The thermal nonequilibrium processes in full state-to-state chemical kinetics

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The full state-to-state chemical kinetics in thermal nonequilibrium gas involves the consideration of all relevant models of processes including vibrational energy exchange, dissociation and chemical exchange reactions. The most well-justified and realistic simulation of full state-specific reactions is successful in solution of the particular dynamic collision problems by means of quasiclassical trajectory method. The appropriate considered models include the description of processes in high temperature air mixture with corresponding formulas. The specific equilibrium constant in state-to-state chemical kinetics may be used for determination of the rate constant of back reactions when the rate constants of forward reactions are known with application of recommended detailed balance relations. The concrete examples of numerical realizations of state-to-state processes in air are presented. The modeling of state-specific reactions has been examined and discussed over many years publications on Minsk School-Senimar.

Introduction

The considerable deviations from Boltzmann distribution over vibrational levels populations of molecules are the result of various strong and sharp actions on a gas, such as shock waves, supersonic nozzle flows and jets, laser irradiation, powerful electrical discharges, intensive combustion, and so on. Under these conditions the most appropriate processes description is provided by state-to-state kinetics.

The necessity of considering the state-to-state kinetics approach stems from the role of vibration-vibrational VV-energy exchange in a medium of reacting gas molecules, when VV-energy exchange proceeds relatively slowly so that the Boltzmann distribution is not established even on the lower vibrational levels. Fast VV-energy exchange leads to the Boltzmann distribution with one- or multi-temperature mode kinetics (see [1]). The main examples of solutions of state-to-state kinetics problems in lasers are examined in [2], and state-to-state kinetics in shock waves and nozzle flows are discussed in [3].

The modeling of processes on state-to-state kinetics has been examined and discussed over some years (see information in Minsk School-Seminar publications [4-10], for example). The most well-justified and detailed processes modeling are based on the solutions of the quasiclassical trajectory method.

Components and processes in full state-to-state kinetics

The mixture components in full state-to-state kinetics includes the molecules $\mathrm{AB}(m,n)$, $\mathrm{CD}(m,n)$, where m,n are the numbers of vibrational levels, A, B, C, D as atoms, and M as non-converting particles (colliders). Here it is proposed that $\mathrm{AB}(m,n)$, $\mathrm{CD}(m,n)$ are diatomic molecules, but polyatomic molecules may be considered by analogy.

The state-to-state processes in high temperature gases are:

- vibration-translational (VT) and vibration-vibrational (VV) energy exchange, which leads to the variations of vibrational states of molecules

$$\mathrm{AB}(m)+\mathrm{M}\leftrightarrow\mathrm{AB}(n)+\mathrm{M},\quad \mathrm{AB}(m)+\mathrm{CD}(m')\leftrightarrow\mathrm{AB}(n)+\mathrm{CD}(n') \tag{1}$$

- dissociation of molecules and recombination of atoms (d-reactions)

$$\mathrm{AB}(m)+\mathrm{M}\leftrightarrow\mathrm{A}+\mathrm{B}+\mathrm{M},\quad \mathrm{CD}(m)+\mathrm{M}\leftrightarrow\mathrm{C}+\mathrm{D}+\mathrm{M} \tag{2}$$

- chemical exchange reactions of simple and double exchange in direct and backward directions (e-reactions)

$$\mathrm{AB}(m)+\mathrm{C} \leftrightarrow \mathrm{AC}(n)+\mathrm{B}, \quad \mathrm{AB}(m)+\mathrm{CD}(m') \leftrightarrow \mathrm{AC}(n)+\mathrm{BD}(n') \tag{3}$$

- excitation and deactivation of electronic state of atoms and molecules, ionization and recombination of ionized components, radiation and its absorption, interaction of gas with solid and liquid surfaces and so on. These processes are not considered here, but they are needed to be taken into account in the kinetics problems in gas dynamics.

The modeling of above indicated state-to-state processes (1)–(3) is provided by relevant set of coefficients in correspondent kinetic equations for calculation of populations $N(m,n)$ on considered vibrational levels of reacting molecules.

The vibrational VT- and VV-energy exchanges (1) are usually simulated by generalized Schwartz – Slawsky – Herzfeld (SSH) theory (see [1], p.95); also it is possible to use Adamovich (see [1], p.99) or Gorbachev [11] models. The review and examination of many state-to-state rate coefficients models of dissociation and recombination d-reactions (2) and bimolecular e-reactions of chemical exchange (3) have been considered in the base of state-to-state models [12] (see short descriptions and references in [9,13]).

Application of quasiclassical trajectory (QCT) method results

The most well-justified and realistic modeling of state-to-state processes in thermally nonequilibrium gas are based on the solutions of dynamic collision problems by means of quasiclassical trajectory (QCT) method (see [5, 14–17] as examples).

For extensive simulation of elementary chemical reactions in thermally nonequilibrium gas by QCT method there is a need for considerable computer support with the set of potential energy surface analytical functions under multivariant initial conditions with statistic retrieval, and so on.

The problems of practical using of these results remain, because their presentations are limited to numerical and graphic demonstrations without simple analytical model approximation over gas temperature T and vibrational level numbers m, n. Only two state-specific kinetics models, Losev γ–model [6] and Levitsky model [18,19], are the function-approximated results based on QCT method, but without the fixing of concrete vibrational level states of reaction products.

In accordance with Losev γ-model, process of dissociation $\mathrm{AB}(m)+\mathrm{M}\rightarrow \mathrm{A}+\mathrm{B}+\mathrm{M}$ is described by the formula

$$k_d(T,m)=k_d^0(T)\exp\left(\frac{\gamma E_m}{T}\right)\times\frac{\left[1-\exp(\gamma-1)\frac{\theta}{T}\right]\left[1-\exp\left(-\frac{D_0}{T}\right)\right]}{\left[1-\exp(\gamma-1)\frac{D_0}{T}\right]\left[1-\exp\left(-\frac{\theta}{T}\right)\right]},$$

$$E_m\le D_0,\ k_d^0(T)=A\exp\left(-\frac{D_0}{T}\right)\left[1-\exp\left(-\frac{\theta}{T}\right)\right],$$

where D_0 is the dissociation energy, θ is the characteristic vibrational temperature, E_m is the vibrational energy of m-th level, A [cm^3/mol·s] is pre-exponential factor in the Arrhenius form for the equilibrium rate constant. Values of this model parameters and coefficients for dissociation are:

AB	M	A		
O_2	O_2	2.2×10^{16}	$\theta = 2240$	$\gamma = 1.25$
	O	7.8×10^{16}	$D_0 = 59380$	
	N,N_2,NO	3.6×10^{15}		
N_2	N_2,O_2,NO	3.2×10^{16}	$\theta = 3354$	$\gamma = 0.8$
	N,O	7.1×10^{16}	$D_0 = 113000$	

The estimating of parameter γ for other dissociation reactions is $\gamma=1.0$. The example of level factor $k_m(T)/k_0(T)$ (where $k_0=k_{m=0}$) for this model is in fig.1. The solution of dynamic problem for dissociation in shock waves were used for this model. The results are in good agreement with data obtained by Esposito et al. [15] for this process.

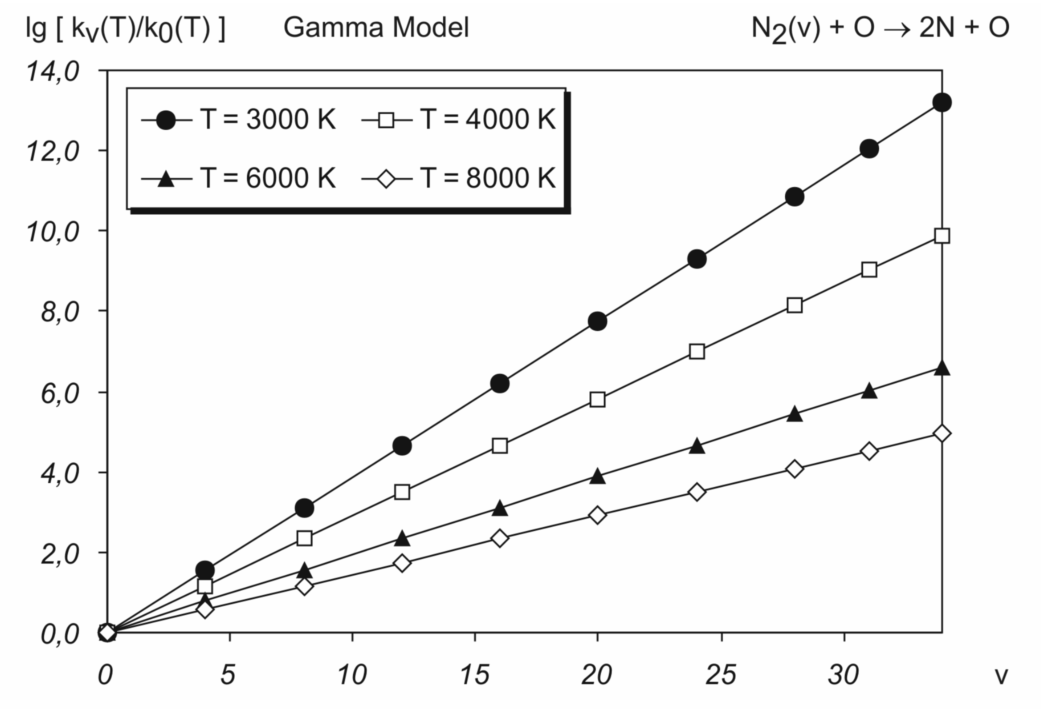

Figure 1. Level factor $k_v(T)/k_0(T)$ for dissociation $N_2 + O \rightarrow 2N + O$ calculated by γ-model at the different translational temperatures $T = 3000$, 4000, 6000, 8000 K as the function of vibrational level numbers

The Levitsky model for dissociation and chemical exchange reactions is described with the formula

$$\left.\begin{matrix} k_d(T,m) \\ k_e(T,m) \end{matrix}\right\} = A(T)\exp\left[-\frac{E - \alpha E_m}{\beta T} \cdot \bar{\theta}(E - \alpha E_m)\right],$$

where $E = D_0$ for dissociation reactions and $E = E_a$ for exchange reactions (E is in Kelvin), α, β are the parameters describing participation of vibrational and translational energies in reactions. The value $\bar{\theta} = \bar{\theta}(x)$ is Heaviside function [$\bar{\theta} = 1$ for $x \geq 0$, $\bar{\theta} = 0$ for $x < 0$]. The pre-exponential factor $A(T)$ is close to the collision frequency per one concentration of particles $Z = \pi R_0^2 \left(8kT/\pi\mu\right)^{1/2}$, where R_0 is the gas kinetic radius, μ is the reduced mass of collision particles (see [1], p.31). The examples of necessary parameters values are:

Reaction	E [K]	α	β
$N_2(m)+O \to N+N+O$	113200	1.0	0.85
$O_2(m)+N \to O+O+N$	59380	1.0	0.92
$N_2(m)+O \to NO+N$	37133	0.52	0.9
$O_2(m)+N \to NO+O$	3829	0.12	0.46

To our regret, Levitsky model for exchange reactions does not include the information on rate coefficients for fixed levels on reaction products, and cannot be used in full state-to-state kinetics descriptions.

The results of QCT method application for chemical exchange reactions (3) in full approach are presented in [5,10,14,17,20,21] with fixed vibrational states of reagents and as well as products.

The software complex "MD Trajectory" has been created and is being used in the modeling of some chemical exchange reactions in full approach (see [22]). This complex is based on the parallized supercomputer cluster system at Moscow State University. The some results of its application for full state-to-state kinetics at high temperatures are demonstrated in figs. 2–6. The level numbers n,m are denoted here by v and w, correspondingly.

Figures 2 and 3 present the probability $P(v,w)$ of exchange reactions with transfer $v \to w$. The relation between rate coefficients k_{vw} and reaction probability $P(v,w)$ has the aspect:

$$k_{vw} = (8kT/\pi\mu)^{1/2}\, \sigma_0 P(v,w) \cdot N_A \; \left[\mathrm{cm^3/mol \cdot s}\right].$$

Here σ_0 is the average cross section of elastic collisions between reagent particles, μ is the reduced mass in these collisions, N_A is the Avogadro number.

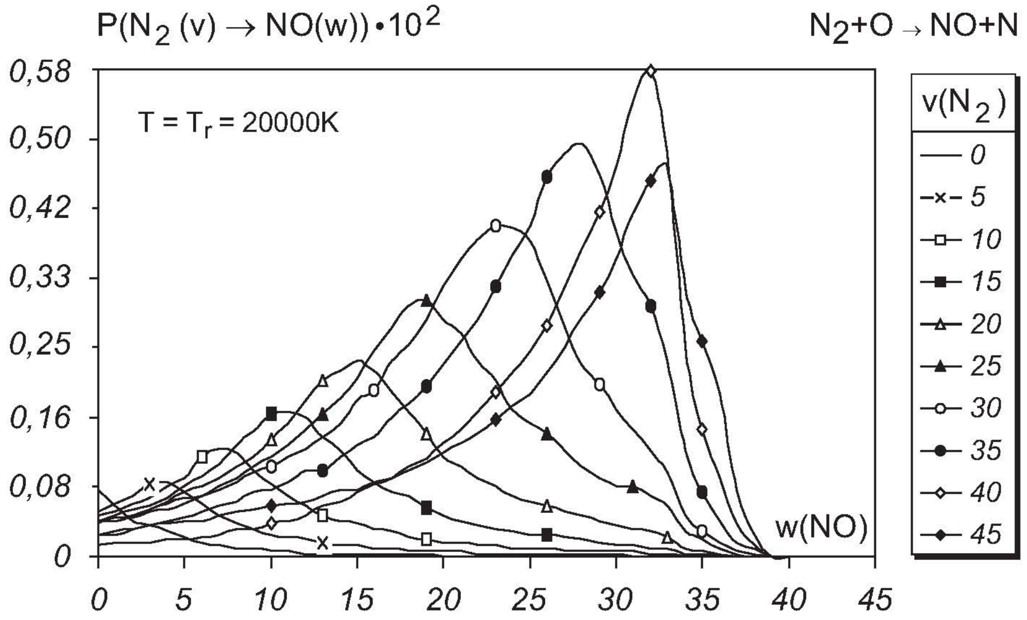

Figure 2. The distribution of NO molecules over vibrational states w at different vibrational states v of N_2 molecules for exchange reaction $N_2(v)+O \rightarrow NO(w)+N$, $T=T_r=20000\,K$

(T_r is the rotational temperature here and below)

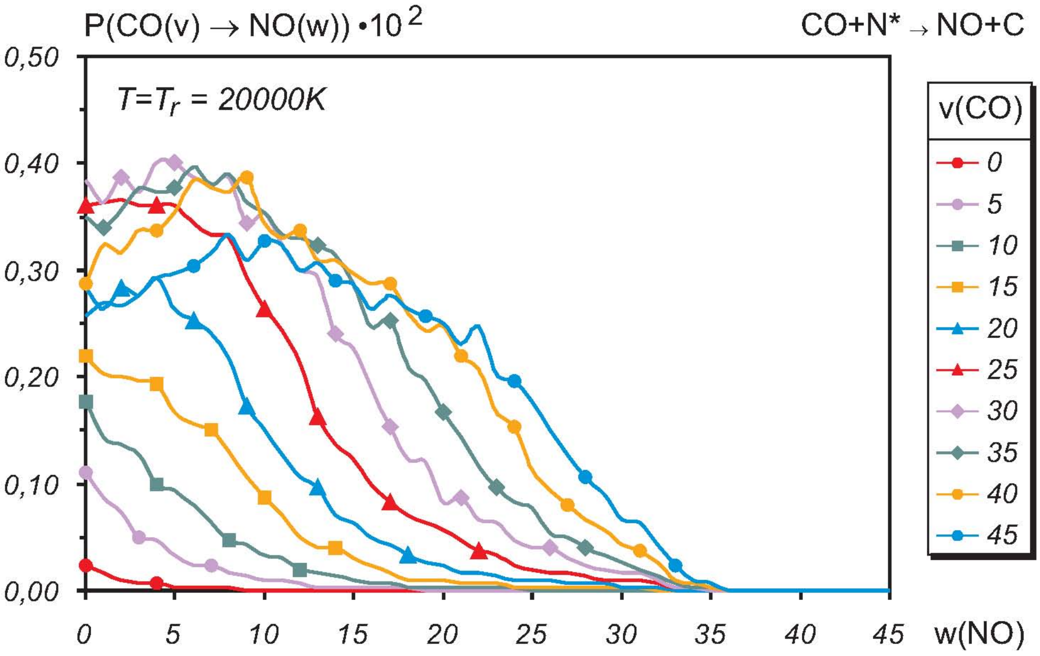

Figure 3. The distribution of NO molecules over vibrational states w at different vibrational states v of CN molecules for exchange reaction $CO+N^* \rightarrow NO+C$, $T=T_r=20000\,K$

(N^* is the electron-induced $N(^2D)$ atom)

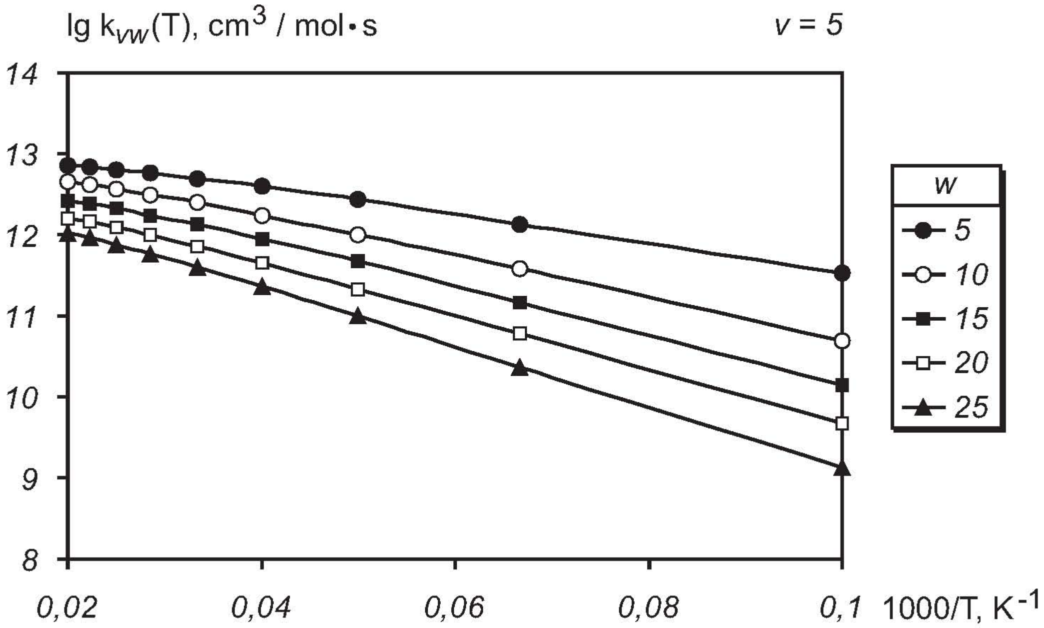

Figure 4. State-to-state rate coefficients on the reaction $N_2(\upsilon) + O \rightarrow NO(w) + N$

for $v = 5$ at different values w

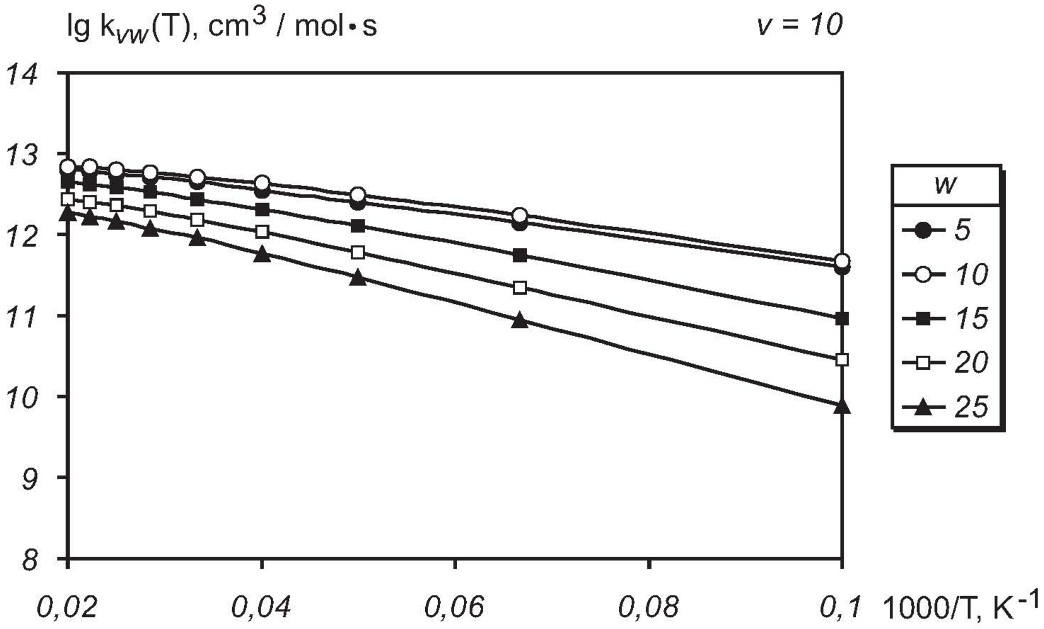

Figure 5. The same in Figure 4, but $v = 10$

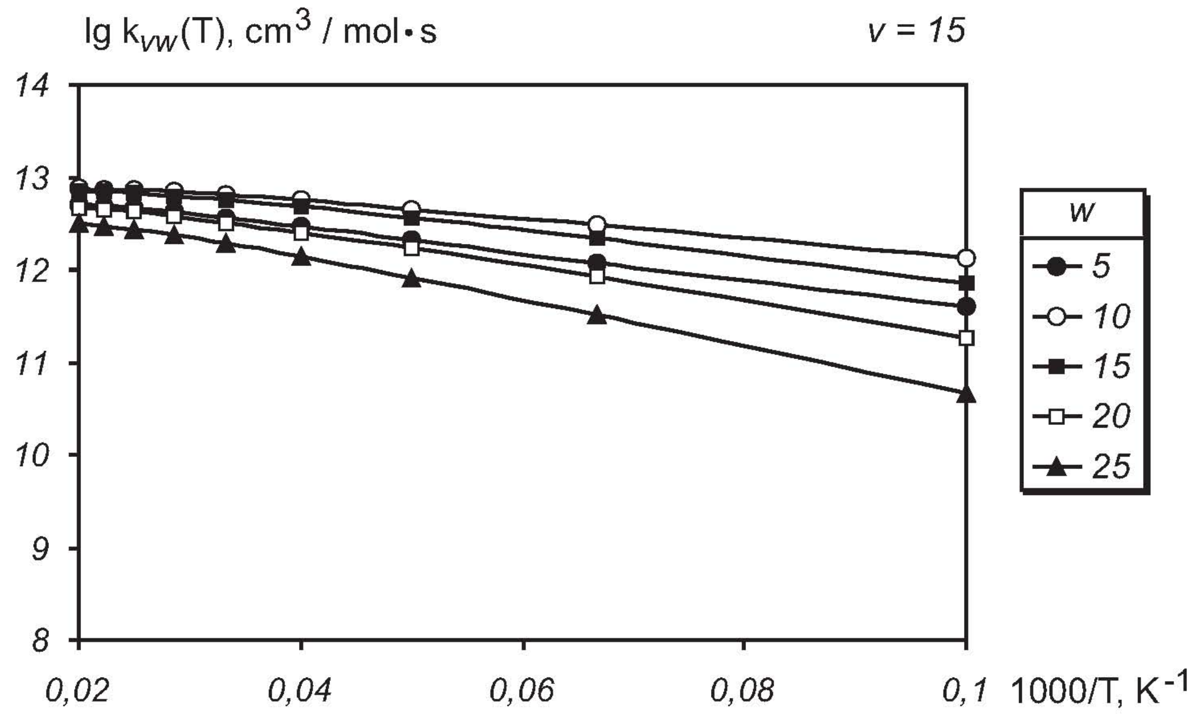

Figure 6. The same in Figure 4, but $v = 15$

The approximated formula of rate coefficient $k(T, m, n)$ as a model on full state-to-state exchange reactions may be defined by the difference between the energy of vibrational excitation of molecules reagents E_m and reaction products E_n. The test variant of this simple formula is

$$k(T,m,n) = A(T)\exp\left[-\lambda(m,n)\frac{E_m - E_n - \Delta E_0}{T}\right],$$

where value ΔE_0 is the reaction heat (endothermicity), $A(T), \lambda(m,n)$ are the model parameters determined by the calculated results of dynamic collision method for concrete chemical exchange reactions, and normalized with thermal equilibrium rate constant $k_e^0(T)$.

Detailed balance relations

The existing information on state-to-state rate coefficient of chemical reactions is insufficient for description of full kinetics even in air. The useful mechanism of these reactions using the results of QCT method includes reactions $N_2(m) + O \rightarrow NO(n) + N$ [22] and $O_2(m) + N \rightarrow NO(n) + O$ [21], as well as indicated above dissociation models.

The knowledge of rate coefficients on reactions in back direction is required for creating the full mechanism of state-specific kinetics. These rate coefficients on back reactions (k_r for recombinations, k_b for back exchange reactions) are determined by the relations of detailed balance:

- For reactions of dissociation and recombination of diatomic molecules

$$\frac{k_{dm}^{\mathrm{AB-M}_s}}{k_{rm}^{\mathrm{A-B-M}_s}} = \frac{Q_v^{\mathrm{AB}}(T)}{\exp\left(-E_m^{\mathrm{AB}}/kT\right)} \times \begin{cases} \dfrac{K_p(T)}{kT} & -\ (1) \\ \left(\dfrac{N^{\mathrm{A}}N^{\mathrm{B}}}{N_{\mathrm{AB}}}\right)_{eq} & -\ (2) \end{cases}$$

- For reactions of simple exchange (m □ m')

$$\frac{k_{fmm'}^{\mathrm{AB-C}}}{k_{bmm'}^{\mathrm{AC-B}}} = \frac{Q_v^{\mathrm{AB}}(T)\exp\left(-E_m^{\mathrm{AC}}/kT\right)}{Q_v^{\mathrm{AC}}(T)\exp\left(-E_m^{\mathrm{AB}}/kT\right)} \times \begin{cases} K_p(T) & -\ (1) \\ \left(\dfrac{N^{\mathrm{AC}}N^{\mathrm{B}}}{N^{\mathrm{AB}}N^{\mathrm{C}}}\right)_{eq} & -\ (2) \end{cases}$$

- For reactions of double exchange (mn □ $m'n'$)

$$\frac{k_{fmn,m'n'}^{\mathrm{AB-CD}}}{k_{bm'n',mn}^{\mathrm{AC-BD}}} = \frac{Q_v^{\mathrm{AB}}Q_v^{\mathrm{CD}}}{Q_v^{\mathrm{AC}}Q_v^{\mathrm{BD}}} \frac{\exp\left[-\left(E_{m'}^{\mathrm{AC}}+E_{n'}^{\mathrm{BD}}\right)/kT\right]}{\exp\left[-\left(E_m^{\mathrm{AB}}+E_n^{\mathrm{CD}}\right)/kT\right]} \times \begin{cases} K_p(T) & -\ (1) \\ \left(\dfrac{N^{\mathrm{AC}}N^{\mathrm{BD}}}{N^{\mathrm{AB}}N^{\mathrm{CD}}}\right)_{eq} & -\ (2) \end{cases}$$

(1) for reactions in simple gases, with no components other than those participating in the reactions under analysis;

(2) for reactions in complex mixture with other components.

The value of an equilibrium constant of chemical reactions $K_p(T)$ in terms of partial pressures of reacting components for reactions in simple gases is discussed in Chapter 8 [23]. The values, indicated by indices «*eq*» correspond to the equilibrium number densities of components in complex mixture. The superscripts are indicated the types of reagents and reaction products. Here Q_v is the partition function over vibrational states, E_m, E_n are the vibrational energy of *m*-th and *n*-th vibrational levels, respectively.

Conclusion

The full state-to-state chemical kinetics in thermal nonequilibrium gas involves the consideration of all relevant models of processes including vibrational energy exchange, dissociation and chemical exchange reactions. The most well-justified and realistic simulation of full state-specific reactions is successful in solution of the particular dynamic collision problems by means of quasiclassical trajectory method. The appropriate considered models include the description of processes in high temperature air mixture. The specific equilibrium constant in state-to-state chemical kinetics is being applied for determination of the rate constant of back reactions when the rate constants of forward reactions are known as mentioned above.

The comparison of the results obtained by means of the level approach with those based on multi-temperature and one-temperature kinetics shows the essential difference between these approaches in the region close to strong shock wave front. The values of this difference may exceed many thousands degrees for gas temperature, and many hundreds kW/m^2 for heat flux (see [3]). These differences are explained by the underestimation of the temperature value with the use of the two-temperature and one-temperature approaches because the quasi-stationary distribution is assumed to be immediately behind a shock wave front. These approaches do not consider the real delay of vibrational excitation at the start of relaxation zone. Recombination during the flow expansion in nozzles and jets leads to the formation of highly nonequilibrium level distributions.

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