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Modeling of Catalytic Reactions on Silica Surfaces with Consideration of Slip Effects

A. Daiß,* H.-H. Frühauf,† and E. W. Messerschmid‡
University of Stuttgart, 70550 Stuttgart, Germany

A detailed surface chemistry model is presented for the reactions of N_2, O_2, NO, N, and O on a silica surface. The model distinguishes adsorption, desorption, and recombination reactions according to the Eley–Rideal and Langmuir–Hinshelwood mechanisms as well as dissociative adsorption reactions of the molecular species. The model parameters are adjusted by comparison of predicted recombination coefficients for N and O with experimentally determined recombination coefficients. For the calculation of surface heating rates of re-entry vehicles, the model is implemented into a multiple-temperature Navier–Stokes code and coupled with a slip model to take into account rarefaction effects at high altitudes. Computational results obtained with the surface chemistry model for Shuttle-equivalent hyperboloids are compared to Shuttle flight data.

Nomenclature

$\bar{c}$ = average particle velocity
E = activation energy
F = energy flux
f = velocity distribution function
G = particle energy
H = enthalpy
h = Planck constant
I = moment of inertia
K = equilibrium constant
k = rate coefficient or Boltzmann constant
l = vibrational level
m = particle mass
n = particles per unit surface area
P = steric factor
Q = partition function
s = sticking coefficient
T = temperature
v = particle velocity
Z = particle flux per unit surface area
$\boldsymbol{\alpha}$ = accommodation coefficient
$\boldsymbol{\beta}$ = chemical energy accommodation coefficient
γ = recombination coefficient
θ = characteristic vibrational temperature
σ = symmetry number
ψ = mole fraction
$\dot{\omega}$ = reaction rate per unit surface area

Subscripts

Ad = adsorption
AS = adsorbed atom and active site
DA = dissociative adsorption
Des = desorption
ER = Eley–Rideal mechanism
LH = Langmuir–Hinshelwood mechanism
r = rotation
S = active site
t = translation
v = vibration
W = wall

Superscripts

$+$ = fluxes going to the surface
$-$ = fluxes coming from the surface
0 = conditions at an empty surface

Introduction

THE modeling of gas-phase and surface processes in nonequilibrium re-entry flows has a strong influence on the heat fluxes and surface temperatures calculated with numerical flow simulation codes. While the differences in stagnation point heat fluxes computed with different gas-phase chemistry models may attain up to 25%, the differences obtained with a different assumption concerning the catalytic behavior of the surface may be even larger. For flow cases with a high degree of dissociation in the boundary layer the heat fluxes calculated for non- and fully catalytic surfaces will differ by more than a factor of 2. Therefore, reliable models are needed for the description of surface reactions in nonequilibrium flows to accurately predict the heat transfer to the surface of a re-entry vehicle.[1] For silicon–dioxide surfaces the existing experimental data indicate that the recombination coefficients for atomic oxygen and nitrogen strongly increase with increasing surface temperature and then rapidly decrease after reaching a maximum at a temperature of about 1600 K. This non-Arrhenius temperature dependence cannot be explained by a single-step reaction mechanism. At least a two-step reaction mechanism involving adsorption/desorption and recombination reactions is required to describe this behavior.[2–5]

Various models have been proposed for the description of surface reactions of air species on silicon–dioxide surfaces.[1–6] These models can be separated into purely phenomenological ones, for instance, the models of Scott[1] and Zoby[6] and models that are based on mechanistic considerations.[2–4] While the phenomenological models try to match the available experimental data by an Arrhenius-type surface temperature-dependent expression for the overall recombination coefficients of the atomic species, the mechanistic models consider a probable reaction mechanism that is commonly thought to be constituted of an adsorption/desorption process of the atomic species N and O and surface recombination reactions according to the Eley–Rideal (ER) or Langmuir–Hinshelwood (LH) mechanism and subsequent desorption of the recombined molecules.

However, in the slip flow regime caused by the temperature jump between the surface and the adjacent gas phase, highly

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*Research Engineer, Institut für Raumfahrtsysteme.

†Senior Scientist, Institut für Raumfahrtsysteme.

‡Professor, Institut für Raumfahrtsysteme. Member AIAA.

excited and fast molecules may hit the surface and thus may also give rise to dissociative adsorption processes and in the upper slip flow regime even to dissociation reactions. Additionally, the occurrence of the temperature jump effect raises the question of which temperature should be introduced in the rate coefficients of the various surface reaction processes.

Since the energy balance at the surface is not only affected by the reaction rates, but also by the amount of energy inherent to the molecules that leave the surface after recombination reactions, the $\boldsymbol{\beta}$ for these reactions are needed also.[7] In most of the current surface reaction models, $\boldsymbol{\beta}$ is assumed to be one,[1,2,4,5] although Melin and Madix suggest in their work,[7] at least for recombination reactions of oxygen atoms on metal oxide surfaces, that the accommodation coefficient can be much less then unity.

The objective of this work is to present a detailed surface chemistry model for the reactions of air species on silicon–dioxide surfaces distinguishing adsorption, desorption, recombination, and dissociative adsorption reactions. The relevance of the different elementary reaction steps will be studied for the continuum and the slip flow regime. Also an estimate will be given for β and the energies stored in the internal and translational degrees of freedom of molecules being formed in surface recombination reactions.

Finally, simulation results obtained with the presented model and the multiple-temperature Navier–Stokes code URANUS[8] will be shown for axisymmetric flows around Shuttle-equivalent hyperboloids.

Catalysis Model for Silica Surfaces

At the interface of a silicon–dioxide/air system various chemical processes may occur. Nitrogen and oxygen atoms can be adsorbed at special locations on the surface, called active sites, which they may leave after some time because of migration processes or thermal desorption from the surface (Fig. 1). They may also be involved in recombination reactions according to the ER and LH mechanisms (Figs. 2 and 3). In the ER mechanism a gas-phase atom strikes an occupied active site and recombines with the adsorbed atom by forming a gas-phase molecule. In contrast to this, the LH mechanism describes a recombination reaction where a migrating surface atom collides with another surface atom to form a gas-phase molecule. If the thermal energy in the gas phase next to the surface is high enough, the reverse process of the ER mechanism, the dissociative adsorption (Fig. 2), becomes important. A gas-phase molecule hits the surface and forms an adsorbed atom and a gas-phase atom. Since this process is strongly endothermic it can only happen if the gas-phase temperature is much higher than the usually met surface temperatures ($T_W \leq$ 2000 K). However, in the slip flow regime the temperature jump at the surface can be large enough for the occurrence of this reaction. If the temperature jump becomes very large the dissociation of molecules into gas-phase atoms may take place. This type of reaction is not considered here.

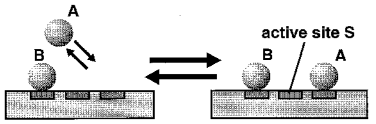

Fig. 1 Adsorption and desorption reaction of A on S.

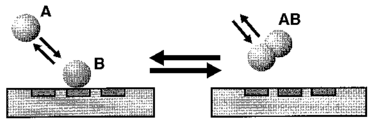

Fig. 2 ER mechanism and dissociative adsorption of AB.

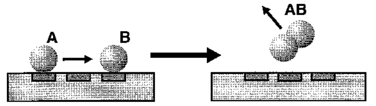

Fig. 3 LH mechanism for AB.

Basic Model Assumptions

The construction of a tractable catalysis model necessitates some simplifications. Therefore, the following assumptions are made concerning the behavior of the adsorbed atoms:

1) The adatoms behave like harmonic oscillators on the surface. They possess different vibrational frequencies $\theta_{\|}$ and $\theta_{\perp}$ for their oscillations parallel and perpendicular to the surface, respectively.

2) The partition function Q_{AS} of the adsorption complex AS can be factorized into a contribution Q_S coming from the surface and a contribution $Q_{\mathrm{Ad},A}$ coming from the oscillations.

3) The vibrational levels are Boltzmann-populated with the surface temperature T_W.

These assumptions allow us to write the partition function of the adsorption complex AS as

$$Q_{\mathrm{AS}} = Q_S \cdot Q_{\mathrm{Ad},A} = Q_S \cdot Q^2_{v,\|}(T_W) \cdot Q_{v,\perp}(T_W) \tag{1}$$

with $Q_{v,\perp}(T_W)$ and $Q_{v,\|}(T_W)$ being the partition functions for the adatom vibrations perpendicular and parallel to the surface

$$\begin{aligned} Q_{v,\perp}(T_W) &= \frac{\exp[-(\theta_{\perp,A}/2T_W)]}{1 - \exp[-(\theta_{\perp,A}/T_W)]} \\ Q_{v,\|}(T_W) &= \frac{\exp[-(\theta_{\|,A}/2T_W)]}{1 - \exp[-(\theta_{\|,A}/T_W)]} \end{aligned} \tag{2}$$

In literature, typical values of $\theta_{\|}$ and $\theta_{\perp}$ for chemisorbed molecules are $\theta_{\|} \approx 100$ K and $\theta_{\perp} \approx 600$ K.[9] In our approach we use the values $\theta_{\|,\mathrm{N}} = 80$ K, $\theta_{\perp,\mathrm{N}} = 600$ K for nitrogen and $\theta_{\|,\mathrm{O}} = 90$ K, $\theta_{\perp,\mathrm{O}} = 600$ K for oxygen.

Also, for the gas-phase particles, simplifications are necessary. It is important to note that they should be consistent with the assumptions made for the modeling of the gas-phase processes:

1) The electronic excitation of the gas-phase particles is neglected, although it might be important for oxygen molecules.

2) For the description of the rotational motion of the gas-phase molecules the infinite rigid rotator model is used.

3) The vibrational motion is sufficiently enough reproduced by the truncated harmonic oscillator model and the vibrational levels of the oscillators are T_v-Boltzmann-populated.

With the previous simplifications one gets for the partition functions of the molecules AB

$$\begin{aligned} Q_{\mathrm{AB}} &= Q_{t,\mathrm{AB}} \cdot Q_{r,\mathrm{AB}} \cdot Q_{v,\mathrm{AB}} \\ &= \left(\frac{2\pi m_{\mathrm{AB}} kT}{h^2}\right)^{3/2} \cdot \left(\frac{8\pi^2 I_{\mathrm{AB}} kT}{\sigma_{\mathrm{AB}} h^2}\right) \\ &\quad \times \left\{\frac{1 - \exp[-(l_D \theta_{\mathrm{AB}}/T_v)]}{1 - \exp[-(\theta_{\mathrm{AB}}/T_v)]}\right\} \cdot \exp\left(-\frac{\theta_{\mathrm{AB}}}{2T_v}\right) \end{aligned} \tag{3}$$

with l_D being the vibrational level just beyond the dissociation limit, and for the atoms A one gets

$$Q_A = Q_{t,A} = \left(\frac{2\pi m_A kT}{h^2}\right)^{3/2} \tag{4}$$

Adsorption/Desorption Reactions

The adsorption reaction of an atom A on an active site S and its corresponding reverse reaction, the thermal desorption, can formally be written as

$$A + S \rightleftharpoons \mathrm{AS} \tag{5}$$

For the rate of adsorption it is supposed that the following expression is valid[2,4]:

$$\dot{\omega}_{\text{Ad}} = s_A Z_A^+ (n_S / n_S^0) \tag{6}$$

Herein s_A is the sticking probability of A striking a vacant S. Z_A^+ denotes the molar flux of A impinging on the surface per area and time unit and n_S/n_S^0 is the ratio of the actual active site concentration to the active site concentration of a completely free surface. For n_S^0, Newman[3] gives the value 2×10^{18} m^{-2}.

The rate of desorption is expressed as a function of the rate coefficient k_{Des} and the concentration of adatoms n_{AS} on the surface

$$\dot{\omega}_{\text{Des}} = k_{\text{Des}} n_{\text{AS}} \tag{7}$$

k_{Des} is determined by using the transition state theory. In the framework of this theory k_{Des} reads

$$k_{\text{Des}} = P_{\text{Des}} \cdot \frac{kT_W}{h} \frac{Q_{\text{AS}}^{\ddagger}}{Q_{\text{AS}}} \cdot \exp\left(-\frac{E_{A-S}}{\Re T_W}\right) \tag{8}$$

with Q_{AS} being the partition function of the adsorption complex AS and $Q_{\text{AS}}^{\ddagger}$ being the partition function of the activated adsorption complex (without the reaction coordinate) that has the form

$$Q_{\text{AS}}^{\ddagger} = Q_S \cdot Q_{v,\|}^2 \tag{9}$$

Using Eq. (1) we get for the rate coefficient of desorption

$$k_{\text{Des}} = P_{\text{Des}} \cdot \frac{kT_W}{h} Q_{v,\perp}^{-1}(T_W) \cdot \exp\left(-\frac{E_{A-S}}{\Re T_W}\right) \tag{10}$$

The parameter P_{Des} is a catchall factor that will be adjusted later.

The sticking coefficient s_A is evaluated by means of equilibrium considerations. In the case of thermodynamic equilibrium, the rates of desorption and adsorption must be equal, thus, $\dot{\omega}_{\text{Ad}} = \dot{\omega}_{\text{Des}}$. Furthermore, the particle flux of A colliding with the surface now satisfies the effusion relation $Z_A^+ = n_A \bar{c}_A / 4$, where n_A is the concentration of A and $\bar{c}_A$ represents their average particle velocity $\bar{c}_A = \sqrt{8kT/\pi m_A}$. Using these two relations together with Eqs. (6) and (7) we get

$$s_A = \frac{4 n_S^0}{\bar{c}_A} \left(\frac{n_A n_S}{n_{\text{AS}}}\right)^{-1} k_{\text{Des}} \tag{11}$$

The ratio of concentrations in Eq. (11) can be expressed by the adsorption/desorption equilibrium constant

$$K_{\text{Ad/Des}} = \frac{n_A n_S}{n_{\text{AS}}} = \frac{Q_A Q_S}{Q_{\text{AS}}} \cdot \exp\left(-\frac{E_{A-S}}{\Re T_W}\right) \tag{12}$$

Introducing this expression into Eq. (11), together with the expressions for the partition functions, gives the final form of the sticking coefficient

$$s_A = P_{\text{Des}} \cdot \frac{n_S^0 h^2}{2\pi m_A k} \cdot \frac{T_W}{T^2} \cdot Q_{v,\|}^2(T_W) \tag{13}$$

where the T of the atoms that hit the surface has been introduced instead of the equilibrium surface temperature T_W to take into account the temperature jump effect. The sticking process is strongly exothermic and no bond has to be broken. We assume, like other authors,[2,10] that the adsorption reaction needs no activation energy. Different values have been given for the desorption energy E_{A-S} in literature.[2,10] In our approach for nitrogen and oxygen we use the values $E_{\text{N}-S} = 250$ kJ/mol and $E_{\text{O}-S}$ 250 kJ/mol, respectively.

ER Mechanism/Dissociative Adsorption

The ER recombination rate $\dot{\omega}_{\text{ER}}$ of an adatom A with a gas-phase atom B

$$\text{AS} + B \rightleftharpoons \text{AB} + S \tag{14}$$

is proportional to molar flux Z_B^+ of B colliding with the surface and it is also proportional to the surface coverage n_{AS}/n_S^0 with A. Hence, we write

$$\dot{\omega}_{\text{ER}} = k_{\text{ER}} \cdot \frac{n_{\text{AS}}}{n_S^0} \cdot Z_B^+ \tag{15}$$

where k_{ER} is the rate coefficient. For the reverse reaction, the dissociative adsorption, the rate is proportional to the flux Z_{AB}^+ of AB and it is also proportional to the surface coverage with vacant S, thus, we have

$$\dot{\omega}_{\text{DA}} = k_{\text{DA}} Z_{\text{AB}}^+ (n_S / n_S^0) \tag{16}$$

The rate coefficient k_{DA} is evaluated by means of a simple collision rate approach. It is supposed that every particle AB that possesses enough energy for surmounting the activation barrier of dissociative adsorption will react when it hits a vacant active site. Assuming that the vibrational energy fully contributes to the activation energy and that only the translational degree of freedom perpendicular to the surface provides energy for the reaction, we get the minimum normal velocity v_z^l of a reacting particle in the vibrational state l

$$v_z^l = \sqrt{\max[2 \cdot (E_{\text{DA}} - \varepsilon^l)/M_{\text{AB}}, 0]} \tag{17}$$

where $\varepsilon^l = \Re \theta_{\text{AB}} l$ is the energy of the oscillator AB in l and E_{DA} is the activation energy of dissociative adsorption. M_{AB} represents the molar mass of the molecule. For simplicity, we have supposed here that the considered surface is perpendicular to the z axis of a Cartesian coordinate system. A v_z-weighted integration of the velocity distribution function f_{AB} over the velocity half-space $-\infty < v_z \leq -v_z^l$ and subsequent summation over all vibrational energy levels gives the flux of molecules that are able to react at the surface. By multiplying the resulting expression with the surface coverage of the vacant active sites, one gets

$$\dot{\omega}_{\text{DA}} = \boldsymbol{\chi} P_{\text{DA}} \sum_{l=0}^{l_D - 1} p^l \int_{-\infty}^{-v_z^l} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_z f_{\text{AB}} \, \mathrm{d}\boldsymbol{v} \cdot \frac{n_S}{n_S^0} \tag{18}$$

with $p^l = \exp(-\varepsilon^l / \Re T_v)$. Two additional factors, $\boldsymbol{\chi}$ and P_{DA}, have been introduced. χ takes into account that a molecule AB can dissociate into $A + BS$, but also into $\text{AS} + B$. Thus, we assign for χ the value 0.5 if $A \neq B$, and 1 if $A = B$. P_{DA} is a catchall factor that includes all of the uncertainties in the modeling and it has to be adjusted by means of comparison with experimental data. An evaluation of Eq. (18) for a Maxwellian velocity distribution function and comparison with Eq. (16) now yields the coefficient

$$k_{\text{DA}}(T, T_v) = \chi P_{\text{DA}} \cdot \Lambda(T, T_v) \cdot \exp[-(E_{\text{DA}}/\Re T)] \tag{19}$$

with Λ being

$$\Lambda(T, T_v) = \frac{Q_v^{\text{DA}}(T^*) + [Q_v^D(T_v) - Q_v^{\text{DA}}(T_v)]\exp(E_{\text{DA}}/\Re T)}{Q_v^D(T_v)} \tag{20}$$

The superscripts DA and D signify that in the vibrational partition functions Q_v of the truncated harmonic oscillators AB, the truncation limits l_{DA} (dissociative adsorption) and l_D (dissociation) have to be introduced, respectively. The pseudotemperature T^* is defined by $1/T^* = 1/T_v - 1/T$. Similar to the sticking coefficient s_A, the rate coefficient k_{ER} is evaluated from equilibrium considerations. Under this special condition $\dot{\boldsymbol{\omega}}_{\mathrm{ER}}$ must satisfy the equality $\dot{\omega}_{\mathrm{ER}} = \dot{\omega}_{\mathrm{DA}}$ and the flux of particles B can be calculated from $Z_B^+ = n_B\bar{c}_B/4$. From Eqs. (15) and (16) and the previous relations, one gets

$$k_{\mathrm{ER}} = \frac{\bar{c}_{\mathrm{AB}}}{\bar{c}_B}\left[\frac{n_{\mathrm{AS}}n_B}{n_{\mathrm{AB}}n_S}\right]^{-1} k_{\mathrm{DA}} \tag{21}$$

Once again the ratio of the concentrations is expressed by the equilibrium constant

$$K_{\mathrm{ER/DA}} = \frac{n_{\mathrm{AS}}n_B}{n_{\mathrm{AB}}n_S} = \frac{Q_{\mathrm{AS}}Q_B}{Q_{\mathrm{AB}}Q_S}\cdot\exp\left(\frac{\Delta H_{\mathrm{ER}}}{\mathcal{R}T_W}\right) \tag{22}$$

Introduction of the partition functions and some algebraic manipulations finally give

$$k_{\mathrm{ER}} = \boldsymbol{\chi}P_{\mathrm{DA}}\frac{m_{\mathrm{AB}}}{m_B}\Lambda(T_W)\cdot Q_{r,\mathrm{AB}}(T_W)\cdot Q_{v,\|}^{-2}(T_W)$$
$$\times\, Q_{v,\perp}^{-1}(T_W)\cdot Q_{v,\mathrm{AB}}(T_W)\cdot\exp\left(-\frac{E_{\mathrm{ER}}}{\mathcal{R}T}\right) \tag{23}$$

In the Boltzmann factor T of B hitting the surface has been introduced instead of T_W, since the activation barrier of the recombination process has to be overcome by the kinetic energy of B.

The activation energies E_{ER} and E_{DA} are still unspecified. We use the semiempirical correlation of Hirschfelder[11] for their estimation from the desorption energy E_{A-S}.[10] The relation of Hirschfelder reads

$$E_{\mathrm{ER}} = 0.055\cdot E_{A-S} \tag{24}$$

The calculated activation energies E_{ER} are then corrected to give best agreement with experimental data. If E_{ER} is known one can determine the activation energy of the dissociative adsorption by $E_{\mathrm{DA}} = -\Delta H_{\mathrm{ER}} + E_{\mathrm{ER}}$. Numerical values for the activation energies of nitrogen are $E_{\mathrm{ER,2N\to N_2}} = 24.94$ kJ/mol and $E_{\mathrm{DA,N_2\to 2N}} = 716.08$ kJ/mol, and for oxygen one gets $E_{\mathrm{ER,2O\to O_2}} = 24.94$ kJ/mol and $E_{\mathrm{DA,2O\to O_2}} = 269.62$ kJ/mol.

LH Mechanism

The modeling of the Langmuir–Hinshelwood mechanism has been adopted from the work of Nasuti and Bruno.[2] Only the determination of the activation energy for surface migration E_m that plays a major role in this model has been modified. For this activation energy we use the rough estimate $E_{m,A} = E_{A-S}/2$.[10] Additionally, a steric factor P_{LH} has been introduced since the modeling of the surface migration process contains some simplifications. The activation energies used in our work are $E_{\mathrm{LH,2N\to N_2}} = 125.0$ kJ/mol and $E_{\mathrm{LH,2O\to O_2}} = 125.0$ kJ/mol.

Average Energy of Recombining Molecules

For the determination of the surface heating of a re-entry body it is not only important to know the surface reaction rates but it is also necessary to know in which state the various particles are formed. For the estimation of the states of particles being formed in the ER recombination we first consider the state of molecules that are vanishing in the reverse process. The average vibrational energy $G_{v,\mathrm{DA}}^+$ of molecules vanishing in dissociative adsorption reactions is given by the following expression:

$$G_{v,\mathrm{DA}}^+ = F_{v,\mathrm{DA}}^+/\dot{\omega}_{\mathrm{DA}}$$
$$= \sum_{l=0}^{l_D-1}\varepsilon^l p^l\int_{-\infty}^{-v_z^l}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_z f_{\mathrm{AB}}\,\mathrm{d}\boldsymbol{v}$$
$$\Bigg/\sum_{l=0}^{l_D-1}p^l\int_{-\infty}^{-v_z^l}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_z f_{\mathrm{AB}}\,\mathrm{d}\boldsymbol{v} \tag{25}$$

where $F_{v,\mathrm{DA}}^+$ is the vibrational energy flux transported by molecules AB that vanish in dissociative adsorption reactions. Analogically, one finds for the average translational energy $G_{t,\mathrm{DA}}^+$

$$G_{t,\mathrm{DA}}^+ = F_{t,\mathrm{DA}}^+/\dot{\omega}_{\mathrm{DA}}$$
$$= \sum_{l=0}^{l_D-1}p^l\int_{-\infty}^{-v_z^l}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_z\frac{\boldsymbol{v}^2}{2}f_{\mathrm{AB}}\,\mathrm{d}\boldsymbol{v}$$
$$\Bigg/\sum_{l=0}^{l_D-1}p^l\int_{-\infty}^{-v_z^l}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} v_z f_{\mathrm{AB}}\,\mathrm{d}\boldsymbol{v} \tag{26}$$

with $F_{t,\mathrm{DA}}^+$ being the translational energy flux of the reacting molecules AB. In the thermodynamic equilibrium the rates of the ER recombination and the dissociative adsorption must be equal, hence, $\dot{\omega}_{\mathrm{ER}} = \dot{\omega}_{\mathrm{DA}}$. Moreover, the average vibrational excitation and the average translational energies have to be equal for the direct and the reverse process, hence, $G_{v,\mathrm{DA}}^+ = G_{v,\mathrm{ER}}^-$ and $G_{t,\mathrm{DA}}^+ = G_{t,\mathrm{ER}}^-$. Using these arguments we get for the average vibrational excitation and the average translational energy of particles that come into being within the ER mechanism under equilibrium conditions

$$G_{v,\mathrm{ER}}^- = \frac{(l_{\mathrm{DA}}^2\mathcal{R}\theta_{\mathrm{AB}}/2)}{l_{\mathrm{DA}} + [Q_v^D(T_W) - Q_v^{\mathrm{DA}}(T_W)]\exp(E_{\mathrm{DA}}/\mathcal{R}T_W)}$$
$$+ \frac{[Q_v^D(T_W)L^D(T_W) - Q_v^{\mathrm{DA}}(T_W)L^{\mathrm{DA}}(T_W)]}{l_{\mathrm{DA}} + [Q_v^D(T_W) - Q_v^{\mathrm{DA}}(T_W)]}\times\exp\left(\frac{E_{\mathrm{DA}}}{\mathcal{R}T_W}\right) \tag{27}$$

with

$$L^D(T_W) = \mathcal{R}\theta_{\mathrm{AB}}\left\{\frac{\exp[-(\theta_{\mathrm{AB}}/T_W)]}{1 - \exp[-(\theta_{\mathrm{AB}}/T_W)]}\right.$$
$$\left. - \frac{l_D\cdot\exp[-(l_{D,\mathrm{AB}}\theta_{\mathrm{AB}}/T_W)]}{1 - \exp[-(E_{A-B}/\mathcal{R}T_W)]} + \frac{1}{2}\right\} \tag{28}$$

For the determination of $L^{\mathrm{DA}}(T_W)$ the dissociation energy E_{A-B} in Eq. (28) has to be replaced by the activation energy E_{DA} of the dissociative adsorption.

The molar translational energy of a molecule being formed in the ER recombination reads

$$G_{t,\mathrm{ER}}^- = (2\mathcal{R}T_W + E_{\mathrm{DA}})$$
$$- \frac{\mathcal{R}\theta_{\mathrm{AB}}l_{\mathrm{DA}}^2/2}{l_{\mathrm{DA}} + [Q_v^D(T_W) - Q_v^{\mathrm{DA}}(T_W)]\exp(E_{\mathrm{DA,AB}}/\mathcal{R}T_W)}$$
$$- \frac{l_{\mathrm{DA}}\mathcal{R}\theta_{\mathrm{AB}}[Q_v^D(T_W) - Q_v^{\mathrm{DA}}(T_W)]\exp(E_{\mathrm{DA}}/\mathcal{R}T_W)}{l_{\mathrm{DA}} + [Q_v^D(T_W) - Q_v^{\mathrm{DA}}(T_W)]\exp(E_{\mathrm{DA}}/\mathcal{R}T_W)} \tag{29}$$

These values are not exact under nonequilibrium conditions because the energies of the molecules AB coming into being in the recombination reaction are also affected by the kinetic energy of the recombining atoms B. Since the energy of B is usually much smaller than the energy values $G_{v,\mathrm{ER}}^-$ and $G_{t,\mathrm{ER}}^-$

calculated for AB under equilibrium conditions, the nonequilibrium values of AB will not be strongly affected by the kinetic energy of B and, thus, the equilibrium values can be used as a quite reasonable approximation even for thermal nonequilibrium situations. The LH recombination reaction is an endothermic process. Therefore, it is assumed that molecules that are formed within this process do not possess any excess energy and we assign the values $G^{-}_{v,\mathrm{LH}} \approx e_v(T_W)$ and $G^{-}_{t,\mathrm{LH}} \approx 2RT_W$ for the average vibrational and translational excitation, where $e_v(T_W)$ is the molar average vibrational energy of Boltzmann-populated truncated harmonic oscillators.

The rotational degrees of freedom are assumed to be in equilibrium with the surface conditions for all considered reactions, hence, $G^{-}_{r,\mathrm{LH/ER}} \approx RT_W$.

Results

Extensive parameter studies have been carried out to adjust the coefficients P_{Des}, P_{DA}, and P_{LH}. First, the case of a pure nitrogen system N/N$_2$ is studied. In Fig. 4 the recombination coefficient $\gamma'_{\mathrm{N}\to\mathrm{N}_2}$, which is defined by

$$\gamma'_{\mathrm{N}\to\mathrm{N}_2} = (Z^+_{\mathrm{N}} - Z^-_{\mathrm{N}})/Z^+_{\mathrm{N}} \tag{30}$$

and the energy recombination coefficient $\gamma_{\mathrm{N}\to\mathrm{N}_2}$, which is the product of $\gamma'_{\mathrm{N}\to\mathrm{N}_2}$ times the average energy accommodation coefficient $\beta_{\Sigma,\mathrm{N}\to\mathrm{N}_2}$, are plotted as a function of the inverse surface temperature $1/T_W$ together with experimental results of Refs. 1 and 12. The steric factors are $P_{\mathrm{Des,N}} = 0.1$, $P_{\mathrm{DA,N}} = 0.01$, and $P_{\mathrm{LH,N}} = 0.02$. The partial pressures of N and N$_2$ in the gas phase are $p_{\mathrm{N}} = 10/100/1000/10{,}000$ N/m^2 and $p_{\mathrm{N}_2} = 0$ N/m^2. Each time it is assumed that thermal equilibrium exists between the surface, the gas phase, and the different degrees of freedom.

The recombination coefficients show the typical rollover at a temperature of about 1600 K. Furthermore, one can see that γ' and γ differ strongly at low temperatures where the ER mechanism is dominant, but lie closely together where the LH mechanism becomes the more important process. This can be explained by the fact that in the model presented the accommodation coefficient $\beta_{\mathrm{LH,N}\to\mathrm{N}_2}$ of the LH mechanism is unity, whereas the ER mechanism has a much smaller value $\beta_{\mathrm{ER,N}\to\mathrm{N}_2}$ of about 0.2. The values of $\beta_{\mathrm{ER,N}\to\mathrm{N}_2}$ and $\beta_{\Sigma,\mathrm{N}\to\mathrm{N}_2}$ shown in Fig. 5 are calculated from the terms $G^{-}_{v,\mathrm{ER/LH}}$ and $G^{-}_{t,\mathrm{ER/LH}}$.

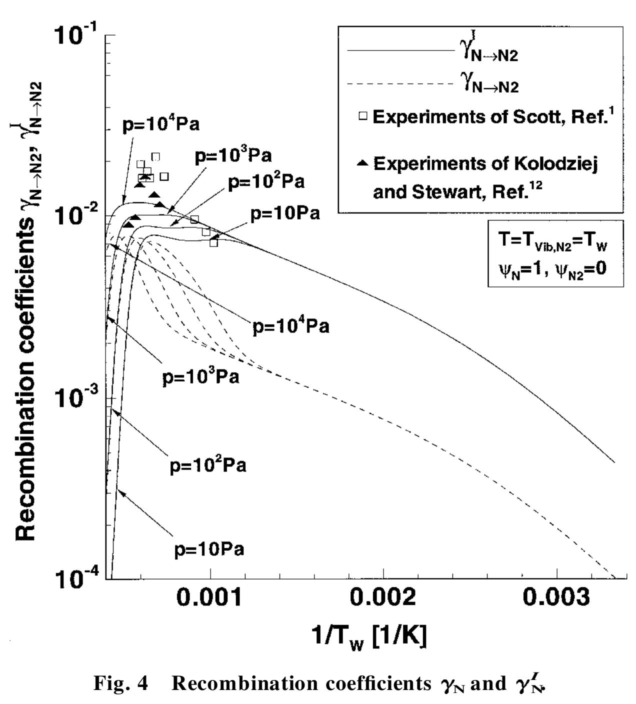

Fig. 4 Recombination coefficients γ_{N} and γ'_{N}.

For a pure oxygen system the same investigations have been carried out as for nitrogen. The steric factors used are $P_{\mathrm{Des,O}} = 0.1$, $P_{\mathrm{DA,O}} = 0.01$, and $P_{\mathrm{LH,O}} = 0.02$.

In Fig. 6 the comparison between the calculated recombination coefficients $\gamma_{\mathrm{O}\to\mathrm{O}_2}$ and $\gamma'_{\mathrm{O}\to\mathrm{O}_2}$ and the experimental values of γ'_{O} from Kolodziej and Stewart[12] and Dickens and Sutcliffe[13] is shown. As one can see, good agreement is found between the experimental data and the calculated values for the chosen set of steric factors.

The same features that have been depicted for nitrogen are found for oxygen, although the differences between the two coefficients γ' and γ are not as much pronounced in this case. This arises from the fact that the coefficient $\beta_{\mathrm{ER,O}\to\mathrm{O}_2}$ is about 0.4 (Fig. 7) and thus is much closer to unity than the value for nitrogen.

Also, the influence of the gas-phase composition on the recombination coefficient has been investigated for an O/O$_2$ system. In Fig. 8 the recombination coefficient $\gamma_{\mathrm{O}\to\mathrm{O}_2}$ is shown as

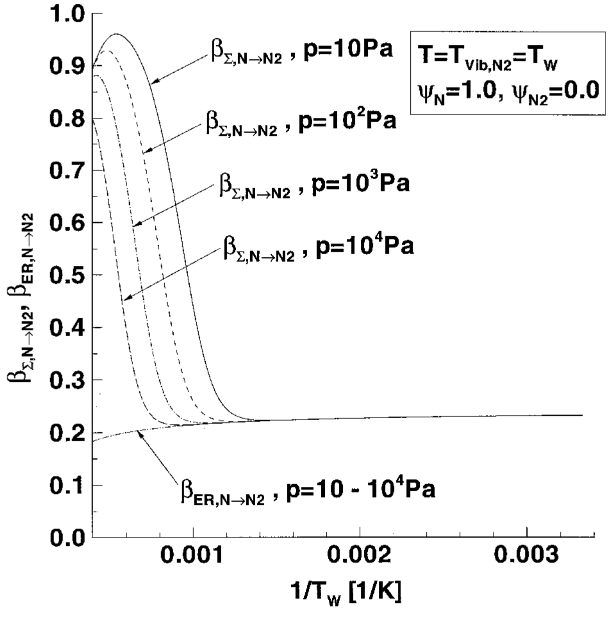

Fig. 5 Energy accommodation coefficients $\beta_{\mathrm{ER,N}\to\mathrm{N}_2}$ of the ER mechanism and $\beta_{\Sigma,\mathrm{N}\to\mathrm{N}_2}$ of the entire recombination process.

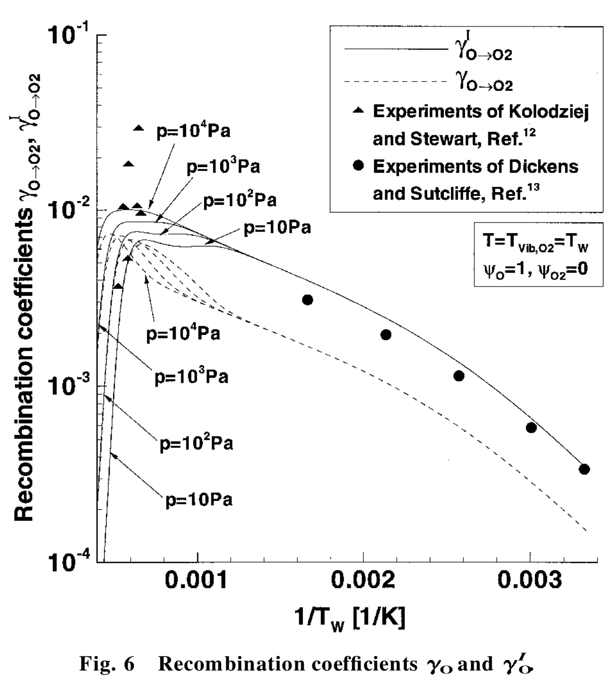

Fig. 6 Recombination coefficients γ_{O} and γ'_{O}.

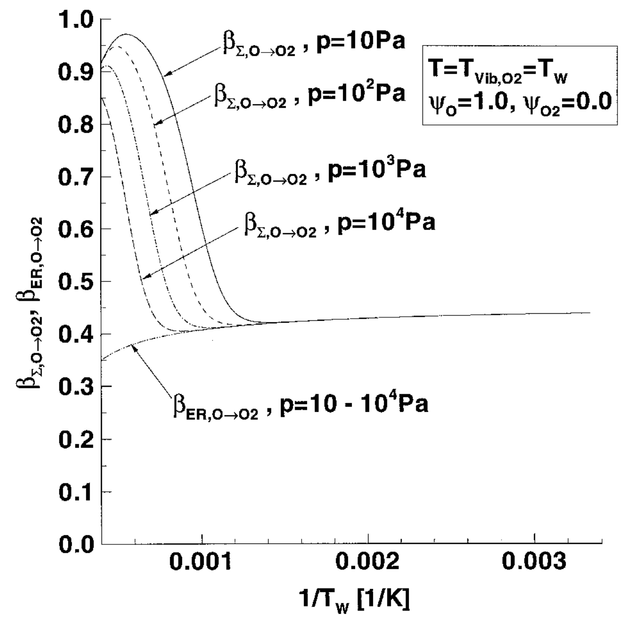

Fig. 7 Energy accommodation coefficient $\beta_{ER,O\to O_2}$ of the ER mechanism and $\beta_{\Sigma,O\to O_2}$ of the entire recombination process.

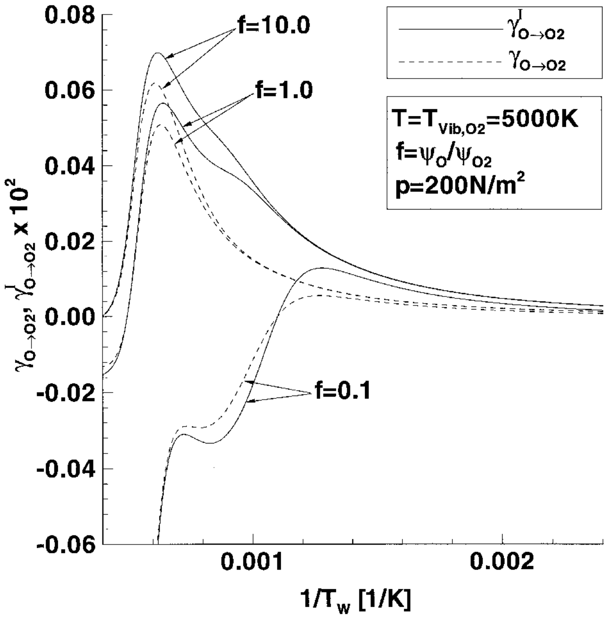

Fig. 8 Influence of the gas-phase composition on the recombination coefficients $\gamma_{O\to O_2}$ and $\gamma'_{O\to O_2}$.

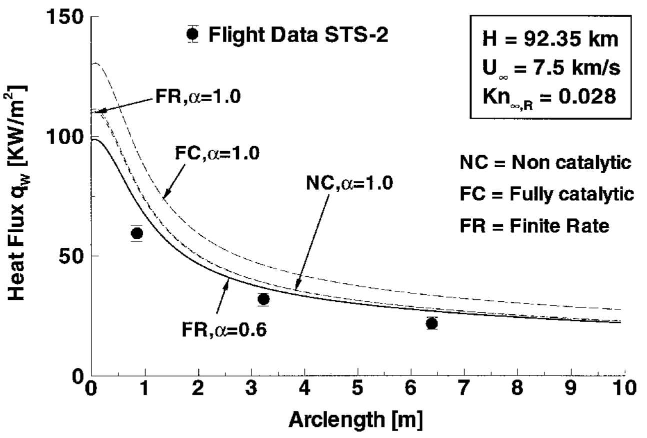

Fig. 9 Heat flux distribution for a Shuttle-equivalent hyperboloid and STS-2 freestream conditions of the trajectory point 92.35 km.

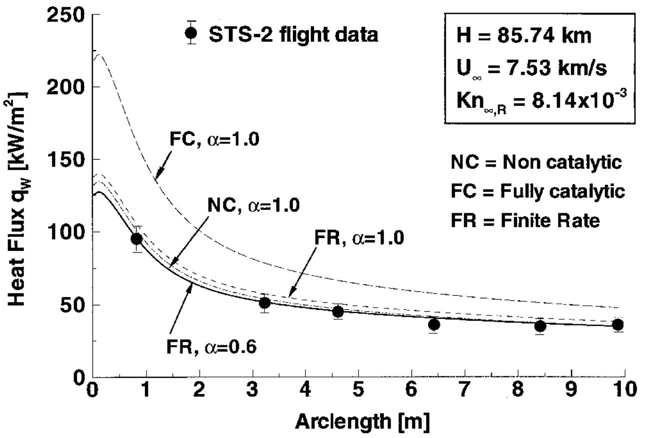

Fig. 10 Heat flux distribution for a Shuttle-equivalent hyperboloid and STS-2 freestream conditions of the trajectory point 85.74 km.

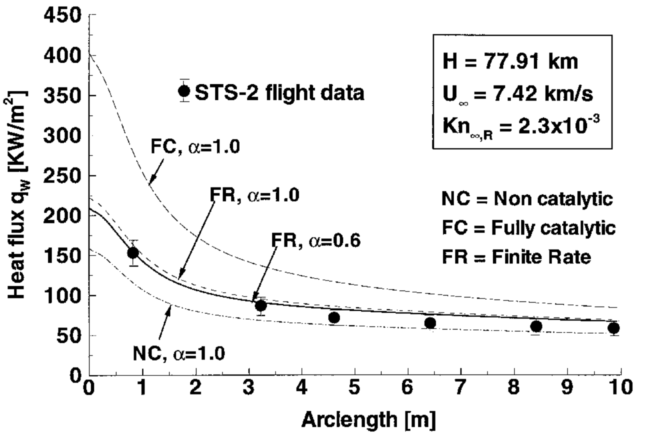

Fig. 11 Heat flux distribution for a Shuttle-equivalent hyperboloid and STS-2 freestream conditions of the trajectory point 77.91 km.

a function of the inverse surface temperature $1/T_W$ for different mole fraction ratios $f = \psi_O/\psi_{O_2}$. Since the translational temperature of the particles impinging on the surface is chosen to be 5000 K and the pressure $p = p_O + p_{O_2}$ is 200 N/m^2, this can be seen as a typical low-density case. Furthermore, the vibrational temperature is assumed to have the same value as the translational temperature ($T_{v,O_2} = T$). One can see that the recombination coefficient defined earlier becomes negative for small ratios f because more atomic oxygen is formed in dissociative adsorption reactions than vanishes in recombination reactions. This means that in low-density flows the catalytic surface reactions may also have the potential to reduce surface heat fluxes.

For further validation of the model the heat flux distributions around Shuttle-equivalent hyperboloids are calculated with the present model for different STS-2 trajectory points and compared to STS-2 flight data (Figs. 9–12). The calculations are performed with the slip model of Refs. 14 and 15 and for the calculations the particles that leave the surface after scattering processes are assumed to be fully ($\alpha = 1.0$) or partly accommodated ($\alpha = 0.6$) to the surface conditions. Furthermore, a radiation equilibrium surface with a surface emissivity of $\varepsilon = 1.06 \times 0.85 \approx 0.9$ has been used. In Fig. 9 the heat flux distribution along the hyperboloid is displayed for the trajectory point $H = 92.35$ km. Since the Knudsen number for this trajectory point is 0.028, it can be considered as a typical slip flow test case. As one can see the agreement between the cal-

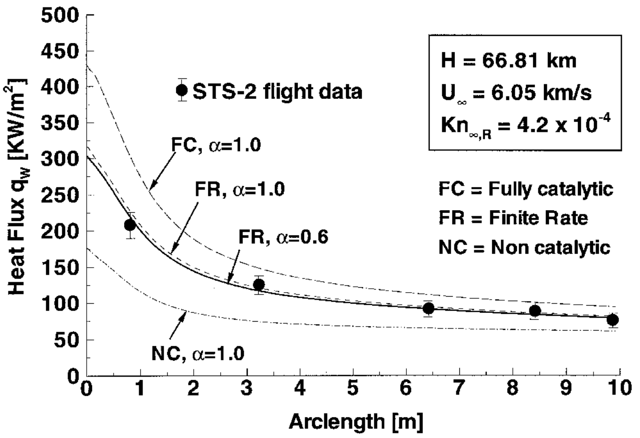

Fig. 12 Heat flux distribution for a Shuttle-equivalent hyperboloid and STS-2 freestream conditions of the trajectory point 66.81 km.

culated and measured heat flux is quite poor. However, in contrast to other catalysis models the presented model gives a heat flux that is almost the same as the heat flux calculated with the noncatalyic boundary condition. Because of the strong influence of $\boldsymbol{\alpha}$ for this test case a possible reason for the discrepancies between the experimental and computational results might be that the accommodation coefficient is smaller than $\alpha = 0.6$. Furthermore, for the trajectory point $H = 92.35$ km it has been found that the modeling of the chemical processes in the gas phase has an important influence on the calculated heat fluxes.

The rate of dissociative adsorption is not high enough to produce a significant decrease of the heat flux in comparison with the noncatalytic case.

The heat flux distributions calculated for the trajectory points $H = 85.74$, 77.91, and 66.81 km are shown in Figs. 10–12, respectively. It becomes apparent that the catalysis model predicts distributions that are in very good agreement with the experimental values. The shift of the catalytic behavior from the noncatalytic case at high altitudes to the fully catalytic case at low altitudes is well described. It is also interesting to see that the influence of α strongly decreases with decreasing Knudsen number.

Conclusions

A detailed catalysis model has been developed that distinguishes adsorption, desorption, and recombination reactions because of the Eley–Rideal and Langmuir–Hinshelwood mechanisms as well as dissociative adsorption reactions. Furthermore, an expression for the estimation of $\boldsymbol{\beta}$ of the Eley–Rideal mechanism has been derived. The model shows a strong dependence of the recombination coefficient on the gas-phase temperature and the chemical composition of the gas phase. This dependency is because of the modeling of the sticking coefficient of the adsorption reaction and the rate coefficient of the dissociative adsorption reaction.

Surface heat flux comparisons have been made between Shuttle flight data and computational results for the model, which show a rather poor agreement in the slip flow regime and a good agreement in the continuum regime. The poor agreement in the slip flow regime is probably a result of the uncertainties in the values of the accommodation coefficients.

Because of the low surface temperatures in the slip flow regime, the dissociative adsorption does not lead to a significant decrease of the calculated heat fluxes.

Acknowledgments

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