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Nonequilibrium Kinetics and Heat Transfer in O_2/O Mixtures near Catalytic Surfaces

E. Kustova* and E. Nagnibeda†
St. Petersburg University, 198904, St. Petersburg, Russia
and
I. Armenise‡ and M. Capitelli§
University of Bari, 70126 Bari, Italy

Nonequilibrium vibrational-chemical kinetics and heat transfer in an O_2/O mixture near the surface of a space vehicle under reentry conditions are studied. Vibration-translation, vibration-vibration energy exchange, dissociation-recombination processes in the gas phase as well as heterogeneous recombination, dissociation, and deactivation of vibrational states on a silica surface are taken into account. The effect of nonequilibrium kinetics and surface catalysis on the total heat flux and averaged dissociation-rate coefficients is examined. It is shown that both heterogeneous recombination and dissociation on the surface must be incorporated in the kinetic scheme. The contribution of thermal conductivity, thermal and mass diffusion, and vibrational energy diffusion to the heat transfer is evaluated. In particular, vibrational energy diffusion near the surface is found to play an important role.

Nomenclature

c_i = mass fraction of molecules at the ith vibrational level
c_O = mass fraction of atoms
c_p = constant pressure specific heat, J · kg^{-1} · K^{-1}
D, $D_{\alpha\beta}$ = diffusion coefficients, m^2 · s^{-1}
D_{T_α} = thermal diffusion coefficients, m^2 · s^{-1}
f^* = stream function
i = vibrational quantum number
k = Boltzmann constant, J · K^{-1}
$k_{\mathrm{diss}}^{(M)}$ = averaged rate coefficient of dissociation by the collision with a partner M, m^3 · s^{-1}
$k_{\mathrm{eq}}^{(M)}$ = thermal equilibrium Arrhenius dissociation-rate coefficient, m^3 · s^{-1}
$k_{i,\mathrm{diss}}^{(M)}$ = state-to-state dissociation-rate coefficient, m^3 · s^{-1}
m = molecular mass, kg
m_O = mass of atoms, kg
n = total number density, m^{-3}
n_i = number density of molecules at the ith vibrational level, m^{-3}
n_O = number density of atoms, m^{-3}
Pr^* = Prandtl number, $Pr^* = \mu c_p / \lambda'$
p = pressure, Pa
$\boldsymbol{q}$ = total heat flux, W · m^{-2}
Sc^* = Schmidt number, $Sc^* = \mu / \rho D$
S_i, S_T = source terms
T = gas temperature, K
$\boldsymbol{V}_i$ = diffusion velocity of molecular species at ith vibrational level, m · s^{-1}
$\boldsymbol{V}_O$ = diffusion velocity of atomic species, m · s^{-1}
v = macroscopic gas velocity, m · s^{-1}
γ_{deact} = heterogeneous deactivation probability
γ_{diss} = heterogeneous dissociation probability
γ_i = probability of heterogeneous recombination to the level i
ε_i = vibrational energy of a molecule, J
$\langle \varepsilon_{\mathrm{rot},i} \rangle$ = averaged rotational energy, J
ε^O = energy of oxygen atom formation, J
η = body-normal coordinate
θ = reduced temperature, $\theta = T/T_e$
λ' = thermal conductivity coefficient, W · m^{-1} · K^{-1}
μ = shear viscosity coefficient, Pa · s
ξ = body-parallel coordinate
ρ = density, kg · m^{-3}

Subscripts

e = parameters at the external edge of boundary layer
O = atomic
O_2 = molecular
w = parameters at the surface

Introduction

THERMAL protection of hypersonic reentry vehicles is a vital problem of modern aerothermochemistry. It requires adequate models of transport properties in extremely nonequilibrium conditions. In particular, heat transfer and diffusion around a body entering a planetary atmosphere should be evaluated taking into account nonequilibrium vibrational-chemical kinetics in the boundary layer and gas-surface interaction.

Many papers are devoted to this problem, and at the present time different models of heat and mass transfer near reentering bodies exist.[1] Such models are most commonly based on phenomenological expressions for the total heat flux and its dependence on the surface catalyticity (see Refs. 2–4). In some papers the transport kinetic theory is used for heat-flux calculations, but these considerations are usually restricted to small deviations from thermal equilibrium.[5] Strong deviations from equilibrium over vibrational degrees of freedom have been studied in Refs. 6 and 7 on the basis of different quasi-stationary vibrational distributions. However, these approaches are not sufficiently rigorous because in boundary layers under reentry conditions the vibrational distributions are far from equilibrium and

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*Associate Professor, Mathematics and Mechanics Department, Bibliotechnaya pl. 2.

†Professor, Mathematics and Mechanics Department, Bibliotechnaya pl. 2.

‡Researcher, Chemistry Department, Centro di Studio per la Chimica dei Plasmi del CNR, Via Orabona 4.

§Professor, Chemistry Department, Centro di Studio per la Chimica dei Plasmi del CNR, Via Orabona 4.

quite different from the quasi-stationary distributions.[8–10] A more accurate kinetic theory model of dissociation-vibration coupling in the boundary layer is proposed in Refs. 11 and 12. Nevertheless, the influence of nonequilibrium kinetics in the gas phase and at the surface on the macroscopic gas flow parameters and heat flux is still not clearly understood.

Recently we have considered this problem in the frame of the kinetic theory of gases in the state-to-state approximation[13,14] This study includes three consequent steps. First, the state-to-state transport kinetic theory has been developed[15] and applied to the boundary-layer problem.[13] Then, in Ref. 13, nonequilibrium state-to-state vibrational distributions obtained in Ref. 8 have been inserted in the transport theory algorithms as input data for the heat-transfer evaluation. The catalytic activity of the surface has also been described in the state-to-state approximation, and probabilities of heterogeneous recombination on the silica surface calculated by means of quantum-classical method[16–18] have been preliminary used for the transport properties computation.[14]

The present paper extends and completes the study started in Ref. 13. We consider the flow of O_2/O mixture with vibration-vibration (VV) and vibration-translation (VT) energy exchange, dissociation and recombination in the boundary layer, and focus the main attention on the dependence of the heat transfer and diffusion on the mechanism of nonequilibrium processes at the surface. Compared to our previous preliminary study,[14] the present paper presents a more realistic model for heterogeneous reactions at a silica surface. First, recombination of oxygen atoms is permitted to proceed through any O_2 vibrational level.[16,17] Also, the processes of O_2 dissociation and deactivation of its vibrational levels at the wall are taken into account. The influence of these features on the transport properties in the O_2/O mixture is estimated.

Further important characteristics of a reacting flow are the averaged chemical reaction-rate coefficients. Under strongly nonequilibrium conditions these quantities depend on the actual vibrational state populations. In the present paper the effect of state-to-state distributions and surface catalyticity on the dissociation-rate coefficients in the boundary layer is also studied.

Transport Properties in the State-to-State Approach

We consider a binary mixture of dissociating O_2 molecules and recombining O atoms and suppose that equilibration of the translational and rotational energies proceed much more rapidly with respect to vibrational relaxation and dissociation-recombination processes. The later processes are assumed to have characteristic times comparable with the residence time of a particle in the boundary layer. The complete set of equations of a nonequilibrium flow follows from the kinetic equations and contains in this case the equations of detailed vibration-chemical kinetics for vibrational level populations of molecular species, number density of atomic species, and conservation equations of the momentum and total energy. These equations and corresponding transport terms are given in Ref. 15. In Ref. 15 it has been shown that in the state-to-state approximation the diffusion velocities of each vibrational state instead of diffusion velocities of molecular chemical species must be introduced. A similar approach has been proposed previously in Ref. 19; however, the diffusion velocities are calculated by using Fick's law instead of rigorous expressions given by the kinetic theory.

In the boundary-layer approximation the state-to-state transport terms can be simplified. Thus, the diffusion velocities of oxygen molecules at different vibrational levels $\boldsymbol{V}_i$ and oxygen atoms $\boldsymbol{V}_O$ and the total heat flux $\boldsymbol{q}$ take the following form[14]:

$$\boldsymbol{V}_i = -(D_{ii} - D_{O_2-O_2})\nabla\left(\frac{n_i}{n}\right) - D_{O_2-O_2}\nabla\left(\frac{n_{O_2}}{n}\right) - D_{O_2-O}\nabla\left(\frac{n_O}{n}\right) - D_{T_{O_2}}\nabla \ln T \tag{1}$$

$$\boldsymbol{V}_O = -D_{O-O}\nabla\left(\frac{n_O}{n}\right) - D_{O_2-O}\nabla\left(\frac{n_{O_2}}{n}\right) - D_{T_O}\nabla \ln T \tag{2}$$

$$\boldsymbol{q} = -\lambda'\nabla T - p\left[D_{T_{O_2}}\nabla\left(\frac{n_{O_2}}{n}\right) + D_{T_O}\nabla\left(\frac{n_O}{n}\right)\right] + \sum_i\left(\frac{5}{2}kT + \langle\varepsilon_{\mathrm{rot},i}\rangle + \varepsilon_i\right)n_i\boldsymbol{V}_i + \left(\frac{5}{2}kT + \varepsilon^O\right)n_O\boldsymbol{V}_O \tag{3}$$

One can see that diffusion velocities and total heat flux depend not only on the gradients of gas temperature but also on the gradients of all level populations and number density of atoms with corresponding diffusion coefficients. The method of the calculation of the transport coefficients in the state-to-state approach is given in Refs. 15 and 20, where after some simplifications they are expressed in terms of n_i, n_O, T, and elastic collision integrals (see Refs. 15 and 20 for the details). All diffusion and heat conductivity coefficients are computed using the nonequilibrium vibrational distributions found in the boundary layer in Ref. 10. The nonequilibrium kinetics in the boundary layer is considered in the next section.

Equations of State-to-State Kinetics in the Boundary Layer

To evaluate state-to-state distributions in the boundary layer around a reentering body, the equations for the vibrational level populations and atomic number density have been coupled with fluid dynamic equations, and some simplifications have been carried out. A stationary flow in the vicinity of the stagnation point has been considered, and boundary-layer equations have been obtained using the Lees–Dorodnitsyn coordinate transformation[21,22]:

$$\xi = \int_0^x \rho_e v_e \,\mathrm{d}x, \qquad \eta = \frac{v_e}{\sqrt{2\xi}}\int_0^y \rho \,\mathrm{d}y \tag{4}$$

Introducing these variables, one can write the boundary-layer equations in the one-dimensional form:

$$c_i'' + f^*Sc^*c_i' = S_i, \qquad i = 0, 1, \ldots, 33 \tag{5}$$

$$\theta'' + f^*Pr^*\theta' = S_T \tag{6}$$

where Eqs. (5) for $i = 0, 1, \ldots, 32$ are the equations for the mass fractions of molecules at the bounded vibrational levels, $i = 33$ corresponds to atomic mass fraction c_O, and Eq. (6) is the energy conservation equation. The derivatives have been done with respect to the surface normal coordinate η.

In Eqs. (5) and (6) the left-hand side describe the diffusive and convection terms. The Schmidt and Prandtl numbers are supposed to be constant: $Sc^* = 0.49$, and $Pr^* = 0.71$. The source terms S_i and S_T describe, respectively, vibrational energy exchanges and dissociation-recombination processes in the gas phase as well as at the surface. Among vibrational energy exchanges only the single-quantum ones have been retained[10]:

$$O_2(i) + O_2(k) \rightleftharpoons O_2(i-1) + O_2(k+1) \tag{7}$$

$$O_2(i) + O_2 \rightleftharpoons O_2(i-1) + O_2 \tag{8}$$

$$O_2(i) + O \rightleftharpoons O_2(i-1) + O \tag{9}$$

$$O_2(i) + \mathrm{wall} \rightarrow O_2(i-1) + \mathrm{wall} \tag{10}$$

Following the ladder-climbing model, the pseudolevel located just above the last bounded level of a molecule has been introduced, and it has been supposed that dissociation and recombination proceed only through this level.[8] Finally, dissociation and recombination reactions in the gas phase are treated as VV and VT energy exchange processes involving the pseudolevel. Recombination and dissociation at the catalytic surface are described by two main mechanisms: the Eley–Rideal mechanism[10,17]

$$O + O^* \rightleftharpoons O_2(i) + \mathrm{wall} \tag{11}$$

and the Langmuir–Hinshelwood one[10,17]

$$O^* + O^* \rightleftharpoons O_2(i) + \text{wall} \tag{12}$$

O^* is an adatom of the surface. Another possible mechanism

$$O_2(i) + \text{wall} \longrightarrow O + O \tag{13}$$

has also been taken into account.

Boundary Conditions

Now we consider the boundary conditions for Eqs. (5) and (6). At the external edge of the boundary layer, the gas temperature is fixed as a parameter T_e, and the level populations are supposed to follow the thermal equilibrium Boltzmann distribution with the gas temperature T_e. On the surface the gas temperature is also fixed at $T = T_w$. Regarding the mass fractions of vibrational species and atoms, three different models are investigated.

The first model assumes that the surface is totally noncatalytic. This model is referred hereafter as nCnDnD (no catalyticity, no dissociation, no deactivation). In this case the derivatives of both vibrational level populations and atom mass fractions, with respect to the coordinate η normal to the surface, are equal to zero:

$$\left.\frac{\partial c_i}{\partial \eta}\right|_w = 0, \qquad i = 0, 1, \ldots, 33 \tag{14}$$

Then, a partially catalytic silica surface has been considered; the processes of heterogeneous recombination and dissociation [Eqs. (11–13)] as well as oxygen molecules deactivation [Eq. (10)] have been taken into account. This model is subsequently called CDD (catalyticity + dissociation + deactivation). In this case, the conditions for c_i and c_O at the wall read[10]

$$\left.\frac{\partial c_i}{\partial \eta}\right|_w = -\frac{\gamma_i}{D}\sqrt{\frac{kT}{2\pi m}}c_O + \gamma_{\text{diss}}c_i - \gamma_{\text{deact}}c_i + \gamma_{\text{deact}}c_{i+1}$$

$$i = 0, 1, \ldots, 32 \tag{15}$$

$$\left.\frac{\partial c_O}{\partial \eta}\right|_w = \frac{\Sigma_i \gamma_i}{D}\sqrt{\frac{kT}{2\pi m}}c_O - \sum_i \gamma_{\text{diss}}c_i \tag{16}$$

where recombination coefficient γ_i represents the ratio of the flux of atoms recombining on the surface to the flux of atoms impinging the surface; the diffusion coefficient D is assumed to be independent of the vibrational level number, and the values of the diffusion coefficients are taken from Refs. 23 and 24. We would like to note that in the right-hand sides of Eqs. (15) and (16) the first term is from recombination at the surface, the second one is due to heterogeneous dissociation, and the third and fourth ones in Eq. (15) are caused by deactivation at the wall.

Finally, the model taking into account only heterogeneous recombination [direct reactions Eqs. (11–13)] has been studied, and this model is named as CnDnD (catalyticity, no dissociation, no deactivation).

For a silica surface the probability of oxygen recombination to each vibrational level has been calculated by Armenise et al.[10] and Cacciatore et al.[16,17] by means of quantum-classical molecular dynamics approach. The dissociation probability γ_{diss} as well as the deactivation one γ_{deact} have been estimated in Ref. 10. The procedure proposed in Ref. 10 can give some overestimation of the dissociation probability at the same time underestimating the deactivating probability.

The rate coefficients of the gas phase reactions [Eqs. (7–9)] are the same as the ones used in Ref. 9. In the last paper the results of accurate quantum-classical calculations of rate coefficients performed in Refs. 25 and 26 have been interpolated in a wide temperature range, and simple analytical formulas for the rate coefficients have been proposed.

Results

Equations (5) and (6) for c_i, c_O, T with boundary conditions in Eqs. (14–16) have been solved numerically using a finite difference method described in details in Refs. 8 and 10. A uniform grid is used to divide the coordinate η normal to the surface into 80 steps. The derivatives in the system are approximated with central differences. The nonlinear system is solved in an iterative way: in each step i of a generic iteration, the unknowns are calculated taking into account their values both in the cell $(i-1)$, calculated in the preceding step of the same iteration, and in $(i+1)$ calculated in the preceding iteration. The code has been validated using different grids and varying the limit values of $\eta = 4$, 8, 16. It has been shown[8,10] that the numerical method itself is sufficiently precise. However, the accuracy of the results depends significantly on the state dependent rate coefficients of considered processes [Eqs. (7–13)] and the surface recombination coefficients. The sensitivity of the vibrational distributions and macroscopic flow parameters to the input data is discussed in Refs. 9 and 10.

Finally the variables c_i, c_O, T as well as their gradients have been found along the coordinate η. Then, this solution has been inserted into the kinetic transport theory algorithm[15,20] to compute the diffusion and heat conductivity coefficients and the total heat-flux. The heat-flux sensitivity to the catalytic properties of the surface has been studied, and some interesting effects have been observed.

In the present section we discuss the nonequilibrium vibrational distributions, gas temperature, and then heat fluxes and dissociation-rate coefficients calculated using the three surface catalyticity models already discussed: CDD, CnDnD, and nCnDnD. The conditions at the high temperature edge of the boundary layer are $T_e = 7000$ K, $p_e = 1000$ Pa, while the wall temperature is $T_w = 1000$ K.

First, let us consider the reduced O_2 level populations n_i/n vs vibrational quantum number i for different values of coordinate η ($\eta = 0$ at the surface, $\eta = 8$ at the external edge of a boundary layer). Figures 1a–1c present n_i/n for three cases: Fig. 1a gives the results for the CDD model (catalytic wall with dissociation and deactivation); Fig. 1b corresponds to CnDnD model (catalytic wall neglecting dissociation and deactivation); Fig. 1c displays the results obtained by means of nCnDnD model (completely noncatalytic wall). These figures show the evolution of vibrational distributions across the boundary layer starting from the extremely nonequilibrium distribution in the vicinity of the wall toward the thermal equilibrium imposed at the external edge. The results for the noncatalytic wall (Fig. 1c) look similar to those reported for a five-species mixture[9] (N_2, N, O_2, O, NO). The vibrational distributions present long declining plateaux as a result of the recombination process in the gas phase. Near the surface (curves 1–2) the plateau is quite stable. However, the concentration of molecules is very small in all of the points of the boundary layer. Distributions change dramatically when recombination at the surface is taken into account (Fig. 1b). This reaction leads to a significant increase of O_2 concentration close to the surface and thus to much higher populations than in the preceding case. The vibrational distribution at the surface is not completely smooth because of the form of the used state-to-state rate coefficients of the recombination catalytic process.[10] In the case of the complete CDD model (Fig. 1a), heterogeneous dissociation diminishes noticeably the concentration of molecules and therefore level populations near the wall compared to the CnDnD model. The distinction between vibrational distributions at the surface in cases a) and b) is mainly caused by dissociation; the influence of deactivation on the distribution is shown to be weak.[10] For the CDD model the nonsmooth distribution at $\eta = 0$ is very pronounced; this behavior is caused by the nonmonotonous character of recombination probabilities[10] and, perhaps, some overestimation of the dissociation-rate coefficient.

Figures 2a and 2b present the gas temperature T and molecular oxygen molar fraction n_{O_2}/n across the boundary layer for all three models considered. As expected, in the case of complete kinetics (CDD model) the temperature close to the surface is higher than in the remaining cases because recombination and deactivation processes raise the gas temperature as the surface is approached. The concentration of molecules under the noncatalytic boundary

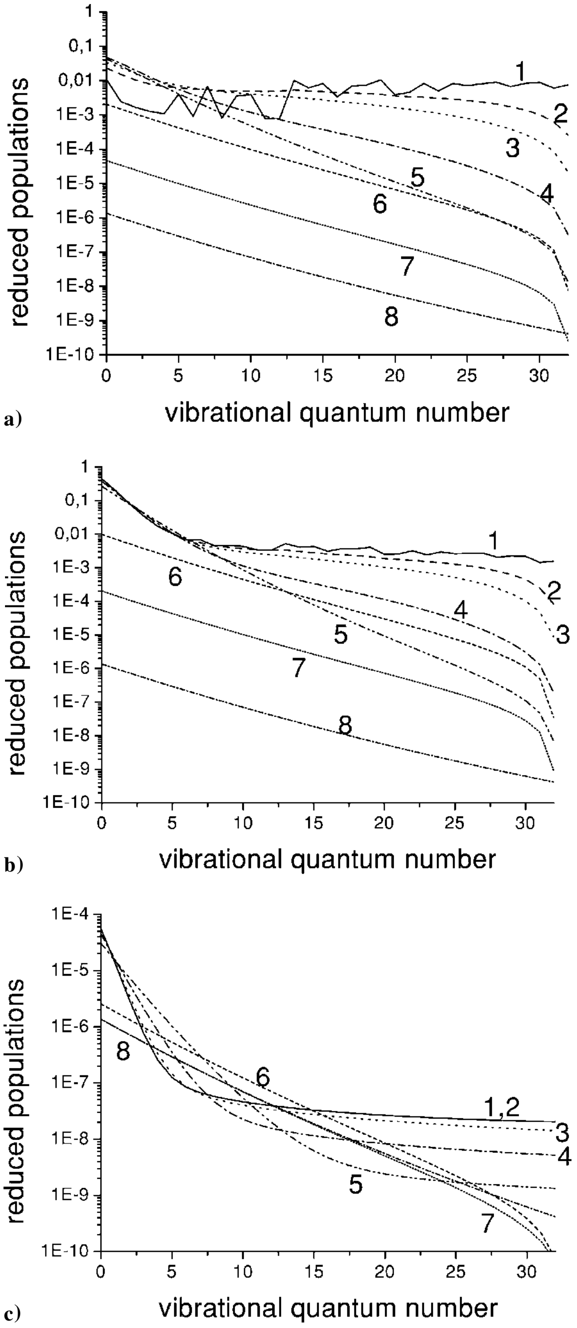
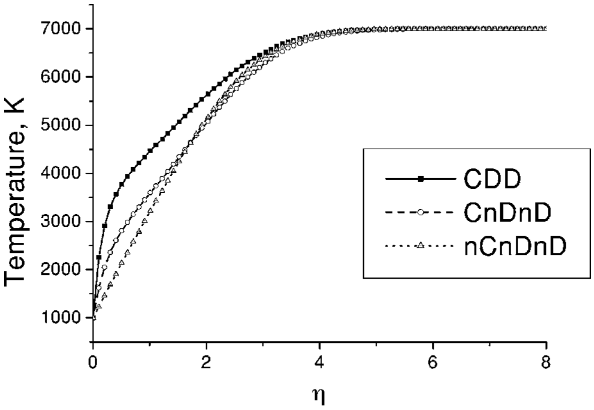
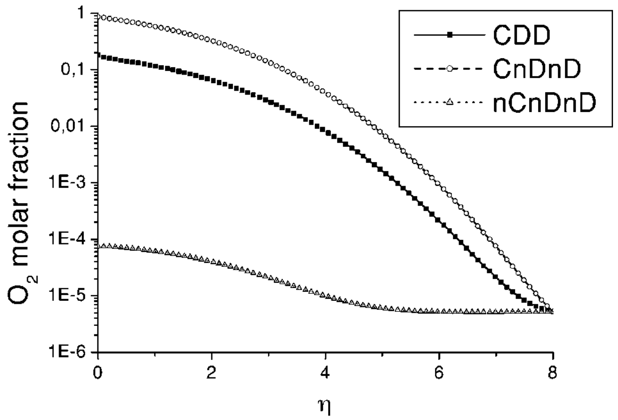


Fig. 1 Reduced level populations n_i/n as functions of i at different η: a) –CDD; b) –CnDnD; c) –nCnDnD. Curves 1: $\eta = 0$; 2: $\eta = 0.1$; 3: $\eta = 0.2$; 4: $\eta = 0.5$; 5: $\eta = 1$; 6: $\eta = 4$; 7: $\eta = 6$; 8: $\eta = 8$.

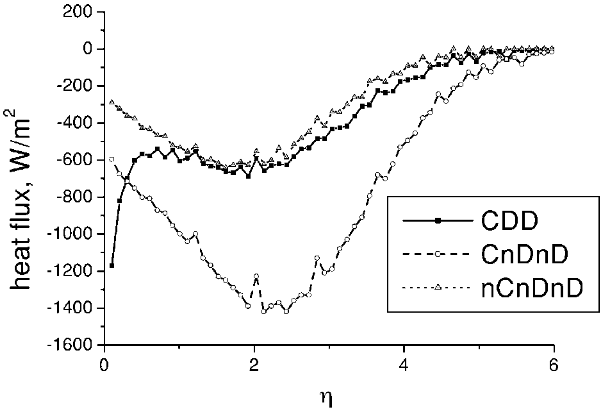


a) Gas temperature

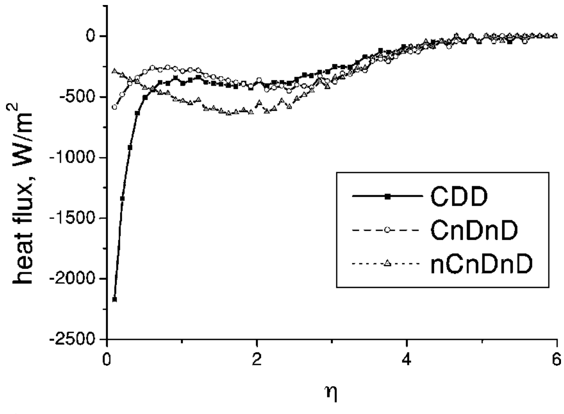


b) O_2 molar fraction

Fig. 2 Functions of η.



a) Total heat flux



b) Fourier flux

Fig. 3 Functions of η.

conditions is very low and increases quite weakly toward the wall as a result of the gas phase recombination. Comparison of curves CDD and CnDnD shows a competition of heterogeneous dissociation and recombination: neglecting dissociation at the surface leads to an overestimation of O_2 concentration. Let us emphasize that the gradients of chemical species concentrations computed by means of CnDnD model are much higher compared to other models; this fact is responsible for overstating the contribution of diffusion processes to the heat flux in this case.

Figures 3a and 3b depict the total heat flux (Fig. 3a) and Fourier flux caused by thermal conductivity $q_F = -\lambda' \nabla T$ (Fig. 3b) calculated using the current three surface interaction models. It is seen that near the surface the CDD model gives a qualitatively different behavior of the heat flux compared to the other two models. For the CDD model the absolute value of q at the surface is much greater, then it decreases rapidly with η, and for $\eta > 1$ the solutions obtained with the CDD and nCnDnD models become close to each other. Comparison of the total fluxes obtained with the CDD scheme and neglecting dissociation and deactivation (CnDnD) shows an essential discrepancy practically in the whole range of η. These peculiarities can be explained after examination of the contribution of various processes to the heat flux. First, let us consider the Fourier flux (Fig. 3b). A noticeable difference between the Fourier fluxes obtained using the CDD and CnDnD models manifests itself only close to the surface; at $\eta > 1.5$ the two fluxes are nearly the same. Such a behavior near the wall is governed by the temperature gradients: the CDD models give the highest temperature gradient at $\eta < 1$. A significant distinction between the total fluxes given by the CDD and CnDnD models shows the important role of heterogeneous dissociation and deactivation in the case of a partially catalytic surface. Recombination at the surface augments considerably the concentration of molecules, and this effect must be compensated by the corresponding reverse process. Taking into account only recombination at the wall and neglecting dissociation at the same time leads to an inadequate description of the heat flux. Thus, a strong discrepancy between the total heat fluxes for CDD and CnDnD models (see Fig. 3a) is dictated mainly by the different character of the O_2 and O concentration gradients (in the CnDnD case the gradients are too high). Concerning the case of a completely noncatalytic surface (nCnDnD), the heat flux is determined only by thermal conductivity; the values of q and q_F coincide within 1%, which means that if one neglects recombination, dissociation, and deactivation at the wall, then in some cases it is sufficient to use the Fourier law for the heat-flux evaluation. Nevertheless, one should be careful using such an approximation: in Ref. 13 it is shown that for a N_2/N mixture the contribution of diffusion processes can reach 60–65% even if the surface is absolutely noncatalytic. Finally, one can conclude that although the nCnDnD model gives a good agreement with the CDD scheme at $\eta > 1$ it is better to use the CDD model and the expression in Eq. (3) instead of the Fourier law (especially near the wall) in order to get satisfactory accuracy.

The next figures (Figs. 4a and 4b) represent the contribution of various transport processes to the total energy transfer. Among the diffusion processes one can distinguish thermal diffusion, mass diffusion of chemical species, and diffusion of vibrational energy by excited molecules. In Fig. 4a the CDD model is considered, and in Fig. 4b CnDnD models are considered. The corresponding plot for the nCnDnD model is not reported because from the preceding discussion it is clear that in this case the contribution of diffusion to the heat flux is negligible. Figure 4 shows that for both the CDD and CnDnD models the heat flux is scarcely affected by thermal diffusion (its maximum contribution does not exceed 6% in the vicinity of the surface and then decreases to 3%). For the CDD model (Fig. 4a) the influence of mass diffusion of atoms is also small, and the main role in the heat transfer belongs to heat conductivity and diffusion of vibrational energy. Near the wall a competition of these two processes is observed. In the case of CnDnD model, the contribution of heat conductivity, mass diffusion, and diffusion of vibrational energy is of the same order of magnitude. A similar tendency has been found in Ref. 14 where the partially catalytic surface without dissociation has been considered for different conditions.

The subsequent discussion is devoted to the rate coefficients of dissociation in the gas phase. In many essentially nonequilibrium flows a non-Arrhenius temperature dependence of averaged dissociation-rate coefficients has been discovered.[9,27,28] The present investigation confirms this statement. The global-rate coefficients can be expressed in terms of the state-to-state coefficients[28]

$$k_{\text{diss}}^{(M)} = \frac{1}{n_{O_2}} \sum_i n_i k_{i,\text{diss}}^{(M)} \tag{17}$$

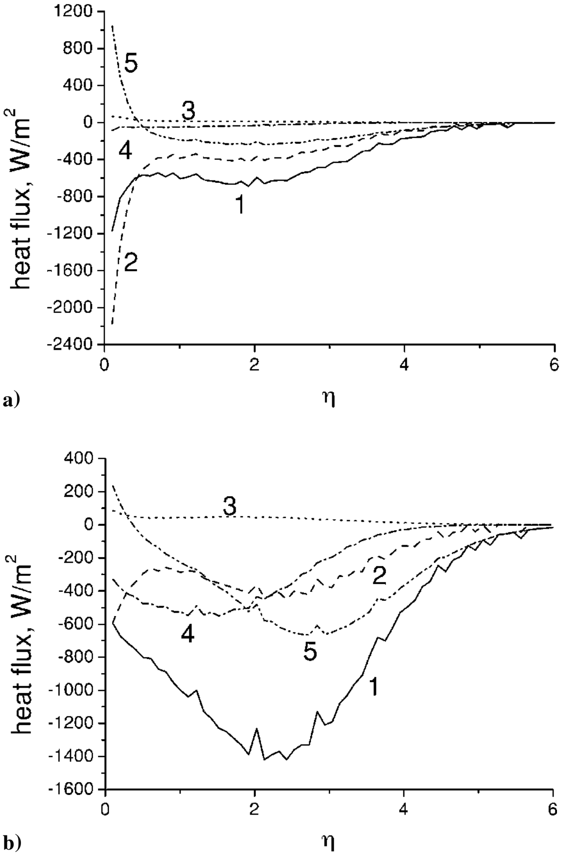


Fig. 4 Contribution of various processes to the heat flux: a) CDD and b) CnDnD models. Curves 1: total heat flux; 2: Fourier flux; 3: flux caused by thermal diffusion; 4: flux caused by mass diffusion of atoms; 5: flux caused by diffusion of vibrational energy.

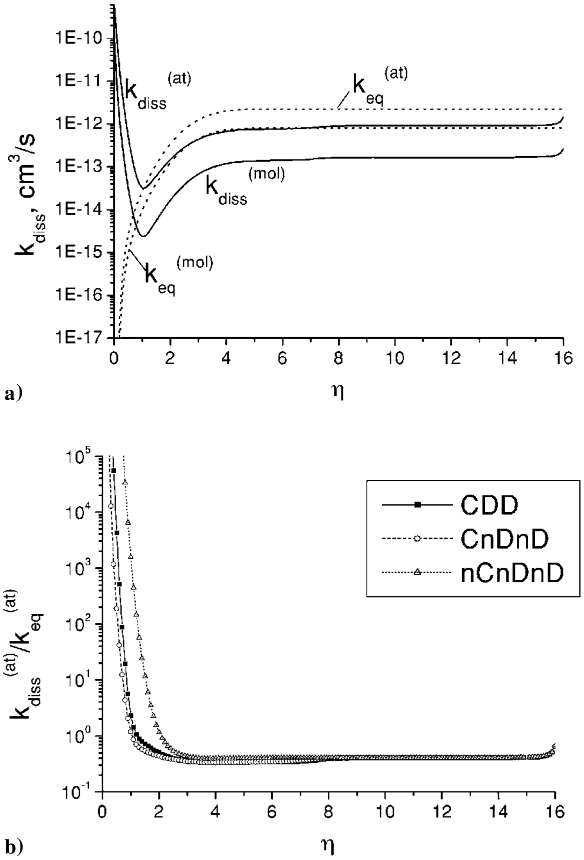


Fig. 5 Averaged dissociation-rate coefficients $k_{\text{diss}}^{(M)}$ (cm^3/s) and corresponding Arrhenius coefficients for a) CDD model and b) ratio $k_{\text{diss}}^{(\text{at})}/k_{\text{eq}}^{(\text{at})}$ for three models as functions of η.

For the ladder-climbing model, as dissociation proceeds only through the last bounded level L, this definition is reduced to the following one:

$$k_{\text{diss}}^{(M)} = (n_L/n_{O_2})k_{L,\text{diss}}^{(M)} \tag{18}$$

Coefficient $k_{L,\text{diss}}^{(M)}$ is determined by the rate coefficients of VV and VT vibrational energy exchanges.

Figure 5a plots the averaged rate coefficients $k_{\text{diss}}^{(\text{mol})}$ and $k_{\text{diss}}^{(\text{at})}$ for dissociation through the collisions with molecules and atoms, respectively, across the boundary layer (CDD model). The corresponding thermal equilibrium Arrhenius-rate coefficients $k_{\text{eq}}^{(\text{mol})}$ and $k_{\text{eq}}^{(\text{at})}$ are also presented. One can see a quite different behavior of the rate coefficients calculated using the state-to-state distributions compared to the Arrhenius ones, close to the surface the curves have an opposite tendency. Figure 5b displays the ratio $k_{\text{diss}}^{(\text{at})}/k_{\text{eq}}^{(\text{at})}$ computed for the three models already discussed. It can be noticed that taking into account heterogeneous recombination dissociation and deactivation produces a decrease of the ratio $k_{\text{diss}}^{(\text{at})}/k_{\text{eq}}^{(\text{at})}$ in the gas phase.

The limit value $\eta = 8$ is sufficient for the calculation of the main macroscopic parameters: gas temperature, density, species concentrations, and heat flux. The exception is for the dissociation-rate coefficients. These quantities do not converge to the equilibrium values at $\eta = 8$, and for the correct prediction of $k_{\text{diss}}^{(M)}$ a greater limit value $\eta = 16$ has been chosen. It is connected with peculiarities of the ladder-climbing model: in this case the dissociation-rate coefficients are determined mainly by the population of the last vibrational states, and those states are strongly disturbed by dissociation. In the present calculation the populations of the highest 2–3 vibrational levels do not reach their equilibrium values at $\eta = 8$, and therefore coefficients $k_{\text{diss}}^{(M)}$ behave similarly. One can expect that using another dissociation model, for instance, the Treanor–Marrone one, will provide a better convergence and a good accuracy of the solution at $\eta = 8$.

Conclusions

Nonequilibrium vibrational-chemical kinetics and transport properties in the O_2/O mixture flow in the boundary layer adjacent to a catalytic silica surface have been investigated by using the detailed state-to-state approach. Three different models of the catalytic activity have been examined: 1) a partially catalytic surface model, which accounts for heterogeneous recombination, dissociation, and deactivation of excited vibrational states; 2) a model that takes into account only heterogeneous recombination and neglects reverse dissociation process and deactivation at the wall; and finally, 3) a totally noncatalytic model.

The state-to-state vibrational distributions as well as the gas temperature and chemical species concentrations have been computed across boundary layers in the vicinity of a stagnation point. The influence of surface catalyticity models on the vibrational distributions and other macroscopic parameters has been estimated. In all cases essentially nonequilibrium distributions have been found for the conditions investigated. For the case of a noncatalytic surface, the concentration of molecules near the wall as well as its change across the boundary layer are shown to be low. For the catalytic surface neglecting dissociation at the wall leads to excessively high variation of species concentrations and their gradients across the flow. Taking into account all heterogeneous processes provides a fast rise of the gas temperature just near the wall compared to the other two models.

Then the calculated macroscopic parameters and vibrational distributions have been used as input data for evaluation of the total heat flux, which in the state-to-state approach depends on the gradients of all level populations, atomic number density, and gas temperature. The role of surface catalysis and the contribution of various processes to the heat transfer have been estimated. In particular, it is shown that using the noncatalytic boundary conditions gives an underestimation of the heat flux near the surface; in this case the heat transfer is determined mainly by thermal conduction; neglecting dissociation at the surface leads to a big discrepancy between the calculated heat fluxes practically in the whole region considered. The contribution of vibrational energy diffusion to the heat transfer is particularly important when the complete kinetic scheme at the surface is applied. The role of thermal diffusion in the heat flux is quite weak in all cases examined. In conclusion, it can be pointed out that the self-consistent CDD model taking into account heterogeneous recombination, dissociation, and deactivation should be used in order to get adequate values of the total heat flux.

Finally, the nonequilibrium rate coefficient of dissociation in the gas phase across the boundary layer has been calculated, and its temperature dependence is found to be essentially non-Arrhenius for all models of surface catalyticity.

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