and the Eley-Rideal mechanism.[24,25] In this model, a recombination takes place via a collision of a gas-phase oxygen atom with a surface adhered, non-free-to-move oxygen atom. At sufficiently low temperatures where the surface coverage of oxygen atoms can be expected to be high, the reaction would be first order, but at elevated temperatures when the surface atoms thermally desorb at sufficiently high rates, the reaction could, but need not, become second order.

Under the assumption of an L-R mechanism, the reaction would progress in two steps as

$$\mathrm{O} + \underset{S}{|} \rightarrow \underset{S}{\overset{\mathrm{O}}{|}} \qquad (4)$$

$$\mathrm{O} + \underset{S}{\overset{\mathrm{O}}{|}} \rightarrow \underset{S}{|} + \mathrm{O}_2 \qquad (5)$$

so that the two steps represent a redox mechanism with O being both the oxidizer and the reducer. This may be pictured as shown in Fig. 3. The detaching of the molecule is usually considered automatic following recombination because of the excess energy available in the reaction.[12] Time-dependent rate equations can be written that describe each of the processes involved in reactions (4) and (5) as follows:

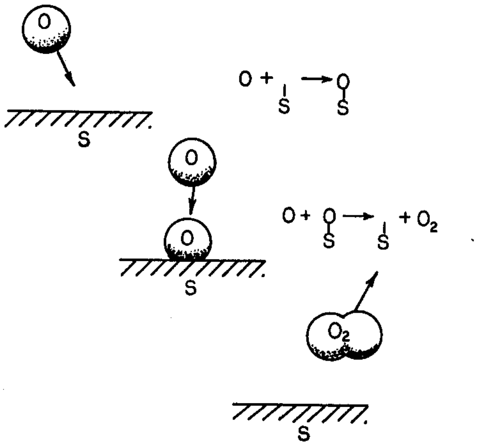

Fig. 3 Schematic representation of the two-step reaction of Eqs. (4) and (5).

$$\frac{\mathrm{d}n_s}{\mathrm{d}t} = \dot{n}_A - \dot{n}_T - \dot{n}_R \qquad (6)$$

where n_s is the surface concentration (particles/cm^2) of atomic oxygen, $\dot{n}_A$ the rate at which atomic oxygen is sticking to the surface, $\dot{n}_T$ the rate at which atoms leave the surface due to thermal boil off (i.e., desorption), and $\dot{n}_R$ the rate at which atoms leave the surface due to recombination reactions with gas-phase oxygen atoms striking the surface-adhered oxygen atoms.

The terms on the right side of Eq. (6) may be described in more detail. The rate at which atoms adhere (stick) to the surface $\dot{n}_A$ is a product of the rate at which gas-phase atoms strike the surface per unit area $\dot{N}$ (the so-called surface impingement rate) times the probability that the strike will result in a stick, S. As noted in Eq. (1), the sticking coefficient is made up of temperature dependent initial sticking coefficient S_o times the fraction of the number of surface sites that are not occupied by either a reactant atom or a poison. The rate at which the gas-phase atoms strike the surface is given by

$$\dot{N} = n(\bar{c}/4) \qquad (7)$$

where n is the gas-phase atom concentration (particles/cm^3), and $\bar{c}$ the average velocity of the particles (atoms or molecules) given by

$$\bar{c} = \sqrt{\frac{8k_BT}{\pi m}} \qquad (8)$$

where k_B is the Boltzmann constant, T the absolute temperature, and m the mass of the particle. The first term is thus given by

$$\dot{n}_A = \dot{N}S_o(1 - \theta_T) \qquad (9)$$

The second term on the right side of Eq. (6), the thermal desorption rate $\dot{n}_T$, is given by

$$\dot{n}_T = \delta\theta \qquad (10)$$

where θ is again the fraction of sites occupied, now with the species being desorbed. According to the theory of absolute reaction rates and assuming the ratio of the activated-complex partition function to the adsorbed-particles partition function is unity, the thermal desorption rate per unit area of covered surface δ is

$$\delta = C_a \frac{k_BT}{h} \exp\left(-\frac{D}{k_BT}\right) \qquad (11)$$

where C_a is the number of adsorption surface sites per unit area, h the Planck constant, and D the thermal desorption energy, taken to be the well depth of the bonded particle.[26] Finally, the third term on the right side of Eq. (6), the recombination desorption rate, is made up of four parts, as follows:

$$\dot{n}_R = \left[\begin{array}{l}\text{surface}\\ \text{impingement}\\ \text{rate}\\ \end{array}\right]\left[\begin{array}{l}\text{impact}\\ \text{probability on}\\ \text{a site occupied}\\ \text{by an atom}\end{array}\right]\left[\begin{array}{l}\text{fraction of}\\ \text{collisions that}\\ \text{have sufficient}\\ \text{energy to react}\end{array}\right]\left[\begin{array}{l}\text{fraction of}\\ \text{sufficiently}\\ \text{energetic collisions}\\ \text{that actually react}\end{array}\right] \tag{12}$$

which is analogous to the collision theory results for homogeneous reactions.[27] These four factors may be written as

$$\dot{n}_R = \dot{N}\theta\left[\exp\left(-\frac{E}{k_BT}\right)\right]P \tag{13}$$

where E is the activation energy and P the steric factor. Taken together, Eq. (6) may be written as

$$\frac{dn_s}{dt} = S_o\dot{N}_0(1-\theta_T) - \delta_0\theta_0 - P\dot{N}_0\theta_0\exp\left(-\frac{E_0}{k_BT}\right) \tag{14}$$

If one were to follow model developments for catalytic recombinations on metal surfaces, rate equations similar to Eq. (14) would be written for each surface-adhering poison (i.e., other atomic or molecular species capable of adhering to surface sites used for recombinations).[17] The total surface coverage fraction would then be given by

$$\theta_T = \theta_0 + \sum_{i=1}^{M}\theta_i \tag{15}$$

where M represents all possible contaminants. The final form of the catalytic-reaction model would result from simultaneously solving the steady-state form of Eqs. (14) and (15) and all of the equations written for the contaminants.[17]

V. Recombination of Oxygen on Silicon Dioxide

Initially, the detailed rate equations just referred to were written and solved at steady state assuming that only diatomic oxygen acted as a poison to the initial (step 1) gas-phase atom adhering at the activation sites on the surface. This would simulate the conditions of the experiments leading to Fig. 1, in which only atomic and molecular oxygen were present in an inert diluent. Using this assumption, we were able to determine parameters that allowed us to match the data of Fig. 1; however, these parameters led to an extremely low number of activation sites, only 1 in 10^7 possible sites based on the surface lattice geometry assuming every surface $\rangle\mathrm{Si} = 0$ represented a possible activation site. Suggestions by Bruno[2] that metal contaminants on the surface may be the activation sites, rather than the silicon dioxide itself, could be thought of as a compatibility argument for the extremely low number of activation sites; however, such metal contaminants are not likely in the experiments leading to the data of Fig. 1. Other objections and a more detailed description of why the poison hypothesis was rejected for the data set of Fig. 1 may be found in Chapter V of Ref. 6.

Having rejected the poisoning hypothesis, a completely new assumption was made. In this new assumption, the catalytic surface was taken to be the silica substrate rather than the silicon dioxide surface (which, as stated in Sec. III, is known to be the oxygen atoms of the complex rather than the silicon). Under this new assumption, diatomic oxygen is not needed as a poison. The mechanism, then, is that a gas-phase oxygen atom actually collides and reacts with a surface oxygen that is part of the surface lattice itself, and they leave the surface as an oxygen molecule. This leaves a hole in the surface required to complete the silicon-dioxide lattice. It is this hole that is the activation site for the gas-phase atom to fill for step 1 [i.e., Eq. (4)].

Although Linnett and Marsden[11] proposed a similar picture for the way in which the surface participates in the reaction as early as 1956, the idea did not seem to take hold, and thinking of the actual surface atoms of the SiO_2 as reactants in the recombination appears to represent a departure from the more-recent ideas regarding surface catalysis for oxygen recombination. If one adapts the new model, however, a number of experimental observations begin to make sense as qualitatively supporting this formulation. The results of Rosner's work (see Ref. 10), for example, can be interpreted as support for the idea that the surface sites are the silicon atoms rather than the oxygen atoms. For nitrogen atom recombination on silicon dioxide, Rosner found nitrogen atoms incorporated into the SiO_2 surface as silicon nitrides or silicon oxynitrides. This experimental data supports the hypothesis that the silicon atoms of the silicon dioxide surface are the active surface sites. Other findings sited in Sec. II may be similarly interpreted as supporting the new hypothesis.

Under the new hypothesis, the problem becomes far more tractable; only Eq. (14) needs be solved at steady state, where the only θ of interest is that for the oxygen, and these are the oxygen of the SiO_2 surface matrix. Equation (14) in this simplified form becomes

$$\frac{dn_s}{dt} = \dot{N}S_o(1-\theta) - \delta\theta - P\dot{N}\theta\exp\left(-\frac{E}{k_BT}\right) \tag{16}$$

In steady state, Eq. (16) may be solved for the fraction of surface that is covered by oxygen atoms in the form

$$\theta = \frac{S_o\dot{N}}{S_o\dot{N} + \delta + P\dot{N}\exp\left(-\frac{E}{k_BT}\right)} \tag{17}$$

The recombination coefficient γ is given as two times the rate at which oxygen atoms are desorbed from the surface by recombinations (the two accounts for the disappearance of two gas phase atoms for each recombination, one in the reaction and a second to fill a void somewhere in the silicon dioxide surface, thereby maintaining steady state) divided by the atom impingement rate,

$$\gamma = 2P\theta\exp\left(-\frac{E}{k_BT}\right) \tag{18}$$

Substituting from Eq. (17) yields

$$\gamma = \frac{2PS_o\dot{N}\exp\left(-\frac{E}{k_BT}\right)}{S_o\dot{N} + \delta + P\dot{N}\exp\left(-\frac{E}{k_BT}\right)} \tag{19}$$

Physiochemical Parameters

A quick check of Eq. (19) with reference back to Eq. (11) reveals that there are now four physiochemical parameters that must be determined in order to fully determine the model because the number of surface sites C_a is now taken to be the subsurface silicon atoms of the surface matrix structure. It should be noted that these four parameters themselves could include more than a single term so that the actual number of terms to be determined is greater than four. There are a number of characteristics of the mathematical form of the model, Eq. (19), that simplify the task of determining the parameters. At low temperatures, for example, the surface can be assumed to be fully covered so that γ is given by

$$\gamma \simeq 2P \exp\left(-\frac{E}{k_B T}\right) \tag{20}$$

or

$$\log \gamma = \log 2P - 0.4343 \frac{E}{k_B}\left(\frac{1}{T}\right) \tag{21}$$

Equation (21) can thus give P and E directly from slope and intercept information contained in Fig. 1. As pointed out in Sec. II, Greaves and Linnett[8] noted that the slope is nonlinear, and this observation led them to suggest that the apparent activation energy E [wholesale use of Eq. (21)] increased from 1 kcal/mole at room temperature to 13 kcal/mole at 573 K. Because exothermic recombination reactions are usually considered to have relatively low activation energies, 13 kcal/mole seems high.[27] Further, it seems improbable that the activation energy alone would change so markedly over the temperature range since the Arrhenius form comes from that portion of the kinetic energy of the gas-phase energy sufficient to penetrate an energy barrier.[27] In addition, if an activation energy of 13 kcal/mole were to be imposed at room temperature, the steric factor needed to accommodate the data of Fig. 1 would be 73, but by definition cannot be greater than unity. If the activation energy is taken to be constant, then the alternative is that the steric factor have a temperature dependence, for which there is some precedence in the literature.[28]

The combined parameters that seemed to most closely match the nonlinear behavior of the data in Fig. 1 were an activation energy E of 1 kcal/mole, independent of temperature, and a steric factor of

$$\begin{aligned} P &= 0.0000224 \exp(0.00908\, T) \qquad & T \le 925 \text{ K} \\ &= 0.1 & T \ge 925 \text{ K} \end{aligned} \tag{22}$$

This form gives rise to a steric factor of 0.0003414 at 300 K with a gradual rise to 0.1 at 925 K. Above 925 K, the steric factor is held at 0.1. One might interpret such a change in the steric factor to mean that the number of surface atoms of acceptable geometric orientation for a recombination to proceed rises from roughly 1 in 3000 at room temperature to 1 in 10 at elevated temperatures. Although geometry is the normal kinetic interpretation of steric factor, and may not be incompatible with the changing character and orientations of the surface lattice with temperature noted in Sec. III, the nature of this temperature dependence should be the subject of further investigation. In fact, in kinetic reaction theory, although geometry is most often sited as the rationale, the steric factor is meant to be a catchall for effects not directly accounted for in the other terms.

The remaining parameters, the thermal desorption energy D, and the temperature-dependent form of the initial sticking coefficient principally affect the high-temperature end of the curve. From the choice of P and E, based on slope, as described earlier, we know that the third term in the denominator of Eq. (19) will eventually begin to dominate, yielding a γ of roughly the functional form

$$\gamma \simeq 2S_o \tag{23}$$

Equation (23) continues to yield first-order recombination rate dependence. It should also be noted that the crossover to the dependence of γ approximated by Eq. (23) is needed in order to flatten the curve, as noted in Sec. II. The magnitude of γ at the high end is useful in helping to identify the form of S_o. Further, the low-temperature character of γ remains nearly unaffected by the choice of S_o, as will be demonstrated in the following.

Although recombination of oxygen on silicon dioxide has not demonstrated second-order characteristics, the model in its present form could accommodate such behavior. At temperatures still higher than those referred to earlier, thermal desorption can begin to affect the recombination process. Referring again to Eq. (19), when the thermal desorption becomes large enough to dominate, the form of γ can be approximated by

$$\gamma \simeq \frac{2PS_o\dot{N} \exp\left(-\dfrac{E}{k_B T}\right)}{\delta} \tag{24}$$

and the recombination process becomes second order.

The form of δ is given by Eq. (11). The choice for C_a is that suggested by Hochstrasser and Antonini[29] of 5×10^{14} sites/cm^2. It should be noted, however, that Newman[7] places the number of surface sites to be more like 2×10^{14} and changes with temperature as the structure of the silicon dioxide changes. Such changes in surface sites are absorbed into the catchall steric factor; it seems far more sensible to fix the number of surface sites, even if somewhat incorrect, in much the same way that the plan-form area of a wing is fixed for the purposes of defining lift and drag coefficients even though it may in fact change in the case of Fowler flaps, for example. To this end, C_a was specified as 5×10^{14} and unchanging with temperature; this leaves only the well depth to be determined.

Since no second-order behavior has been reported up to 1100 K,[8,11] the thermal desorption well depth must be sufficiently high to be consistent with this finding. Under the premise of the model, that the reactant oxygen is that of the surface lattice of the SiO_2, this well depth should also be consistent with the bonding energy of the Si and the O. Wells[20] gives the Si—O bond energy in the SiO_2 molecule as 108 kcal, therefore, each half-bond strength would be 54 kcal. As a reasonable estimate of the bonding of the oxygen to the silicon in the surface matrix of the silicon dioxide, 150% of the half-bond strength was chosen as thermal desorption well depth, i.e., 81 kcal/mole. Since this is only an estimate, the effect of changes in this parameter will be addressed later.

Using 81 kcal/mole for the thermal desorption well depth, the functional form of S_o may be explored. Although the form of the initial sticking coefficient reported by Antonini[18] was that for molecular oxygen on fresh silicon dioxide, it served as a starting point for our work. Further, based on our new view of the catalytic nature of the silicon dioxide, it seemed to us that the creation of a fresh surface by breaking the glass yielded a stickable surface by virtue of the disruption of the SiO_2 matrix, thereby creating dangling Si bonds on the surface. It seems likely, then, that the chemisorption of O_2 was really a dissociative adsorption and could be viewed as similar to adsorption of atomic species. Further, such a representation of the nature of the adsorption surface would also explain why the surface in its natural state, i.e., fully oxygen populated, would not give rise to chemisorption.

Using Antonini's formulation, we explored the effect of modifying the exponential constant and the premultiplier using the previously determined form/value of the parameters P and E, and 81 kcal/mole for D. First the exponential constant was modified as

$$S_o = 0.1 \exp(-\,0.001\, TL) \tag{25}$$

The results of letting $L = 2, 3$, and 4 are given in Fig. 4 along with the data of Fig. 1.[8] Then the premultiplier was modified as

$$S_o = 0.01\, L \exp(-\,0.002\, T) \tag{26}$$

and $L = 3, 5$, and 7. The results of this exercise are shown in Fig. 5 along with the data of Fig. 1. It appears that an exponential constant of 0.002 and a premultiplier of 0.05 best fit the data.

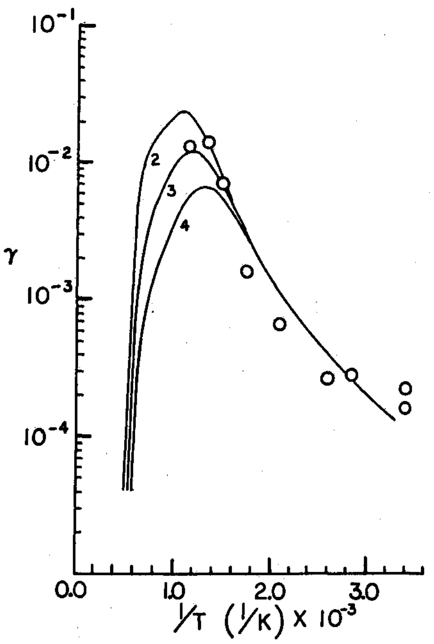

Fig. 4 Effect of modifying the exponential constant in Eq. (25): L = 2, 3, 4.

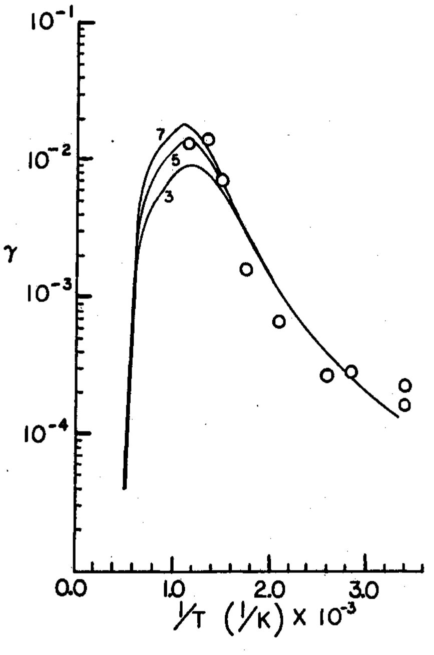

Fig. 5 Effect of modifying the premultiplier in Eq. (26): L = 3, 5, 7.

With all parameters now determined, it is possible to explore the effect of changing the thermal desorption well depth; this is done in Fig. 6, where D is varied from 45 kcal/mole (below the half-bond energy for a SiO_2 molecule) to 85 kcal/mole with intermediate steps of 55, 65, and 75 kcal/mole. It can be seen that 81 kcal/mole is as good a choice as any. Examination of Figs. 4–6 demonstrates the near imperceptible effect of the choice of S_o and D on the low-temperature portion of the curve.

The final choice of physiochemical parameters is given in Table 1. The final curve fit is shown in Fig. 7.

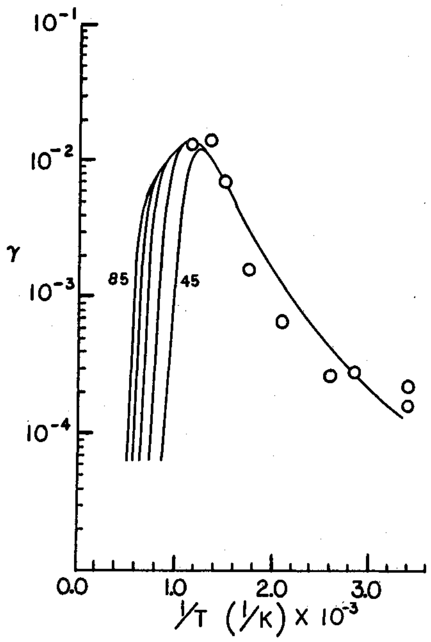

Fig. 6 Effect of modifying the thermal desorption well depth of Eq. (11) on the recombination coefficient: D = 45, 55, 65, 75, 85.

Table 1 Values/form of the physiochemical parameters for catalytic recombination of O_2 on SiO_2

Parameter	Value
P, steric factor	0.0000224 exp (0.00908 T) (maximum value = 0.1)
E, activation energy	1 kcal/mole = 6.949×10^{-21} J/atom
S_o, initial sticking coefficient	0.05 exp (-0.002 T)
C_a, surface sites	5×10^{14} sites/cm^2
D, thermal desorption energy	81 kcal/mole = 5.629×10^{-19} J/atom

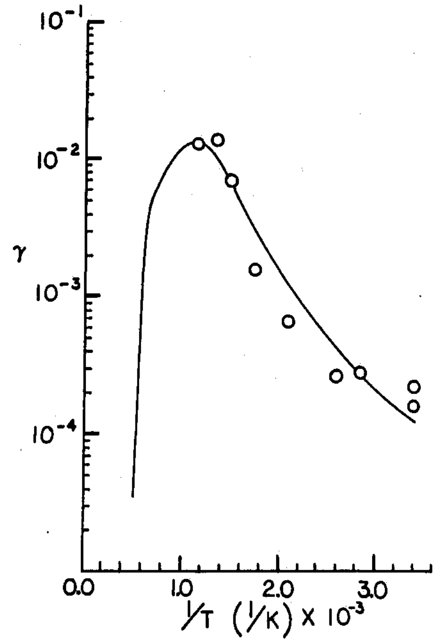

Fig. 7 Final oxygen-recombination-on-silicon-dioxide model (the curve) compared to the data of Ref. 8.

VI. Discussion

As shown by Fig. 7, the model is capable of satisfactorily matching the data of Ref. 8 over the entire range of experimental observation. Unlike Fig. 1, however, the model predicts a drop-off in γ at temperature above 900 K (i.e., $1/T$ of 1.1×10^{-3}). This drop-off eventually leads to a change in reaction character away from first-order and toward second-order behavior, another characteristic not experimentally ob-

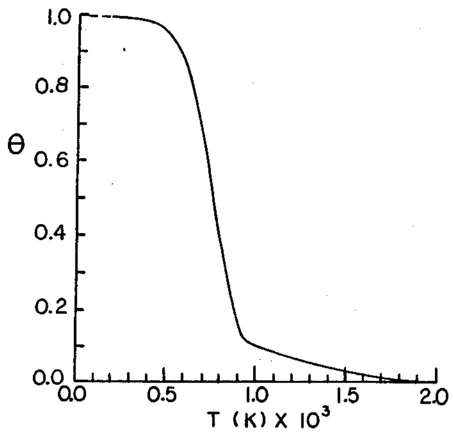

Fig. 8 Fractional surface coverage of atomic oxygen vs temperature for the experimental conditions of Ref. 8.

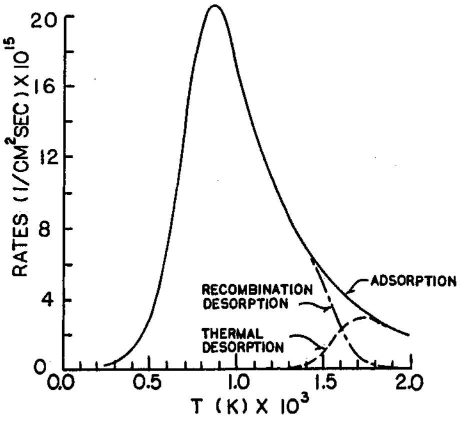

Fig. 9 Absolute rates of adsorption, thermal desorption, and recombinative desorption of oxygen for the experimental conditions of Ref. 8: the behavior for $T > 1100$ K is derived by extrapolation of the model fit to the data of Ref. 8.

served. It is of interest to examine the causes of this behavior in more detail, and, unlike models obtained by simple curve fitting of the data, our model allows for looking at underlying details of the physical mechanism. This is done in Figs. 8 and 9 for the experimental conditions of Ref. 8.

Figure 8 is a plot of the predicted steady-state surface coverage of oxygen atoms attaching to the dangling Si bonds. At room temperature, the surface is completely intact (i.e., completely covered). This coverage drops off rapidly at temperatures above 500 K, until at the height of recombination activity (~900 K) the surface coverage is approximately 0.1; that is, the surface is made up of 90% dangling Si bonds. Figure 9 yields even more information by examining the absolute rates of adsorption and desorption by both recombinative and thermal processes. From Fig. 9, it is clear that up to the height of recombinative activity, and even beyond, the only meaningful desorption is by recombinative activity and the recombination rates just match the adsorption rates; however, up until approximately 900 K, the rates are principally driven by the ability to recombine and after this point the rates are driven by the ability of the surface to recapture atomic oxygen. It is only above about 1200 K that the reaction begins to be influenced by thermal desorption, approximately 300 K above that of experimental observations. It is interesting to note that the temperature above which the thermal desorption is active enough to almost completely deplete the surface of oxygen atoms (~1900 K) is nearly coincident with the temperature at which silicon dioxide liquefies. To us, this fact seems to give some credibility to the notion that thermal desorption and second-order behavior is to be expected, if not yet observed. (See Epilogue for further comments.)

VII. Concluding Remarks

In this paper we have attempted to present and describe the rationale behind our model for recombination of oxygen on silicon dioxide. The form of the model allows for a computation of recombination rate as a function of local gas and surface properties. This form can be incorporated into a complete computational scheme describing the global nonequilibrium, reacting, real-gas environment in which the surface activity forms but one boundary condition. In fact, this has been done in Ref. 6 in a manner similar to that described in Refs. 30 and 31. Because of the involved description of the model given in this paper, the computational results of Ref. 6, originally intended to be contained in this paper, are now the intended subject of a future paper.

In order to explain our interpretation of the importance of our work in modeling the recombination of oxygen on silicon dioxide, let us start by understating its importance; we will then take the liberty of, perhaps, overstating its importance. First, it might be said that, since the reaction has been shown to be first order, little utility has been gained by a complicated model requiring the determination of four physiochemical parameters when a simple curve fit in temperature would yield an equally computational-adequate model. This is a true statement if the only consideration is computational utility.

In favor of the more physically descriptive model presented here, we start by recalling the ability to interpret the reactivity in terms of phenomena taking place on the surface itself (as was done earlier with the help of Figs. 8 and 9) rather than only in terms of the activity in the gas phase. To us, however, the significance of the model goes well beyond simply describing this particular reaction. First, the reaction, as viewed in our model, offers new insight into the way that surface recombinative catalysity operates on a ceramic material as opposed to a metal. Second, if the reaction operates as we suggest, the suggested mechanisms offer reasonable insight into rational analytic approaches that might be taken to investigate possible electronic states that the desorbing molecular oxygen might assume. Since such electronic character directly impacts the thermal load on the surface, this is clearly an important consideration for re-entry studies.

Beyond the implications to the oxygen recombination process, the model also offers insight into how nitrogen recombination might operate. These implications, in fact, formed the basis for the study of nitrogen recombination on silicon dioxide by Newman[7]; these results are the intended subject for a forthcoming paper. Equally important is the implications that the model has on the ability to model, not only the nitrogen-alone recombinative reaction, but the competing reaction of oxygen and nitrogen on silicon dioxide to form O_2, N_2, and NO (nitric oxide).

Epilogue

During the final stage of editing the manuscript for this paper, Carl D. Scott, Associate Editor for this journal, brought to our attention a paper we had overlooked. Because of the importance of this reference to the model presented here, we mention it briefly. Although the material tested was a reaction-cured borosilicate glass (RCG) rather than pure silica, Kolodziej and Stewart[32] present experimental data indicating that a sharp rolloff and decline in the recombination coefficient of oxygen on RCG takes place at temperatures above 1400 K. They mention among other possible explanations that this behavior could be due to the heterogeneous recombination crossing over from first-order to second-order surface kinetics. They also report that the rapid decline in recombination coefficient is coincident with noticeable structural changes in the RCG, i.e., at temperatures above 1400 K the RCG gradually transforms with increasing temperature, going through a phase change from a hot, rigid material to a very viscous liquid. These data and reports are in complete agreement with the predicted behavior based on our model (cf., comments at the end of Sec. VI). Although this does not prove that our model is correct, it lends strong corroborative support for its validity.

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