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Model for Oxygen Recombination on Reaction-Cured Glass

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This article briefly reviews the model for recombination of oxygen on a silicon-dioxide surface presented in detail in a previous paper. Data for oxygen recombination on reaction-cured glass (RCG), a silicon-dioxide-based material, is presented and compared with the Si-O_2 recombination model. The model is modified slightly to better represent the oxygen-RCG system, but the essential feature of the model, the participation of the oxygen of the surface matrix itself, remains unchanged. The ramifications of the model toward the production of excited molecular oxygen is examined as it may pertain to surface heating during a re-entry. Data indicating that the predicted production of singlet-delta oxygen, and no higher-electronic-state oxygen is given in support of the model.

I. Introduction

A NUMBER of papers (e.g., Refs. 1–3) have pointed out the importance of being able to model the catalytic recombination of oxygen and nitrogen on silica-based materials because of the role that these reactions play in re-entry heating. Because the energies of molecular oxygen and nitrogen are less than that of two atoms of oxygen and nitrogen, respectively, when these species recombine, the excess energy can be transferred directly to the surface, representing an additional heat load.[4] Silicon dioxide is the principal material making up the Space Shuttle thermal-protection-tile surface; to be more precise, the surface is a borosilicate reaction-cured glass (RCG). Although RCG is reported to contain some (3–7%) B_2O_3,[5,6] as will be shown here, this surface reacts catalytically similar to pure silicon dioxide.

In a previous paper a model for the recombination of oxygen on silica (silicon dioxide) was presented.[3] In that paper a new mechanism involving the surface oxygen of the silicon-dioxide matrix itself was proposed, and the detailed rate equations describing the proposed mechanism were written and solved at steady state. The predicted rates were shown to match catalytic data specifically collected for the silicon-dioxide/oxygen system.[7]

In this article, the mechanism for pure silica is extended to RCG by modifying some of the coefficients to more closely match recently published data for RCG. In doing so the fundamental character of the model was preserved; specifically, the chemical well depth for surface atomic oxygen remained unchanged.

Since the model of Ref. 3, as modified for RCG, appears to properly portray the catalytic behavior of oxygen on RCG, it is appropriate to explore the possible excited species of diatomic oxygen that the model allows. Such production of excited species can influence the prediction of re-entry heating, because under certain conditions energy contained in the excited species may not transfer to the surface.[8] The electronically excited states that the catalytically recombined O_2 can take on are examined by looking at the exotherm/endothermisity of the elementary reactions involved in the recombination process. Implications of the model on the added heat load imposed by catalytic recombination of oxygen on silica-based thermal protection surfaces during a re-entry are briefly discussed.

II. Brief Summary of Recombination Model

The catalytic recombination reaction for oxygen on a silicon dioxide surface of Ref. 3 adopted the Langmuir-Rideal mechanism which can be described by a two-step reaction described by Eqs. (1) and (2) below, and Fig. 1:

$$\begin{array}{l} O + \quad \rightarrow O \\ \quad\;\; | \quad\; | \\ \quad\;\; S \quad S \end{array} \tag{1}$$

$$\begin{array}{l} O + O \rightarrow \quad + O_2 \\ \quad\;\; | \quad\; | \\ \quad\;\; S \quad S \end{array} \tag{2}$$

so that the two steps represent a redox mechanism with O being both the oxidizer and the reducer. If the surface-adhered O atom is, in fact, the oxygen of the silicon-dioxide surface matrix itself, the reaction proceeds via a gas-phase oxygen atom colliding and reacting with a surface-matrix oxy-

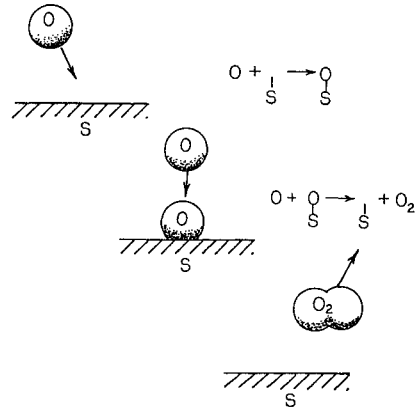

Fig. 1 Schematic representation of the two-step Langmuir-Rideal reaction mechanism of Eqs. (1) and (2).

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

Parameter	Value
P	0.0000224 exp(0.00908 T) (maximum value = 0.1)
E	1.0 Kcal/mole (6.949×10^{-21} J/atom)
S_0	0.05 exp(−0.002 T)
C_a	5.0×10^{14} sites/cm^2
D	81.0 Kcal/mole (5.629×10^{-19} J/atom)

gen. When the two atoms leave as an oxygen molecule, they leave a "hole" in the surface required to complete the silicon-dioxide lattice. It is this hole that represents an unfilled surface activation site for the gas-phase atom to "adhere" for step 1 [i.e., Eq. (1)]. When the rate equation describing these processes is written and solved at steady state (as is done in Ref. 3), the resulting functional form for the recombination coefficient γ is given by

$$\gamma = \frac{2PS_0\dot{N}\exp[-(E/k_BT)]}{S_0\dot{N} + \delta + P\dot{N}\exp[-(E/k_BT)]} \tag{3}$$

where P is the steric factor, S_0 is the clean surface sticking coefficient, $\dot{N}$ is the atomic oxygen surface impingement rate, E is the activation energy, and δ is the thermal desorption rate per unit surface area of filled activation sites. The latter is described by the expression

$$\delta = C_a(k_BT/h)\exp[-(D/k_BT)] \tag{4}$$

where C_a is the number of surface activation sites per unit area (taken as the number of surface oxygens on a silicon-dioxide surface), k_B is the Boltzmann constant, T is the absolute temperature, h is the Planck constant, and D is the thermal desorption energy, taken to be the well depth of the surface-oxygen/silicon surface bond (see Ref. 3 for details). As described in Ref. 3, the physiochemical parameters for oxygen recombination on pure silica were determined to be consistent with known parameters and to match the Greaves-and-Linnett data.[7] These parameters are given in Table 1. As will be described below, these parameters had to be modified for the oxygen/RCG system.

III. Comparison of the Model with New Data

At the time that Ref. 3 was written, the authors were aware of data of the Greaves and Linnett type, that exhibited only monotonic increasing recombination activity with increasing temperature. On the contrary, the model of Ref. 3 predicted that the recombination coefficient curve should fold over above a certain "critical temperature" (depending on the partial pressure of oxygen) and dramatically decline. As described in detail in Ref. 3, at "low" temperatures, thermal desorption, Eq. (4), is low and the depletion of surface oxygen by recombination [third term in the denominator of Eq. (3)] is small compared to the rate of replenishing of the surface oxygen [first term in the denominator of Eq. (3)]; this results in the model predicting first-order behavior at "lower" temperatures (i.e., the reaction rates go at the partial pressure of oxygen to the first power). At some intermediate temperature the depletion of surface oxygen by recombinations begins to compete with the replenishing of surface oxygen, but the model remains first order; however, above the critical temperature referred to above, the model predicts that surface-oxygen depletion via thermal desorption, Eq. (4), dominates the denominator and the reaction should exhibit second-order reaction characteristics (reaction rates going at the partial pressure of oxygen to the second power). As was the case for the monotonic increasing data, the authors were aware of experiments only for the oxygen-silica systems that had demonstrated first-order behavior. At the time of the original writing of Ref. 3, these features of the model were considered to be inconsistent with data and a possible explanation was offered. The explanation was that the requirement for the model to become second order was that appreciable surface-adhered atoms must be thermally desorbed; because, according to the model, such "surface-adhered" atoms would be the surface of the silicon dioxide itself, this meant that the surface should show signs of melting (or softening). It would, therefore, make sense that experiments had been limited to temperatures that did not melt the surface samples. Therefore, our prediction was that if experiments were carried out at high enough temperatures to demonstrate second-order behavior, the critical temperature should be near the melting temperature of the silicon dioxide.

As discussed in the epilogue of Ref. 3, although not for pure silica, a set of experiments had been performed by Kolodziej and Stewart[9] that showed both evidence of second-order behavior and a rollover of catalytic activity at elevated temperatures. Furthermore, it was coincidentally noted that the critical temperature necessary for this behavior to begin to appear was near the softening point for the samples. The surface samples tested were RCG. Because we felt this development was of significance, we compare the model [Eq. (3)] to the data of Kolodziej and Stewart,[9] Marinelli,[10] as well as more-recent data reported by Steward et al.[11] These data along with those of Greaves and Linnett[7] are given in Table 2; some additional information concerning these data is also included in the table. There are additional data for the monotonic increasing portion of the RCG curve by Scott,[1] Stewart et al.,[12] and Willey,[13] but these have not been included. The data from Refs. 7, 9–11, along with the predictions of the Ref. 3 model for a partial pressure of oxygen of 1.0 Torr, are shown in Fig. 2. With the inclusion of the Ref. 11 data (not included in an earlier paper), a statement of the earlier paper[14] indicating that catalytic recombination of oxygen on RCG is virtually identical with that for silica, must be modified. While the data trends appear to be consistent with the physical mechanisms of the Ref. 3 model, some modification of the coefficients of the model appear to be needed.

Of the coefficients contained in the model, the well depth for the bonding of atomic oxygen in the silicon-dioxide surface matrix appeared to be the most well justified of the parameters based on independent physical principles.[3] This meant that the steric factor and the initial sticking coefficient were the best candidates for modification. Thus, we "optimized" only these two coefficients. Adjusting the sticking coefficient and the steric factor in an inverse relationship effected the character of the peak catalycity. Thus, by increasing the sticking coefficient and decreasing the steric factor, the curve of Fig. 2 tended to sharpen the peak and move it to the left. The new "RCG-optimized" coefficients are given in Table 3, with the resulting curves shown in Fig. 3. Further refinement of the number of surface sites by Newman[15] and reported in Ref. 16 is also incorporated into Table 3; however, this change led to only a nearly imperceptible difference in predicted recombination coefficients in the postcritical temperature regime. The fact that the curves for 0.1 and 10 Torr lie on top of one another up to an approximate inverse temperature of 0.6×10^{-3} K^{-1}, and split thereafter, shows that the model is first order up to the critical temperature and second order above it. It should be noted that the critical temperature approximately coincides with the softening point of RCG, consistent with the predictions of Ref. 3.

Although the model of Ref. 3 required some modification of two of the coefficients, the preservation of the well depth for surface-bound oxygen leaves the underlying physics of the model unaltered; i.e., the hypothesis that the oxygen of the silicon-dioxide surface matrix participates in the recombina-

Table 2 Recombination data

Temperature, K	Inverse temperature, 1/K	0 Partial pressure, Torr	Recombination coefficient	Source
893	1.12×10^{-3}	0.11–0.12	0.0123	Greaves and Linnett[7b]
735	1.36×10^{-3}	0.11–0.12	0.0135	(Silica)
658	1.52×10^{-3}	0.11–0.12	0.007	
568	1.76×10^{-3}	0.11–0.12	0.001535	
472	2.12×10^{-3}	0.11–0.12	0.000635	
385	2.6×10^{-3}	0.11–0.12	0.00025	
347	2.88×10^{-3}	0.11–0.12	0.000271	
300	3.333×10^{-3}	0.11–0.12	0.00022	
300	3.333×10^{-3}	0.11–0.12	0.00016	
833	1.2×10^{-3}	[a]	0.001	Stewart et al.[11b]
714	1.4×10^{-3}	[a]	0.0008	(RCG)
606	1.65×10^{-3}	[a]	0.0005	
500	2.0×10^{-3}	[a]	0.00055	
952	1.05×10^{-3}	[a]	0.00135	
1754	0.57×10^{-3}	[a]	0.004	
1667	0.6×10^{-3}	[a]	0.012	
1818	0.55×10^{-3}	[a]	0.0115	
1613	0.62×10^{-3}	[a]	0.015	
1408	0.71×10^{-3}	[a]	0.012	
1408	0.71×10^{-3}	[a]	0.0135	
1500	0.667×10^{-3}	[a]	0.0125	
1515	0.66×10^{-3}	[a]	0.0208	
1640	0.61×10^{-3}	[a]	0.023	
1282	0.78×10^{-3}	[a]	0.0081	
1831	0.546×10^{-3}	6.18	0.0037	Kolokziej and Stewart[9]
1806	0.554×10^{-3}	3.09	0.01007	(RCG)
1742	0.574×10^{-3}	3.09	0.01893	
1726	0.579×10^{-3}	6.18	0.00525	
1644	0.608×10^{-3}	1.76	0.01068	
1617	0.618×10^{-3}	3.09	0.00968	
1592	0.628×10^{-3}	1.76	0.0306	
1450	0.69×10^{-3}	1.76	0.0179	
300	3.33×10^{-3}	1.00	0.0002	Marinelli[10] (RCG)

All data presented here are without error bars; such error is, in some instances, relatively large (e.g., Ref. 9).
[a]Not reported in the reference.
[b]Data obtained from figure in reference; exact numbers could be in error.

tive reaction appears to properly characterize the reaction, as demonstrated in Fig. 3.

IV. Theoretical Possibilities for Excited Oxygen

When a nonequilibrium flow containing atomic species whose natural state is in molecular form (i.e., recombination is exothermic) encounters a surface of lower temperature, two convective processes can contribute to the surface heat load (energy transfer from the fluid to the surface). The first is the normal temperature-gradient (Fourier law) type heat transfer. If the surface acts to catalyze recombination of the atomic species, the excess energy in the reaction may be deposited directly into the surface. To the extent that the branching ratio in the reaction populates states other than those in the ground state of the newly created molecules, not all the available excess energy needs to be deposited in the catalytic surface during the reaction.[1,8] It is not enough that the reaction populate excited states, however, in order for the surface to experience heat rates less than those predicted assuming that all the excess energy is deposited directly at the surface. The reason for this is that if the excited state is such that it is easily collisionally de-excited, the energy not deposited directly will quickly find its way back to the surface via the increased temperature of the flow in the immediate vicinity of the surface. One would either like to have products with very short radiative lifetimes (compared to the mean time between collisions) so that the energy leaves via spontaneous emissions, or have products that are very metastable and relatively nonreacting. Arguments addressing the radiative lifetime vs emission distance from the wall have been discussed in relationship to the "Shuttle Glow" phenomena by Slanger,[17] and are alluded to by Rosner.[8]

It is an experimentally demonstrated fact that surface catalyzed oxygen recombinations produce a large manifold of electronically excited O_2 states on metals[17–19]; however, as will be argued below, recombinations on SiO_2-based materials may preferentially populate only the ground state and the O_2 singlet-delta state. If singlet oxygen is produced, its extreme stability, with a radiative lifetime of 3.7×10^3 s, could make it a good candidate for transporting energy stored in this state far from the wall; however, the singlet-delta state represents only about 20% of the excess energy in the reaction (see Fig. 4).

The new catalytic recombination model of Ref. 3, provides a theoretical framework for why singlet-delta oxygen may be preferentially produced when oxygen is catalytically recombined on silica-based materials. It is possible to examine the elementary reactions involved in the model from a purely thermodynamic point of view; the applicable elementary reactions would be (see Fig. 4):

$$\begin{matrix} \diagdown & \diagdown \\ \text{Si=O} \rightarrow & \text{Si=} \\ \diagup & \diagup \end{matrix} + \text{O}(^3\text{P}) + 81 \text{ Kcal/mole} \qquad (5)$$

$$\text{O}(^3\text{P}) + \text{O}(^3\text{P}) \rightarrow \text{O}_2(^3\Sigma) - 117.6 \text{ Kcal/mole} \qquad (6)$$

$$\text{O}(^3\text{P}) + \text{O}(^3\text{P}) \rightarrow \text{O}_2(^1\Delta) - 95 \text{ Kcal/mole} \qquad (7)$$

$$\text{O}(^3\text{P}) + \text{O}(^3\text{P}) \rightarrow \text{O}_2(^1\Sigma) - 76 \text{ Kcal/mole} \qquad (8)$$

Table 3 Values/form of the physiochemical parameters for catalytic recombination of O_2 on RCG

Parameter	Value
P	0.0002 exp(0.003 T) (maximum value = 0.03)
E	1.0 Kcal/mole (6.949×10^{-21} J/atom)
S_0	1.0 exp(−0.002 T)
C_a	2.0×10^{14} sites/cm^2
D	81.0 Kcal/mole (5.629×10^{-19} J/atom)

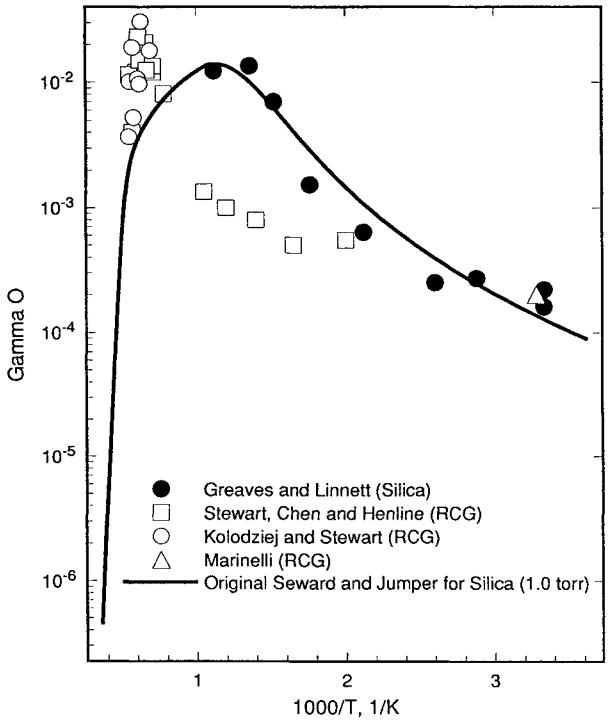

Fig. 2 Comparison of the model with data from Refs. 7 and 9–11, with the model's coefficients optimized for silica as given in Table 1.

From these, it is possible to examine the exotherm/endothermisity of the formation of ground-state oxygen, singlet delta oxygen, and singlet sigma oxygen states.

Ground state: (5) + (6) − 36.6 Kcal/mole exothermic
Singlet delta: (5) + (7) − 14 Kcal/mole exothermic
Singlet sigma: (5) + (8) + 5 Kcal/mole endothermic

From which it can be concluded that the only real candidate for electronic excitation is singlet delta, although singlet sigma might form given a sufficient kinetic energy contribution; such excess kinetic energy is always available from a probability point of view at all temperatures, but far less likely to be produced. This has two ramifications; first it suggests that unlike experiments for oxygen recombination on metals that are known to produce a variety of electronically excited states,[18,19] experiments for oxygen recombination on silicon dioxide and silica-based surfaces should produce only singlet delta (and perhaps a very low yield of singlet sigma) and ground state O_2, but no higher states than these. Furthermore, the model implies that the real energy releasing step in the reaction is the rebuilding of the SiO_2 surface. This would imply that much less "benefit" can be inferred from a fractional thermal accommodation than has been implied in the literature.[2]

In fact, preferential production of singlet-delta oxygen by recombination on a silica-based material has been reported.[20] The surface reported on was Pyrex®, and although some have

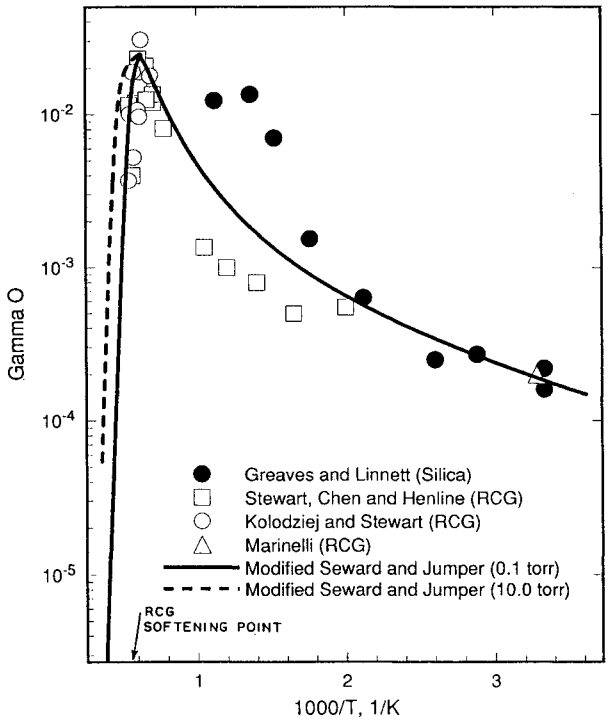

Fig. 3 Comparison of the model with data from Refs. 7 and 9–11, with the model's coefficients optimized for RCG as given in Table 3.

noted that the recombination efficiency of oxygen on Pyrex is somewhat different than either pure silica or RCG, it seems reasonable to suppose that the participation of surface-matrix oxygen would be preserved in the oxygen/Pyrex system. In the experiments reported in Ref. 20, only ground state and singlet-delta oxygen were produced with a yield of singlet-delta oxygen of between 20–36% of the total recombined oxygen, depending on the partial pressure of atomic oxygen. These findings appear to lend credibility to not only the predicted preferential production of singlet-delta, but also to the correctness of the underlying recombination model.

V. Implications of the Model Toward Re-Entry Heating

The implications of the model on prediction of re-entry heating are perhaps less important than the model itself, since extensive computations for re-entry profiles have been made using curve fits of the existing recombination data, like those reported in Ref. 11; however, the model offers some important insights into silica-based surface behavior during re-entry. First, as described above, little benefit in reducing catalytic heating through the production of excited species can be expected, and should not be included in re-entry calculations; thermal accommodation coefficients of nearly unity should be used. Second, the model given by Eq. (3) with the coefficients from Table 3, can easily be incorporated into computational schemes, as reported in Ref. 14, and should not be avoided in favor of simple curve fits. Although the heating predictions using either the model, Eq. (3), or curve fits would yield essentially the same results for the first-order-behavior regime, the transition to second-order behavior depends on the local gas-phase concentration of atomic oxygen in the immediate vicinity of the surface. As demonstrated in Fig. 3, such local partial-pressure differences can change the recombination coefficient by order(s) of magnitude over a small temperature range. As we have noted,[14] and as has been noted by others,[9] the rapid falloff in recombination rate above the partial-pressure-dependent critical temperature has a buffering effect on the heat load. According to the model, the physical reason for the buffering is that at these temperatures, sufficient kinetic (thermal) energy is present in the surface

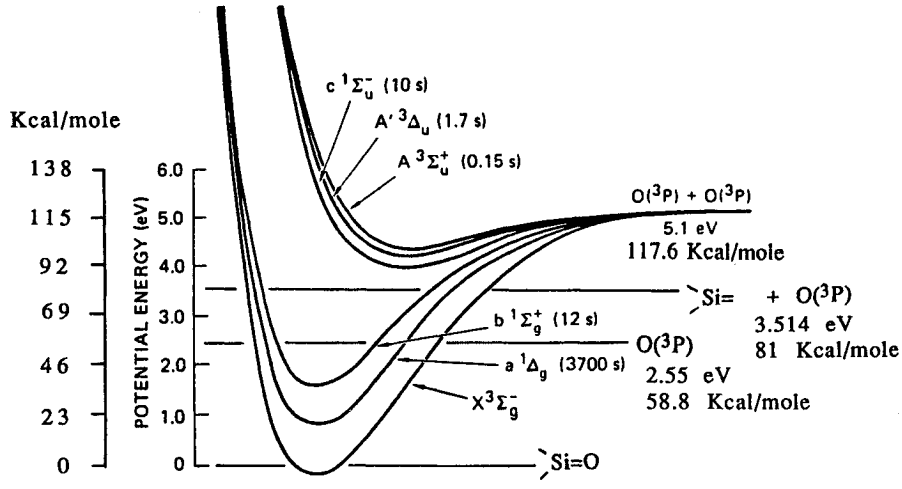

Fig. 4 Energy state diagram for molecular oxygen overlaid with the energy states for two O(^{3}P), a single O(^{3}P), and a broken Si=O bond relative to the surface-bonded Si=O.

atomic oxygen collisions to disrupt the Si=O bond, thereby rendering the surface catalytic; however, one can expect the behavior of the surface to change radically as the temperatures rise above the critical temperature. In effect, once the surface temperature rises above the critical temperature, surface-adhered oxygens required for the reaction are thermally desorbed more rapidly than they can be replenished, and the surface begins to become noncatalytic, thereby buffering the heat load and keeping the temperature from rising further. Using the model with the coefficients of Table 3, or even refined versions of the coefficients, may better define the local dependence of this buffering effect. It should be pointed out that Space Shuttle re-entry data and our own relatively-crude computations,[14] as well as more refined computations by others, have shown that certain locations on the Shuttle may be subjected to temperatures corresponding to the critical temperature during re-entry. Since, at surface temperatures near the critical temperature, catalytic heating accounts for 25–35% of the total re-entry heating,[14,21] proper modeling of the reaction based on local conditions may be important for certain proposed critical re-entry maneuvers.

VI. Concluding Remarks

Data for oxygen recombination on RCG were presented that support the notion that the model of Ref. 3 correctly portrays the physics of the catalytic reaction of oxygen on silica-based surfaces. In particular, the data for RCG demonstrates that the model's prediction that the recombination should dramatically decline and become second order appears to be correct. As such, we may infer that the fundamental concept of the model, the participation of a surface matrix oxygen directly in the reaction, is correct. Such surface-matrix oxygen participation gives specific insight into the extent to which the creation of electronically excited species may be expected to be formed in the reaction; only singlet-delta oxygen is a real candidate. Data on catalytically produced, singlet-delta oxygen on Pyrex was cited in support of this contention; the existence of these data further support the validity of the model. Furthermore, the preferential production of only singlet-delta oxygen greatly limits the extent to which the production of excited species is able to reduce the thermal load imposed on a surface by the transfer of the excess energy of the recombination directly to the surface; it appears that almost all the excess energy will be deposited directly into the surface, the principle energy transfer mechanism being the replenishing of the surface-matrix oxygen by the gas-phase collisions of atomic oxygen. The model also provides an explanation for why the recombination coefficient suddenly drops above a oxygen-partial-pressure-dependent critical temperature. This reduction is due to thermal desorption of the surface-adhered oxygen, and since this oxygen is part of the surface matrix of the silica-based surface, it is not surprising that the critical temperature occurs near the softening temperature of the surface.

Although the existence of this model may offer only subtle differences in computational predictions of surface heating on such surfaces as are used on the Space Shuttle, the adaptability of the model for predictive purposes is relatively straightforward and allows for the inclusion of local conditions into the calculations. We suggest that the use of the model be preferred over simple curve fits of existing data. The real value of the model, however, is that it provides insight into the specific processes involved in the reaction. These specifics have allowed for a prediction of the production of electronically excited species and offer an explanation for why this production should differ from that on metals. Hopefully, the understanding of how oxygen catalytically recombines on silica-based materials may lead to insights on the development of other candidate materials for thermal protection and other purposes.

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