JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 9, No. 2, April–June 1995

Theory and Validation of the Physically Consistent Coupled Vibration-Chemistry-Vibration Model

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A consistent thermochemical relaxation model is presented that has been derived on the basis of $T_{\mathrm{vib},i}$-Boltzmann populated vibrational energy modes and truncated harmonic oscillators. A persistent application of these two assumptions to all types of chemical reactions with molecular reactants leads to the coupled vibration-chemistry-vibration model (CVCV model), which specifies multiple temperature rate constants and vibrational energies transferred due to chemical reactions in a consistent way. The simple analytic expressions obtained for both rate constants and transferred vibrational energies enable to account for thermal nonequilibrium not only in dissociation, but also in exchange and associative ionization reactions. The model assumptions as well as the introduced model parameters are evaluated by comparisons with a state-selective model calculation and an experimental result.

Introduction

AS a consequence of the rapid energy transformation across the bow shock in front of a hypersonic vehicle, the flow is out of thermodynamic equilibrium. Rotational, vibrational, and electronic DOF become excited and chemical reactions commence. In airflows, chemistry is mainly characterized by impact dissociation (D) $AB + C \rightleftharpoons A + B + C$, exchange ($E$) $AB + C \rightleftharpoons AC + B$, associative ionization (AI) $A + B \rightleftharpoons AB^+ + e^-$, and electron impact ionization (EI) $A + e^- \rightleftharpoons A^+ + 2e^-$ reactions.[1] Since internal energies contribute to overcome the activation threshold, their distribution functions affect chemical rates. In order to determine the population of the internal energy states it would be most physical to regard particles in a particular internal quantum state as particles of a particular chemical species and inelastic collisions as chemical reactions. However, establishing a conservation equation for each state-selected species (master equation) results in prohibitively large and costly solution algorithms. For that reason, such detailed models are not suited for hypersonic design calculations and simplifications have to be sought that nevertheless adequately allow for the effects of excited internal DOF on chemistry and vice versa.

In order to drastically reduce the problem it is common practice to assume that electronic DOF are excited in the ground state dominantly (i.e., all of the collisional processes occur on a single potential energy surface), and that rotational modes are quickly equilibrated with translational modes.[2] On the other hand, at conditions where these approximations hold, vibrational equilibration needs many more collisions and can occur with time scales of the same order of magnitude as dissociation and ionization reactions. Since these phenomena influence each other, a coupled consideration of chemistry and vibrational excitation is imperative in order to predict relaxation processes accurately.

Following these understandings, in the present study we confine ourselves to investigate the interdependence of chemistry and vibrational excitation. Starting from kinetic theory we discuss our recently developed coupled vibration-chemistry-vibration (CVCV) model,[3,4] which couples vibration-chemistry-vibration effects in a physically consistent way. Then, the model assumptions are reviewed by comparisons with a state-selective model calculation and an experimental result obtained in a high-enthalpy shock tunnel.

Fundamental Relationships

Extending previous work[5-7] we examine the influence of vibrational excitation not only on D, but also on E reactions. With regard to vibrational and chemical relaxation processes of nitric oxide this is indispensable since the presence of NO is governed by this type of reaction. Considered are the following reactions:

$$AB(v) + C \rightleftharpoons AC(w) + B \tag{1}$$

$$AB + C \rightleftharpoons AC + B \tag{2}$$

where the former, state-selected reaction (1) is part of the overall reaction (2) and describes the decomposition of a molecule AB excited in the particular vth vibrational quantum state and the production of a molecule AC excited in the wth vibrational state and vice versa. In both reactions (1) and (2) a vibrationally excited, rotationless molecule collides with a nonvibrating particle in order to overcome the activation threshold and, consequently, to react. The customary rate equation formulation

$$-\frac{\partial c_{\mathrm{AB}}}{\partial t} = \underbrace{c_{\mathrm{AB}} c_{\mathrm{C}} k_f}_{\dot{\omega}_{\mathrm{va,AB}}} - \underbrace{c_{\mathrm{AC}} c_{\mathrm{B}} k_b}_{\dot{\omega}_{\mathrm{app,AB}}} \tag{3}$$

defines the time rate of change of AB molecules by means of the bulk rate constants k_f and k_b. Since we count all particles in moles, the variable c_i represents the concentration of species X_i in mole/m^3. The quantities $\dot{\omega}_{\mathrm{va,AB}}$ and $\dot{\omega}_{\mathrm{app,AB}}$ mark the molar decomposition and production rates, respectively. The question to be answered is, how vibrational excitation influences the reaction process.

Vibration-Chemistry Coupling

Summing up the rates of all collisional processes that destroy (index out) as well as form (index in) a vibrationally

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excited AB molecule leads to the time rate of change of concentration c_{AB} in the form:

$$-\frac{\partial c_{\mathrm{AB}}}{\partial t} = \underbrace{c_{\mathrm{C}} \sum_{v=0}^{v_{\max}} c_{\mathrm{AB}}(v) \sum_{w=0}^{w_{\max}} k(v, w)}_{(\partial c_{\mathrm{AB}}/\partial t)_{\mathrm{out}}} \underbrace{- c_{\mathrm{B}} \sum_{w=0}^{w_{\max}} c_{\mathrm{AC}}(w) \sum_{v=0}^{v_{\max}} k(w, v)}_{(\partial c_{\mathrm{AB}}/\partial t)_{\mathrm{in}}} \tag{4}$$

Notice that formulation (4) proceeds on the assumption that reactions can occur from and up to each vibrational level. The rate constant $k(v, w)$ specifies the reaction in which a v-state excited AB molecule decomposes, and an AC molecule excited in the wth state is formed. The reverse rate constant $k(w, v)$ is linked with $k(v, w)$ by the principle of detailed balance according to

$$k(w, v)c_{\mathrm{AC}}^{E}(w)c_{\mathrm{B}}^{E} = k(v, w)c_{\mathrm{AB}}^{E}(v)c_{\mathrm{C}}^{E} \tag{5}$$

with the superscript E denoting equilibrium. If one introduces the population distribution function of the discrete vibrational states v of a molecule X_i

$$f_i(v) \equiv c_i(v)/c_i \tag{6}$$

Eq. (4) can be rearranged to

$$-\frac{\partial c_{\mathrm{AB}}}{\partial t} = \underbrace{c_{\mathrm{AB}}c_{\mathrm{C}} \sum_{v=0}^{v_{\max}} f_{\mathrm{AB}}(v)k(v, d)}_{(\partial c_{\mathrm{AB}}/\partial t)_{\mathrm{out}}} \underbrace{- c_{\mathrm{AC}}c_{\mathrm{B}} \sum_{w=0}^{w_{\max}} f_{\mathrm{AC}}(w)k(w, d)}_{(\partial c_{\mathrm{AB}}/\partial t)_{\mathrm{in}}} \tag{7}$$

Herein, the totalized rate constants involving the dummy variable d

$$k(v, d) = \sum_{w=0}^{w_{\max}} k(v, w) \qquad k(w, d) = \sum_{v=0}^{v_{\max}} k(w, v) \tag{8}$$

summarize all rates of a state-selected molecule that form the product molecule. A comparison of Eq. (7) with Eq. (3) relates the bulk rate constants k_f and k_b to kinetic theory. For the determination of these quantities, however, the distribution functions $f_{\mathrm{AB}}(v)$ and $f_{\mathrm{AC}}(w)$, or rather their dependence on c_{AB}, c_{C}, c_{AC}, and c_{B} have to be known.

If the molecule AB is dissociated by the impact of particle C [reaction type (D)] the incoming rate of Eq. (4) changes to[6,7]

$$\underbrace{c_{\mathrm{A}}c_{\mathrm{B}}c_{\mathrm{C}} \sum_{v=0}^{v_{\max}} k(d, v)}_{(\partial c_{\mathrm{AB}}/\partial t)_{\mathrm{in}}} \tag{9}$$

whereas the outgoing rate remains formally unchanged. Thus, the dissociated state A + B + C can be included in our consideration as a threshold of a single state with $f_{\mathrm{A+C}} = 1$. This means that all expressions derived later will be transferable to dissociation reactions if one substitutes $f_{\mathrm{AC}} \rightarrow f_{\mathrm{A+C}} = 1$ and takes into account c_{A} and c_{C}. Since, however, the state-selected rate constants $k(v, d)$ of an exchange reaction differ from those of a dissociation reaction, different bulk rate constant expressions for the diverse types of reactions are expected.

Chemistry-Vibration Coupling

When an AB(v) molecule decomposes by an impact of another particle C, the total vibrational energy content of species AB is diminished by an amount that is equal to the vibrational energy content of this particular state. In our molar counting system this corresponds to $\varepsilon_{\mathrm{vib,AB}}(v)$ in J/mole. On the other side, the reverse formation process increases the vibrational energy by $\varepsilon_{\mathrm{vib,AB}}(v)$. Hence, the vibrational energy loss rate of AB is given by

$$c_{\mathrm{C}} \sum_{v=0}^{v_{\max}} c_{\mathrm{AB}}(v)\varepsilon_{\mathrm{vib,AB}}(v) \sum_{w=0}^{w_{\max}} k(v, w) - c_{\mathrm{B}} \sum_{v=0}^{v_{\max}} \varepsilon_{\mathrm{vib,AB}}(v) \sum_{w=0}^{w_{\max}} c_{\mathrm{AC}}(w)k(w, v) \tag{10}$$

Rearranging expression (10) leads to

$$c_{\mathrm{AB}}c_{\mathrm{C}}k_f \sum_{v=0}^{v_{\max}} \frac{k(v, d)}{k_f} f_{\mathrm{AB}}(v)\varepsilon_{\mathrm{vib,AB}}(v) - c_{\mathrm{AC}}c_{\mathrm{B}}k_b \sum_{v=0}^{v_{\max}} \varepsilon_{\mathrm{vib,AB}}(v) \sum_{w=0}^{w_{\max}} \frac{k(w, v)}{k_b} f_{\mathrm{AC}}(w) \tag{11}$$

With the abbreviations introduced in Eq. (3) for the production and decomposition rates, $\dot{\omega}_{\mathrm{app,AB}}$ and $\dot{\omega}_{\mathrm{va,AB}}$, as well as the further definitions

$$G_{\mathrm{va,AB}} \equiv \sum_{v=0}^{v_{\max}} \frac{k(v, d)}{k_f} f_{\mathrm{AB}}(v)\varepsilon_{\mathrm{vib,AB}}(v) \tag{12}$$

$$G_{\mathrm{app,AB}} \equiv \sum_{v=0}^{v_{\max}} \varepsilon_{\mathrm{vib,AB}}(v) \sum_{w=0}^{w_{\max}} \frac{k(w, v)}{k_b} f_{\mathrm{AC}}(w) \tag{13}$$

the vibrational energy gain rate of a molecule X_i due to chemical reactions j as part of a complex reaction scheme ($j = 1, \ldots, m$) is derived to[5,8]

$$Q_{C-V,i} = \sum_{j=1}^{m} (\dot{\omega}_{\mathrm{app},ij}G_{\mathrm{app},ij} - \dot{\omega}_{\mathrm{va},ij}G_{\mathrm{va},ij}) \tag{14}$$

The quantities $G_{\mathrm{va},ij}$ and $G_{\mathrm{app},ij}$ denote the vanishing and appearing vibrational energies, which are on average lost or gained by a molecule X_i being destroyed or created in a chemical reaction j. The application of the principle of detailed balance determines $G_{\mathrm{app},i}$ as a function of $k(v, w)$: introducing the distribution function (6) into the detailed balance relation (5) yields:

$$k(w, v) = k(v, w)[f_{\mathrm{AB}}^{E}(v)/f_{\mathrm{AC}}^{E}(w)](1/K_e) \tag{15}$$

wherein $K_e = (c_{\mathrm{AC}}^{E}c_{\mathrm{B}}^{E})/(c_{\mathrm{AB}}^{E}c_{\mathrm{C}}^{E})$ denotes the equilibrium constant. On the other hand, K_e is fixed by the ratio k_f^E/k_b^E following from Eq. (3) at equilibrium conditions. Both inserted into definition (13) give

$$G_{\mathrm{app,AB}} = \frac{k_b^E}{k_b} \sum_{w=0}^{w_{\max}} \frac{f_{\mathrm{AC}}(w)}{f_{\mathrm{AC}}^{E}(w)} \sum_{v=0}^{v_{\max}} \frac{k(v, w)}{k_f^E} f_{\mathrm{AB}}^{E}(v)\varepsilon_{\mathrm{vib,AB}}(v) \tag{16}$$

Of course, vanishing and appearing vibrational energies coincide at equilibrium ($G_{\mathrm{va,AB}}^{E} = G_{\mathrm{app,AB}}^{E}$).

Vibration-Chemistry-Vibration Coupling

As has been outlined, vibrational level population determines chemical rate constants, which, in turn, affect the vibrational energy gain rate due to chemical processes $Q_{C-V,i}$. Since this rate again implies redistribution of vibrational states, both phenomena define the vibration-chemistry-vibration coupling. If the distribution function $f_i(v)$ and the state specific energies $\varepsilon_{\text{vib},i}(v)$ are known, the bulk rate constants k_f and k_b, as well as the transferred energies $G_{\text{va},i}$ and $G_{\text{app},i}$ still depend on the vibrational state-specific rate constants $k(v, w)$. Thus, as a simple fact from chemical kinetics, energy values and rate constants are coupled and must not be modeled independently of each other.

Basic Physical Assumptions

Vibrational Distribution Function

At equilibrium the population distribution function of vibrational energy states is known as a Boltzmann distribution determined by the translational/rotational temperature T

$$f_i^E(v, T) = \frac{c_i^E(v)}{c_i^E} = \frac{\exp[-\varepsilon_{\text{vib},i}(v)/\Re T]}{Q_{\text{vib},i}(T)} \tag{17}$$

with $Q_{\text{vib},i}(T)$ being the vibrational partition function and $\Re$ denoting the universal gas constant. At thermal and chemical nonequilibrium, however, the population deviates from this distribution. In the sixties the master equations have been solved taking into account translational-vibrational (T-V) and vibrational-vibrational (V-V) energy exchange mechanisms. Assuming harmonic oscillators and near adiabatic vibrational transition probabilities the quasi-steady-state (QSS) analysis of Treanor et al.[9] shows that in the absence of chemical reactions vibrational relaxation proceeds via a continuous series of Boltzmann distributions:

$$f_i(v, T_{\text{vib},i}) = \frac{c_i(v)}{c_i} = \frac{\exp[-\varepsilon_{\text{vib},i}(v)/\Re T_{\text{vib},i}]}{Q_{\text{vib},i}(T_{\text{vib},i})} \tag{18}$$

which are characterized by a pseudotemperature $T_{\text{vib},i}$. The temperature $T_{\text{vib},i}$ is called vibrational temperature and deviates from the translational/rotational temperature T at thermal nonequilibrium.

From shock-tube experiments it is well-known that just behind the shock wave chemical reactions are delayed until T-V energy exchange mechanisms have led to advanced excitation. Following Treanors QSS analysis, the $T_{\text{vib},i}$-Boltzmann distribution is a good approximation for the determination of the nonequilibrium rate constants during this T-V energy exchange-dominated period. Note that these are the quantities that have to produce the experimentally observed chemical incubation time.

The reader is reminded that the derivation of the currently most widely employed model for calculating the overall rate of energy exchange between translational and vibrational modes[10-12]

$$Q_{T-V,i} = c_i \left\{\frac{\varepsilon_{\text{vib},i}^E(T) - \varepsilon_{\text{vib},i}}{\langle\tau_i\rangle}\right\} \tag{19}$$

is also based on the foregoing assumptions and also neglects physical features like anharmonicity, nonadiabatic transitions, and multiquantum jumps.[13] In conclusion, expression (18) reflects the consistent population distribution when chemical processes are absent and the Landau–Teller formulation (19) is used to describe vibrational relaxation. The quantity

$$\varepsilon_{\text{vib},i} \equiv \sum_{v=0}^{v_{\max}} f_i(v)\varepsilon_{\text{vib},i}(v) \tag{20}$$

represents the average vibrational energy content of the molecule X_i in J/mole, whereas $\varepsilon_{\text{vib},i}^E(T)$ denotes the average vibrational energy content at local equilibrium. The variable $\langle\tau_i\rangle$ marks the T-V relaxation time.

Keck and Carrier solved the master equations for coupled vibration-dissociation-recombination processes also using the QSS approximation.[14] Lee concluded in consequence of their results that the low vibrational states nearly relax through a series of $T_{\text{vib},i}$-Boltzmann distributions.[11] Recently, Landrum and Candler[15] integrated the master equations in time and confirmed this behavior. Park,[6] as well as Sharma et al.,[16] pointed out that k_f and k_b can be expressed uniquely as functions of T and $T_{\text{vib},i}$, even if the thermodynamic state of the gas changes so rapidly that in particular the low vibrational states do not satisfy the quasi-steady-state condition. In Ref. 6 Park proposes a bimodal distribution model: for low levels a T_{vib}-Boltzmann distribution, for high levels a QSS assumption holds. The border between both regimes is marked by v_{bor}.

Nonequilibrium Rate Constants

With all this knowledge we regard the limiting case $v_{\text{bor}} \rightarrow v_{\max}$. This corresponds to the assumption that all vibrational states of a molecular species X_i are populated according to a Boltzmann distribution characterized by a vibrational temperature $T_{\text{vib},i}$ (assumption $A1$). Then, comparison of Eqs. (3) and (7) yields the bulk rate constants to

$$k_f(T, T_{\text{vib,AB}}) \overset{A1}{=} \sum_{v=0}^{v_{\max}} f_{\text{AB}}(v, T_{\text{vib,AB}})k(v, d) \tag{21}$$

$$k_b(T, T_{\text{vib,AC}}) \overset{A1}{=} \sum_{w=0}^{w_{\max}} f_{\text{AC}}(w, T_{\text{vib,AC}})k(w, d) \tag{22}$$

One realizes that the vanishing and appearing rates of Eq. (3), $\dot{\omega}_{\text{va,AB}}$ and $\dot{\omega}_{\text{app,AB}}$, coincide with the outgoing and incoming rates of Eq. (7). This is not the case when a QSS distribution is supposed.[6]

Relation (21) has already been applied by Park,[1] Jaffe,[2] Treanor and Marrone,[5,8] Olynick and Hassan,[7] Landrum and Candler,[15] and Macheret and Rich,[17] to allow for the effects of thermal nonequilibrium on dissociation reaction rates. We also prefer this formulation to the deviating expressions based on QSS[6,14] or mixed Boltzmann/QSS[6,16] distributions because it yields analytic expressions for rate constants and transferred vibrational energies being easily applicable to computational fluid dynamics (CFD). Up to now no analytic rate constant formulation has been derived with an underlying QSS distribution function.

In order to account for the vibrational effects on reaction rate constants, we follow the proposal of Treanor and Marrone[5,8] and introduce the nonequilibrium factor Ψ according to

$$\Psi \equiv \frac{k}{k^E(T)} \overset{A1}{=} \frac{\sum_{v=0}^{v_{\max}} f_i(v, T_{\text{vib},i})k(v, d)}{\sum_{v=0}^{v_{\max}} f_i^E(v, T)k(v, d)} \tag{23}$$

as a measure of the deviation from thermal equilibrium. The quantity $k^E(T)$ stands for the traditional Arrhenius description

$$k^E(T) = CT^s \exp[-(A/\Re T)] \tag{24}$$

with A being the molar activation energy and C, s representing the Arrhenius coefficients. Consequently, forward and backward rate constants are correlated by

$$\frac{k_f}{k_b} = \frac{\Psi_f k_f^E}{\Psi_b k_b^E} = \frac{\Psi_f}{\Psi_b} K_c(T) \tag{25}$$

From Eq. (23) one sees that the ratio k_f/k_b is a function of both T and $T_{\mathrm{vib},i}$. This non-quasi-steady-state dependence resembles the expression $k_f/k_b = K_e(T^q_{\mathrm{vib}}T^{1-q})$ proposed by Park,[6] but differs from the QSS relation $k_f/k_b = K_e(T)$ of Keck and Carrier.[14]

Oscillator Model

Considering a harmonic oscillator model (assumption $A2$) with its uniform spacing of vibrational states, Eq. (18) together with definition (20) leads to an analytic equation of state of the form[3]:

$$\varepsilon_{\mathrm{vib},i}(T_{\mathrm{vib},i}) \overset{A1,A2}{=} \frac{\mathcal{R}\Theta_{\mathrm{vib},i}}{\exp(\Theta_{\mathrm{vib},i}/T_{\mathrm{vib},i}) - 1} - \frac{D_i}{\exp(D_i/\mathcal{R}T_{\mathrm{vib},i}) - 1} \tag{26}$$

wherein $\Theta_{\mathrm{vib},i}$ represents the characteristic vibrational temperature. This expression has been derived for an oscillator that is truncated at a vibrational state $v_{\max}$ located one level below the dissociation energy D_i of the molecule X_i. For an infinite or simple harmonic oscillator ($v_{\max} \to \infty$, $D_i \to \infty$), the second term of Eq. (26) vanishes. As has been illustrated in Ref. 18, the harmonic oscillator model is well-justified up to $T_{\mathrm{vib},i} = 15{,}000$ K so that anharmonic effects can be expected to be small for re-entry flight conditions. With regard to CFD applications, however, an analytic equation of state is more favorable than a summation formula being left by an anharmonic oscillator model.

The necessity of a consistent thermochemical relaxation modeling can now easily be demonstrated. Provided that both assumptions $A1$ ($T_{\mathrm{vib},i}$-Boltzmann distributions) and $A2$ (harmonic oscillators) are strictly maintained, the derivative of the natural logarithm of the rate constant (21) with respect to $1/T_{\mathrm{vib},i}$ yields[3,4]:

$$-\frac{\partial \ln k_f(T, T_{\mathrm{vib},i})}{\partial(1/T_{\mathrm{vib},i})} \overset{A1,A2}{=} \frac{G_{\mathrm{va},i}}{\mathcal{R}} - \frac{\varepsilon_{\mathrm{vib},i}}{\mathcal{R}} \tag{27}$$

This means that k_f and $G_{\mathrm{va},i}$ are coupled by a simple analytic interrelation. However, many multiple temperature models introduced in the literature do not take into account the foregoing interdependence, although they employ the equation of state (26) and thus suppose $A1$ and $A2$. Expressions like

$$G_{\mathrm{va},i} = G_{\mathrm{app},i} = \gamma_1 \varepsilon_{\mathrm{vib},i} \qquad \gamma_1 \geq 1 \tag{28}$$

$$G_{\mathrm{va},i} = G_{\mathrm{app},i} = \gamma_2 D_i \qquad 0 < \gamma_2 < 1 \tag{29}$$

for the vibrational energies transferred due to chemical reactions with γ_1 and γ_2 being constants are inconsistent with rate constant formulations and accordingly unfit to provide satisfactory results.[4,19] Moreover, they involve an additional model parameter to be adjusted.

Governing Equations

Due to the assumption that the population distribution function is determined by a single relaxation parameter $T_{\mathrm{vib},i}$, the formulation of a global vibrational energy equation

$$\frac{\partial E_{\mathrm{vib},i}}{\partial t} + \nabla(E_{\mathrm{vib},i}\boldsymbol{v}) = -\nabla \boldsymbol{q}_{\mathrm{vib},i} - \nabla(E_{\mathrm{vib},i}\boldsymbol{V}_i) + Q_{T-V,i} + Q_{e-V,i} + Q_{V-V,i} + Q_{C-V,i} \tag{30}$$

for each molecular species X_i is sufficient[10,20] to account for vibrational nonequilibrium. In this equation the conserved quantity is the vibrational energy per unit volume $E_{\mathrm{vib},i} = c_i\varepsilon_{\mathrm{vib},i}$. The first two terms on the right side denote the vibrational energy transport caused by heat conduction within vibrational modes as well as mass diffusion.[11] The source terms Q stand for the energy exchange mechanisms between translational-vibrational, electron-vibrational, vibrational-vibrational, and chemical-vibrational modes, respectively.

Summarizing, we emphasize that any nonequilibrium relaxation model that solves global vibrational energy equations of the form (30) and determines vibrational temperatures by means of the equation of state (26) implicitly assumes $A1$, Boltzmann populated vibrational energy states determined by vibrational temperatures $T_{\mathrm{vib},i}$ and $A2$, harmonic oscillators.

It is the purpose of the subsequent sections to validate a multiple temperature model that is based on these two assumptions and to point out the importance of a physically consistent source term $Q_{C-V,i}$ for any thermochemical relaxation process.

CVCV Model

Recently, we have developed a new thermochemical relaxation model[3,4] by picking up the concepts of Treanor and Marrone[5,8] and extending their dissociation CVDV modeling to exchange and associative ionization reactions. In accordance with other scientists[21,22] we think that their approach seems to be the most physical multiple temperature formulation. A persistent application of the assumptions $A1$ and $A2$ to all types of chemical reactions with molecular reactants has resulted in the CVCV model that couples vibration-chemistry-vibration consistently.

As outlined before, the basis of any modeling is the formulation of the vibrational state specific rate constants $k(v, d)$. We set[3,4]

$$k(v, d) = \Lambda k^E \exp[(\varepsilon_{\mathrm{vib},i}(v)/\mathcal{R})(1/T + 1/U_i)] \qquad \varepsilon_{\mathrm{vib},i}(v) \leq \alpha A \tag{31}$$

$$k(v, d) = \Lambda k^E \exp\{\varepsilon_{\mathrm{vib},i}(v)/\mathcal{R}U_i + \alpha A/\mathcal{R}T\} \qquad \varepsilon_{\mathrm{vib},i}(v) > \alpha A \tag{32}$$

where Λ stands for

$$\Lambda = \frac{\exp(-\alpha A/\mathcal{R}T)Q^{D_i}_{\mathrm{vib},i}(T)}{\exp(-\alpha A/\mathcal{R}T)Q^{\alpha A}_{\mathrm{vib},i}(-U_i) + Q^{D_i}_{\mathrm{vib},i}(T^\star_i) - Q^{\alpha A}_{\mathrm{vib},i}(T^\star_i)} \tag{33}$$

with D_i and A notifying the dissociation energy of the molecule X_i and the activation energy of the reaction, respectively. The quantity

$$Q^{\Upsilon}_{\mathrm{vib},i}(T) \overset{A2}{=} \frac{1 - \exp(-\Upsilon/\mathcal{R}T)}{1 - \exp(-\Theta_{\mathrm{vib},i}/T)} \tag{34}$$

denotes the vibrational partition function of a harmonic oscillator cut off one quantum state below the energy Υ. In accordance with the CVDV modeling of Treanor and Marrone, the variable U_i (with dimension of a temperature) is taken to be a measure of the extent to which the upper vibrational levels are more reactive due to a cross section enlargement at higher excitation. $U_i = \infty$ corresponds to an equal probability assumption or so-called nonpreferential reaction modeling.

The additionally introduced parameter α limits the maximum vibrational energy contribution for overcoming the activation threshold to αA ($0 < \alpha < 1$), and consequently requires a minimum energy contribution, namely $(1 - \alpha)A$, from the translational motion of the particles. This is important for the modeling of exchange reaction rate constants since there are many molecules that store much more vibrational energy than the needed activation energy $A < D_i$. As has been illustrated in Ref. 3, the parameter α implies that chemical reactions remain dependent on translational motion, and hence on T, especially in the case when $T_{\mathrm{vib},i} >> T$.

Inserting expressions (31) and (32) into Eq. (21) and summing up over the limited number of energy levels of a truncated harmonic oscillator (assumption $A2$) by means of a $T_{\mathrm{vib},i}$-Boltzmann distribution (18) (assumption $A1$), leads to a nonequilibrium factor Ψ of the form[3]

$$\Psi(T, T_{\mathrm{vib},i}) = \frac{k(T, T_{\mathrm{vib},i})}{k^E(T)} \overset{A1,A2}{=} \frac{Q^{D_i}_{\mathrm{vib},i}(T)}{Q^{D_i}_{\mathrm{vib},i}(T_{\mathrm{vib},i})} \times \frac{\exp(-\alpha A/\mathscr{R}T)Q^{\alpha A}_{\mathrm{vib},i}(\Gamma_i) + Q^{D_i}_{\mathrm{vib},i}(T^0_i) - Q^{\alpha A}_{\mathrm{vib},i}(T^0_i)}{\exp(-\alpha A/\mathscr{R}T)Q^{\alpha A}_{\mathrm{vib},i}(-U_i) + Q^{D_i}_{\mathrm{vib},i}(T^\star_i) - Q^{\alpha A}_{\mathrm{vib},i}(T^\star_i)} \tag{35}$$

(It is obvious that Ψ as well as $G_{\mathrm{va},i}$ are derived for a single reaction that is characterized by its involved molecular species X_i and its activation energy A. To distinguish these values for many reactions as part of a reaction scheme, an index j is appended.) The pseudotemperatures Γ_i, T^0_i, and $T^\star_i$ are defined by

$$\frac{1}{\Gamma_i} = \frac{1}{T_{\mathrm{vib},i}} - \frac{1}{T} - \frac{1}{U_i} \tag{36}$$

$$\frac{1}{T^0_i} = \frac{1}{T_{\mathrm{vib},i}} - \frac{1}{U_i} \qquad \frac{1}{T^\star_i} = \frac{1}{T} - \frac{1}{U_i} \tag{37}$$

It is emphasized that expression (35) is applicable to all types of chemical reactions with molecular participation: dissociation reactions are characterized by an activation threshold A_j, forward exchange reactions by $A_j < D_i$, and reverse reactions by $A_j \approx 0$. The resulting special expressions for Ψ_j are summarized in Ref. 3. For dissociation reactions ($A_j = D_i$) our formulation (35) coincides with the CVDV-model relationship when α is selected to be unity. Note, however, that the CVDV model has been derived for dissociation reactions only. Thus, the application of CVDV-model expressions to exchange and associative ionization reactions is deficient. Since the activation energies and, consequently, the state-selected rate constants of dissociation and exchange reactions differ considerably from each other, also the corresponding nonequilibrium factors must be different.

Next, inserting the $k(v, d)$ formulations (31) and (32) into Eq. (12) yields the average vibrational energy removal in a decomposition of molecule X_i according to

$$G_{\mathrm{va},i} \overset{A1,A2}{=} \frac{\exp(-\alpha A/\mathscr{R}T)Q^{\alpha A}_{\mathrm{vib},i}(\Gamma_i)L^{\alpha A}_i(\Gamma_i) + Q^{D_i}_{\mathrm{vib},i}(T^0_i)L^{D_i}_i(T^0_i) - Q^{\alpha A}_{\mathrm{vib},i}(T^0_i)L^{\alpha A}_i(T^0_i)}{\exp(-\alpha A/\mathscr{R}T)Q^{\alpha A}_{\mathrm{vib},i}(\Gamma_i) + Q^{D_i}_{\mathrm{vib},i}(T^0_i) - Q^{\alpha A}_{\mathrm{vib},i}(T^0_i)} \tag{38}$$

where the shorthand notation $L^{\Upsilon}_i(T)$ marks the molar vibrational energy content

$$L^{\Upsilon}_i(T) \overset{A1,A2}{=} \frac{\mathscr{R}\Theta_{\mathrm{vib},i}}{\exp(\Theta_{\mathrm{vib},i}/T) - 1} - \frac{\Upsilon}{\exp(\Upsilon/\mathscr{R}T) - 1} \tag{39}$$

of a harmonic oscillator truncated one quantum state below the energy Υ. The reader is reminded that $G_{\mathrm{va},i}(T, T_{\mathrm{vib},i})$ according to Eq. (38) has been derived consistently with the rate constant $k(T, T_{\mathrm{vib},i}) = \Psi(T, T_{\mathrm{vib},i})k^E(T)$, and thus, both expressions fulfill condition (27). Moreover, this is the first time that an analytic expression has been derived that specifies the vibrational energy removal also in exchange reactions.

In order to derive an expression for the average vibrational energy gain $G_{\mathrm{app},i}$, at the formation of a molecule X_i, we refer to relation (16). For dissociation reactions D we apply our formal limit consideration $f_{\mathrm{AC}} \to f_{\mathrm{A+C}} = 1$ discussed previously, and obtain from relation (23) $\Psi_b = k_b/k^E_b \overset{(D)}{=} 1$ and therewith from Eq. (16)

$$G_{\mathrm{app},i} \overset{A1,(D)}{\equiv} \sum_{v=0}^{v_{\max}} \frac{k(v, d)}{k^E_f} f^E_i(v, T)\varepsilon_{\mathrm{vib},i}(v) \tag{40}$$

It is evident that this expression coincides with the relation (12) for $G_{\mathrm{va},i}$ at equilibrium, i.e.,

$$G_{\mathrm{app},i} \overset{A1,(D)}{\equiv} \lim_{T_{\mathrm{vib},i} \to T} G_{\mathrm{va},i}(T, T_{\mathrm{vib},i}) = G^E_{\mathrm{va},i}(T) \tag{41}$$

The limit $T_{\mathrm{vib},i} \to T$ of Eq. (38) entails the exchange of Γ_i against $-U_i$ and T^0_i against $T^\star_i$. Thus, $G_{\mathrm{app},i}$ still depends on the translational temperature. For exchange reactions E we approximate the detailed rate constants $k(v, w)$ as a fraction of the totalized rate constant $k(v, d)$ according to

$$k(v, w) = F(w)k(v, d) \tag{42}$$

This assumption states that the probability of producing a particular w-state excited product molecule does not depend on the vibrational state of the disintegrating molecule. For future considerations also an approach $F(v, w)$, which depends on both v and w, would be conceivable. Inserting relation (42) into Eq. (16) leads to

$$G_{\mathrm{app},i} \overset{A1,(E)}{\equiv} \frac{G^E_{\mathrm{va},i}(T)}{\Psi_b} \sum_{w=0}^{w_{\max}} \frac{f_s(w, T_{\mathrm{vib},s})}{f^E_s(w, T)} F(w) \tag{43}$$

wherein, the index s denotes the molecular reactant of the reverse reaction. One realizes that formulation (42) leads to a decoupling of v and w modes in Eq. (16). Certainly, the detailed balance relationship (15) is also affected by our approach (42), and a summation over all energy states v provides

$$F(w) = f^E_s(w, T)[k(w, d)/k^E_b] \tag{44}$$

If one substitutes this probability function $F(w)$ into Eq. (43), one obtains with regard to the expressions (22) and (23)

$$G_{\mathrm{app},i} \overset{A1,(E)}{\equiv} G^E_{\mathrm{va},i}(T) \tag{45}$$

In conclusion, both Eqs. (41) and (45) refer the average vibrational energy gain at the formation of a molecule to the average vibrational energy removal at local equilibrium. Notice, only for dissociation reactions ($A = D_i$) and the choice $\alpha = 1$, our $G_{\mathrm{app},i}$ expression reduces to $G_{\mathrm{app},i} = L^{D_i}_i(-U_i)$, which is the T-independent proposal of Treanor and Marrone.[8] For a more detailed description of the CVCV model, the reader should consult the original literature.[3-5,8]

Validation of the CVCV Model

Calibration of the CVCV-Model Parameters

Up to now, no recommendation has been made for the CVCV-model parameters α and U_i. The reader is reminded that if α and U_i are prescribed, the rate constants k_f and k_b, as well as the transferred vibrational energies $G_{\mathrm{va},i}$ and $G_{\mathrm{app},i}$ are uniquely determined. In order to estimate these parameters roughly, we compared[4] the CVCV-model approach for the vibrational state-specific rate constants $k(v, d)$ [Eqs. (31) and (32)] with the approach used in the detailed state-selective modeling of Warnatz and Riedel.[23,24] They relate their state-specific rate constants to the dissociation model of Johnston and Birks,[25] which assumes a linear cross section enlargement with increasing excitation. In Ref. 4 we have illustrated that our CVCV-model formulation of $k(v, d)$ agrees fairly well with Warnatz's and Riedel's approach if the model parameters are adjusted to $U_i = D_i/(5\mathscr{R})$ and $\alpha = 0.8$ uniformly for all types of chemical reactions. Let this be a first assessment of the CVCV-model parameters, which of course has to be confirmed by subsequent validation calculations.

Evaluation of the Boltzmann Assumption $A1$

Solving the large number of conservation equations of a state-selective modeling, deviations from the Boltzmann distribution can be computed. Thus, such solutions are suited to evaluate the shortcomings of multiple temperature models based on the Boltzmann assumption $A1$. Notice that the CVCV model describes the coupling of vibration-chemistry-vibration by means of the Boltzmann-averaged quantities Ψ, $G_{\mathrm{va},i}$ and $G_{\mathrm{app},i}$, whereas the detailed model merely uses the state-specific rate constants. In this section a comparison of CVCV-model calculations with state-selective model results shall contribute to sustain the Boltzmann assumption.

We examine Riedel's state-selective model results,[26] which have been obtained for a spatially homogeneous reaction system. The initial conditions $T_0 = 22000$ K, $p_0 = 0.0256$ bar, and $T_{\mathrm{vib},i_0} = 205$ K of the considered isochore adiabatic relaxation process correspond to a postshock condition of a reentry flight with 6.73 km/s speed at an altitude of 71 km. Due to the immense implementation and calculation effort, Riedel applied only a simplified species (N, O, N_2, O_2, NO) model[23,24]:

1) Solely N_2 and O_2 molecules being differently vibrationally excited are treated as different chemical species.

2) Because of statement 1, only their translation-vibration energy transfer is modeled.

3) NO molecules are assumed to be thermally equilibrated.

4) Vibration-vibration energy transfer is neglected.

5) Rotational states are considered to be equilibrated with translation.

Nevertheless, this state-selective modeling ends up in an immense reaction scheme being composed of 502 reactions with 87 different species.

Since the CVCV model is not bound to any specific reaction scheme, we take into account the same 17 overall reactions for the subsequent CVCV-model calculation. N_2 and O_2 molecules are regarded to be in thermal nonequilibrium, NO molecules are considered to be equilibrated ($T_{\mathrm{vib,NO}} = T$). The model parameters are selected to be $U_i = D_i/(5\mathfrak{R})$ and $\alpha = 0.8$, as assessed previously. Translational-vibrational energy exchange is calculated by relation (19) with the relaxation time[27]

$$\langle\tau_i\rangle = \left[\left(\sum_{r=1}^{10} c_r\right) \Bigg/ \left(\sum_{r=1}^{10} \frac{c_r}{\tau_{ir}^{\mathrm{MW}}}\right)\right] + \frac{1}{cN_A\sigma_{\mathrm{vib},i}\bar{v}_i} \tag{46}$$

being determined by the averaged interspecies relaxation times τ_{ir}^{MW} of Millikan and White extended by a correction factor introduced by Park.[28] Finally, for this special calculation we set the source term $Q_{V-V,i}$ in the vibrational energy Eqs. (30) equal to zero, in order to neglect vibration-vibration energy exchange mechanisms as Riedel did.

Figure 1 compares the temperature profiles of both models vs time. Good agreement is obtained for the relaxation of heavy particle temperature T. The vibrational temperatures of N_2 and O_2 calculated by the CVCV model illustrate the strong thermal nonequilibrium character of the process. The distinctly suppressed T_{vib,O_2} profile is a consequence of the strong affect of large vibrational energy removal due to chemical reactions on vibrational excitation. The inelastic cross sections $\sigma_{\mathrm{vib},i}$ determining the T-V relaxation times $\langle\tau_i\rangle$ at high temperatures have been calibrated to be $\sigma_{\mathrm{vib},N_2} = 1.5 \times 10^{-20}$ m^2 and $\sigma_{\mathrm{vib},O_2} = 4.5 \times 10^{-20}$ m^2.

Inserting the vibrational temperatures into the Boltzmann distribution function (18) yields the mole fractions $\psi_i(v)$ of selected vibrational levels v according to

$$\psi_i(v) = \frac{c_i(v)}{c} = \frac{c_i(v)}{c_i}\frac{c_i}{c} \overset{A1}{=} f_i(v, T_{\mathrm{vib},i})\psi_i \tag{47}$$

Figure 2 presents the population of differently vibrationally excited N_2 molecules for the relaxation process considered.

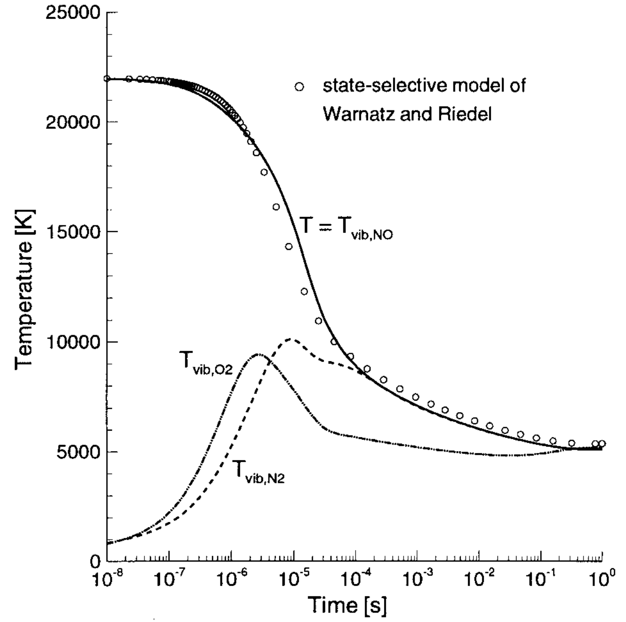

Fig. 1 Heavy particle temperature T and vibrational temperatures T_{vib,N_2}, T_{vib,O_2}, and $T_{\mathrm{vib,NO}}$ of an isochore, adiabatic relaxation process in air characterized by the initial conditions $T_0 = 22{,}000$ K, $p_0 = 0.0256$ bar, and $T_{\mathrm{vib},i_0} = 205$ K.

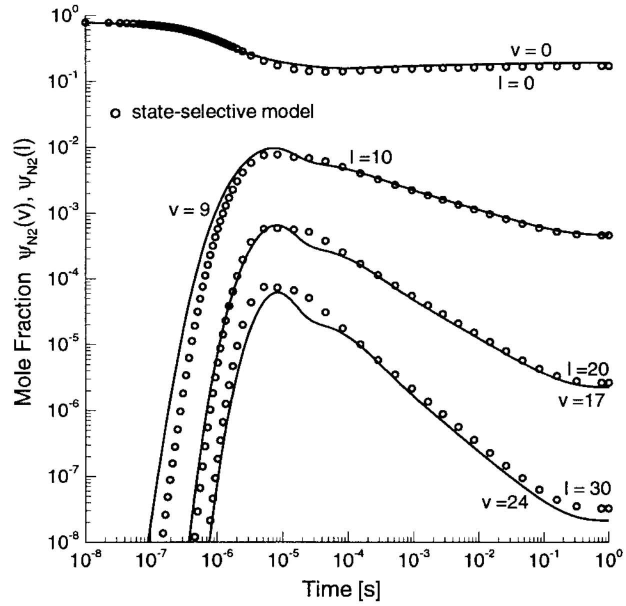

Fig. 2 Population of selected N_2 vibrational energy levels calculated by the state-selective model suggested by Warnatz[23] and Riedel[24] and by the multiple temperature CVCV model.

Mark-points denote the state-selected concentrations obtained as direct solution of the governing equations.[26] Since Riedel applies an anharmonic oscillator (levels l) in contrast to our truncated harmonic oscillator model, the states compared have identical energy content $\varepsilon_{\mathrm{vib},N_2}(l) = \varepsilon_{\mathrm{vib},N_2}(v)$, where $l \neq v$. This plot as well as the O_2 population profiles (not included here) impressively justify the multiple temperature model assumption of quasi-Boltzmann-populated vibrational quantum states. Deviations from the Boltzmann distribution are hardly observable and do not influence the relaxation behavior. The crucial quantities for getting the state-selected mole fractions $\psi_i(v)$, $\psi_i(l)$ in such good agreement are as follows:

1) The inelastic cross sections $\sigma_{\mathrm{vib},i}$ at the beginning of the relaxation process (T-V exchange prevails).

2) The separated vibrational temperatures T_{vib,N_2} and T_{vib,O_2}; a common average vibrational temperature is not sufficient to compute the state-selected concentration profiles as accurate as shown in Fig. 2.

3) The consistent energy terms $G_{\text{va},i}$ and $G_{\text{app},i}$ that prevent an overshoot of vibrational temperatures over the heavy particle temperature T.

In conclusion, the foregoing consideration sustains the multiple temperature CVCV modeling of rate constants $k(T, T_{\text{vib},i})$ and source terms $Q_{C-V,i}$ as well as assists the assessed model parameters $U_i = D_i/(5\mathfrak{R})$ and $\alpha = 0.8$.

In the next section we want to compare CVCV-model calculations with experimental data obtained in a high-enthalpy shock tunnel.[29] For that purpose we have implemented our relaxation model into the fully coupled, 11 species, 5 temperature Navier–Stokes code, upwind relaxation algorithm for nonequilibrium flows of the University of Stuttgart[20] (URANUS).

Calculation of a Shock-Tunnel Experiment

A copper sphere with 0.1 m in diameter has been investigated experimentally in the high-enthalphy shock tunnel of the RWTH Aachen[29] with the goal to provide pressure and heat flux measurements. The freestream conditions are specified by a Mach number of 12.7, a density of 1.6×10^{-3} kg/m^3, and a temperature of 196 K. The gas composition is given by the mole fractions $\psi_{N_2} = 0.789$, $\psi_{O_2} = 0.164$, $\psi_{NO} = 0.038$, and $\psi_O = 0.009$. Atomic nitrogen is negligible.

Figure 3 illustrates the calculated stagnation line distributions of the translational and vibrational temperatures. The reaction scheme and Arrhenius coefficients of Ref. 1 have been used and the CVCV-model parameters have been maintained to be $U_i = D_i/(5\mathfrak{R})$ and $\alpha = 0.8$. Approximating the experimental conditions at the sphere, a fully catalytic surface has been assumed and the wall temperatures have been prescribed to be in equilibrium at 300 K. To account for vibration-vibration energy exchange we set[3,27]

$$Q_{V-V,i} = b \sum_{r \neq i}^{\text{mol}} P_{ri}\sigma_{ir} \frac{c_i c_r}{\sqrt{\mu_{ir}}} \left(\frac{\varepsilon^E_{\text{vib},i}}{\varepsilon^E_{\text{vib},r}} \varepsilon_{\text{vib},r} - \varepsilon_{\text{vib},i} \right) \qquad (48)$$

with $b = N_A\sqrt{8\mathfrak{R}T/\pi}$ and an assessed exchange probability of $P_{ri} = 0.01$. As can be seen, the flow is characterized by strong thermal nonequilibrium. Just behind the shock, vibrational energy modes become excited by dominant T-V energy exchange. At advanced excitation mainly O_2 dissociation commences (see Fig. 4) and vibrational energy removal keeps the vibrational temperature T_{vib,O_2} from overshooting the heavy particle temperature T. The electron temperature T_e calculated by a separate electron energy conservation equation[20] coincides with T_{vib,N_2}, since the coupling of N_2-vibrational modes and electron motion is strong at these conditions.

Steep temperature gradients occur near the wall and have to be resolved by a strongly refined mesh with only 1.2×10^{-8} m spacing at the wall. Nevertheless a convergence rate of six orders of magnitude within 100 iterations is achieved by the URANUS second-order TVD-scheme when vibration-chemistry-vibration is consistently coupled. Moreover, Courant–Friedrichs–Lewy (CFL) numbers up to 10,000 are possible even with the second-order-accurate scheme. The fully converged second-order solution is obtained after 250 iterations. Using a 25×61 mesh this corresponds to 3.8 h CPU on an IBM RISC 6000/550.

The calculated stagnation point Stanton number $St = 0.0444$ is in excellent agreement with the experimental result $St = 0.0445$ of Vetter et al.[29] Grid independence has been verified by a repeated computation on a refined 37×83 grid that showed only a slight deviation (0.12%). A variation of the reaction probability parameter U_i to $U_i = D_i/(0.1\mathfrak{R})$ (i.e., assuming a nonpreferential reaction modeling), however, leads to a stagnation point Stanton number of $St = 0.0465$, and thus, to a deviation of 4.7% from experiment. As illustrated in Fig. 4, the nonpreferential modeling promotes the formation of atomic oxygen, whereas a variation of the parameter α to $\alpha = 1.0$ shows an even more delayed dissociation process.

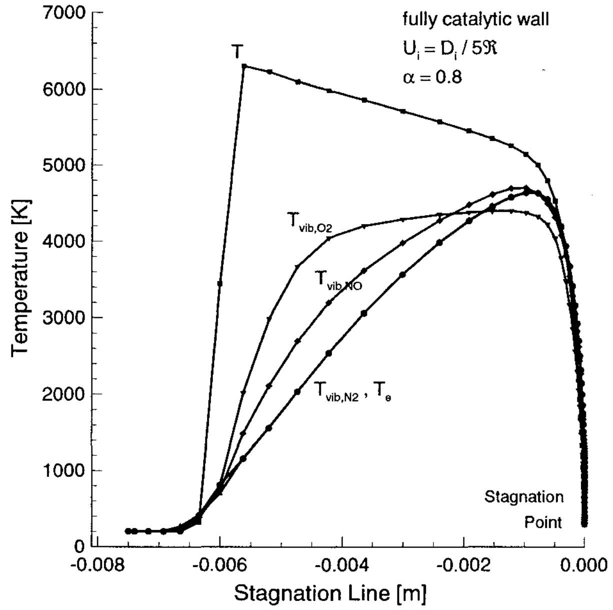

Fig. 3 Translational and vibrational temperatures along the stagnation streamline of the 0.1-m sphere.

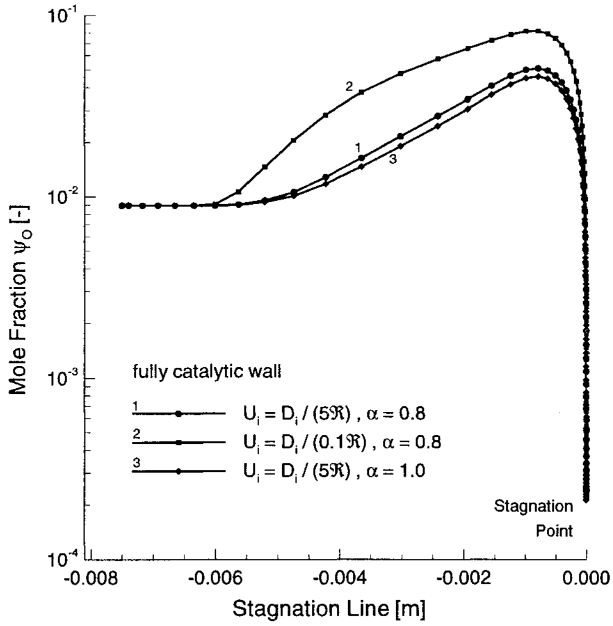

Fig. 4 CVCV-model parameter study depicted by atomic oxygen mole fraction profiles along the stagnation streamline of the 0.1-m sphere.

In order to demonstrate the importance of a physically consistent coupling of chemistry and vibration, we have recomputed the above test case with inconsistent source terms $Q_{C-V,i}$: nonequilibrium factors are again calculated by means of the CVCV-model formulation, but the vibrational energies transferred due to chemical reactions are determined according to Eq. (28) as $G_{\text{va},i} = G_{\text{app},i} = \varepsilon_{\text{vib},i}$ $(\gamma_1 = 1)$. Hence, the influence of chemical reactions on vibrational excitation is modeled inconsistently with regard to the modeling of rate constants. As a consequence, the CFL number could not be increased as fast as in the consistent case, which led to a clear convergence loss. Furthermore, the calculated stagnation point Stanton number changes to $St = 0.0455$ (2.5% deviation from experiment), indicating some loss in accuracy. In conclusion, the stagnation point heat flux indeed reacts upon a variation of the thermochemical modeling, but all deviations obtained are within the measurement accuracy of 5%.

Important Conclusions

A new thermochemical relaxation modeling has been discussed that allows for a physically consistent vibration-chemistry-vibration coupling in chemically reacting flowfields in thermal nonequilibrium. The CVCV model is derived from kinetic theory on the basis of two principal assumptions: 1) the vibrational energy states relax through a series of Boltzmann distributions characterized by a vibrational temperature and 2) the molecules can be approximated as truncated harmonic oscillators. Concluding this study we would like to summarize the most important statements obtained by this simple multiple temperature model:

1) Kinetic theory provides an interdependence between rate constants and vibrational energies transferred due to chemical reactions. The expressions derived differ for dissociation and exchange reactions.

2) The comparison with a state-selective model result sustains the CVCV-model assumption of $T_{\mathrm{vib},i}$-Boltzmann populated vibrational energy states.

3) The CVCV-model parameters $U_i = D_i/(5\Re)$ and $\alpha = 0.8$ yield good agreement with a state-selective model calculation as well as an experimental result. However, more comparisons are necessary to confirm these values.

4) In connection with an efficient CFD code the physically consistent formulation of the source term vector leads to an essentially higher convergence rate.

Further validation of the CVCV model is required to establish confidence in its abilities. In particular, the applicability of the model to expanding flows will be examined in the near future.

Acknowledgments

This work is supported by the Deutsche Forschungsgemeinschaft. The authors wish to express their sincere thanks to U. Riedel of the University of Heidelberg for providing the state-selective model results. Also the advice and assistance of A. Daiß using the URANUS code is gratefully acknowledged.

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