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Citation: **1786**, 150005 (2016); doi: 10.1063/1.4967646

View online: <http://dx.doi.org/10.1063/1.4967646>

View Table of Contents: <http://aip.scitation.org/toc/apc/1786/1>

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Non-equilibrium Reaction Rates in Air Flows Behind Shock Waves. State-to-state and Three-temperature Description

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Abstract. Non-equilibrium reaction rates in the flows of the five-component air mixture $N_2/O_2/NO/N/O$ in the relaxation zone behind shock waves are studied on the basis of the state-to-state, three-temperature and one-temperature kinetic theory approaches. State-dependent rate coefficients for N_2 and O_2 dissociation and Zeldovich exchange reactions are averaged using 1) state-to-state vibrational distributions, 2) two-temperature Treanor distributions and 3) thermal equilibrium distributions. Variation of global reaction rate coefficients obtained in different approaches along the relaxation zone is studied numerically for free stream Mach number $M = 13$ and differences between reaction rate coefficients found in the frame of the state-to-state and more simple kinetic models are evaluated.

INTRODUCTION

In this paper non-equilibrium rates of dissociation and Zeldovich exchange reactions in shock heated air flows are studied in the frame of state-to-state, three and one-temperature flow descriptions. Prediction of non-equilibrium reaction rates in high-temperature air flows is very important for gas dynamic problems. Experiments carried out in shock heated air components [1, 2] show noticeable deviations of reaction rates from the Arrhenius law. However, at present time experimental data for reaction rates obtained under strongly non-equilibrium conditions are limited and available only for one-component molecular gases or binary mixtures of molecules and atoms. Therefore the development of adequate theoretical models for rates of chemical reactions in high-temperature multi-component air flows is of importance.

Non-equilibrium contributions to reaction rates have been studied originally for a spatially homogeneous gas, and then for various gas flows using different molecular distributions over velocities and internal energies. The impact of non-Maxwell velocity distributions on reaction rates is studied in [3, 4, 5, 6, 7, 8].

For two-temperature dissociation rates in a vibrationally excited gas a simple expression was proposed by Park [9] and the Treanor-Marrone model was derived [10] and later generalized for exchange reactions [11] and for the state-to-state approach [12, 13]. Dissociation models based on quasi-stationary Boltzmann or Treanor vibrational distributions are calculated for the flows of shock heated N_2/N and O_2/O mixtures in [14]. Under strong non-equilibrium conditions the more rigorous state-to-state approach [15] is needed for modeling of reaction rates. This approach was used for calculations of dissociation rates in binary mixtures N_2/N , O_2/O in the flows behind shock waves [16] and in nozzles [17, 18]. In the five-component shock heated air flows the influence of state-dependent vibrational level populations on Zeldovich exchange reaction rates is recently evaluated in [19]. Verification of theoretical models for dissociation and exchange reactions in air components on the basis of trajectory calculations is presented in [20, 21].

In the present paper we study global rates of dissociation and exchange reactions in the flows of air mixture $N_2(i)/O_2(i)/NO/N/O$ behind shock waves by averaging state-dependent reaction rate coefficients with vibrational distributions obtained in different approaches. First, governing equations for macroscopic air flow parameters in the relaxation zone behind a shock have been solved numerically in the state-to-state (STS), three-temperature (3T) and one-temperature (1T) kinetic theory approximations for free stream Mach numbers $M = 13$. Then state-dependent

rate coefficients for N_2 and O_2 dissociation and exchange reactions of NO formation were averaged with 1) state-to-state distributions, 2) two-temperature Treanor distributions, 3) thermal equilibrium distributions. Variation of global reaction rate coefficients obtained in different approaches along the relaxation zone is studied numerically and differences between reaction rate coefficients found in the frame of the most accurate state-to-state approach and using more simple models are shown.

GLOBAL RATE COEFFICIENTS FOR DISSOCIATION AND EXCHANGE REACTIONS

We study reaction rates in high-temperature flows of air mixture $N_2(i)/O_2(i)/NO/N/O$ with dissociation, recombination:



and Zeldovich exchange reactions of NO formation:



where i is the vibrational state of a molecule, $M = N_2, O_2, NO, N, O$.

Along with reactions (1)-(5), the kinetic scheme includes $VT(TV)$ vibrational energy exchanges with translation energy as well as VV exchanges of vibrational energies between the same molecular species and VV' exchanges between different species. Since in high-temperature air flows translational-rotational relaxation is known to proceed much faster comparable to vibrational energy transitions and chemical reactions [15], therefore in the present paper distributions over translational and rotational energies are supposed to be equilibrium with the gas temperature T . Under this assumption the general definition for averaged rates of reaction (1)-(5) may be written in the form

$$k_c^r = \frac{1}{n_c} \sum_{i=0}^{l_c} n_{ci} k_{ci}^r(T), \quad c = N_2, O_2, \quad (6)$$

where r indicates the type of chemical reaction, n_c are molecular number densities, n_{ci} are populations of the i th vibrational level of N_2 and O_2 molecules, k_{ci}^r are state-dependent rate coefficients of reactions. These coefficients for considered reactions are proposed in some papers using empirical models or approximations for trajectory calculations (see Refs. in [15, 19, 21]). We are interested in the influence of vibrational distributions on reaction rates in the relaxation zone behind shock waves. For this purpose, reaction rates (6) are considered in the next section using level populations n_{ci} found in the frame of different kinetic theory approaches.

REACTION RATE COEFFICIENTS BEHIND SHOCK WAVES. DIFFERENT APPROACHES

State-to-state approach

Now we consider averaged rate coefficients (6) of reactions (1)-(5) in the relaxation zone behind shock waves in the state-to state approach. First, vibrational level populations n_{N_2i} and n_{O_2i} , number densities n_{N_2} , n_{O_2} , n_{NO} , the gas temperature and velocity were found in numerical simulations of air flows behind plane shock waves in the state-to-state approach. In the frame of this approach the equations for vibrational distributions n_{N_2i} ($i = 0, 1 \dots 47$), n_{O_2i} ($i=0, 1 \dots 36$), number densities of atoms and NO molecules are coupled to the conservation equations for momentum and total energy [22]. Similarly to [22] the flow is assumed to be non-viscous, one-dimensional and steady-state. The solution of flow equations are used as input data for the expressions (6) for global rates of forward reactions (1)-(5).

State-specific rate coefficients of vibrational energy transitions, dissociation and forward exchange reactions entering to the equations of vibrational-chemical kinetics are calculated using the generalized formulas of Schwartz, Slawsky, Herzfeld [23] for energy transitions, the modified Treanor-Marrone dissociation model [10] and the expression proposed in [24] for exchange reactions. Rate coefficients of backward energy transitions and reactions are computed using the detailed balance relations.

Three-temperature approach

Calculations of global non-equilibrium reaction rates according to Eq. (6) is noticeably simplified if level populations are expressed in terms of macroscopic parameters. Experimental data on relaxation times in air components [25, 26] and calculations of vibrational energy transition probabilities [1] show that near-resonant VV vibrational energy exchanges between the same species happen more often comparable to non-resonant VV' exchanges between different molecules. In this case populations n_{ci} may be written in the form of the two-temperature Treanor distributions [27]:

$$n_{ci}^T = \frac{n_c}{Z_c^{vibr}(T, T_1^c)} \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c}\right), \quad (7)$$

T_1^c ($c = \text{N}_2, \text{O}_2$) is the temperature of the first vibrational level, ε_i^c are vibrational energies for anharmonic oscillators counted from the zero-th level energy, k_B is the Boltzmann constant,

$$Z_c^{vibr}(T, T_1^c) = \sum_{i=0}^{l_c} \exp\left(-\frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c}\right)$$

is the partition function.

Vibrational temperature T_1^c is connected with the mean number of vibrational quanta $W_c(T, T_1^c)$ of molecular species c per unit mass:

$$\rho_c W_c(T, T_1^c) = \sum_{i=0}^{l_c} i n_{ci}^T(T, T_1^c), \quad c = \text{N}_2, \text{O}_2. \quad (8)$$

Expressions (7)-(8) make it possible to reduce detailed state-to-state flow description to the three-temperature model in the frame of equations for number densities of species $n_{\text{N}_2}(x)$, $n_{\text{O}_2}(x)$, $n_{\text{NO}}(x)$, $n_{\text{N}}(x)$, $n_{\text{O}}(x)$, temperatures $T(x)$, $T_1^{\text{N}_2}(x)$, $T_1^{\text{O}_2}(x)$ and macroscopic velocity $v(x)$ [28]. The numerical solution of these equations and expression (7) are used as input data for equation (6) for calculation of reaction rate coefficients in the frame of the three-temperature model.

One-temperature approach

If all vibrational energy transitions proceed faster than chemical reactions, the non-equilibrium chemical kinetics may be considered on the background of the maintaining one-temperature Boltzmann vibrational distributions over vibrational energies. In the frame of this regime, one-temperature reaction rates are described by the Arrhenius law:

$$k_c^A = AT^b \exp\left(-\frac{E_a}{k_B T}\right). \quad (9)$$

Parameters A , b , E_a in this expression for considered reactions may be found in [29].

Macroscopic air flow parameters $n_{\text{N}_2}(x)$, $n_{\text{O}_2}(x)$, $n_{\text{NO}}(x)$, $n_{\text{N}}(x)$, $n_{\text{O}}(x)$ satisfy to the equations of the one-temperature chemical kinetics coupled to the conservation equations of momentum and total energy.

RESULTS

The solution of shock heated flow equations in the state-to-state and simplified models are obtained for Mach number $M = 13$ and the following values of the gas temperature, pressure and mixture composition in the free stream: $p_0 = 100$ Pa, $T_0 = 271$ K, $n_{\text{N}_2} = 0.79n$, $n_{\text{O}_2} = 0.21n$, $n_{\text{NO}} = n_{\text{N}} = n_{\text{O}} = 0$, where n is the total number density. Vibrational level populations of nitrogen and oxygen molecules in the free stream are described by equilibrium Boltzmann distributions with the gas temperature T_0 .

The values of flow parameters just behind a shock in the STS approach are found using the Rankine-Hugoniot relations with frozen vibrational distributions and mixture composition within a shock front. In the 3T approach parameters just behind a shock are calculated using conservation equations of momentum, total energy, mixture composition along with the total numbers of vibrational quanta of molecules within a shock front. In the 1T approach chemical composition is conserved within the shock front whereas level populations are described by the Boltzmann distributions with the gas temperature just behind a shock.

Now let us consider the comparison of flow parameters and averaged rate coefficients for dissociation reactions (1) and (2) along with forward and backward reactions (4) and (5) obtained in three approaches in the relaxation zone behind a shock front.

The variation of the gas temperature and number densities of species formed as a result of chemical reactions versus distance from shock front is shown in Fig. 1. It was found that the STS and 3T approaches provided the close values of temperature profile and mixture composition in the beginning of relaxation zone. With increasing x the 3T model provides underestimated temperature values and overestimated NO and atoms number densities compared to the state-to-state description. While the 1T approach based on quasi-stationary Boltzmann distributions do not describes the delay of free atoms formation (see Fig. 1b) which is found in the STS approach and known from experimental results. And on the whole the 1T model leads to a significant underestimation of gas temperature. Incorrect

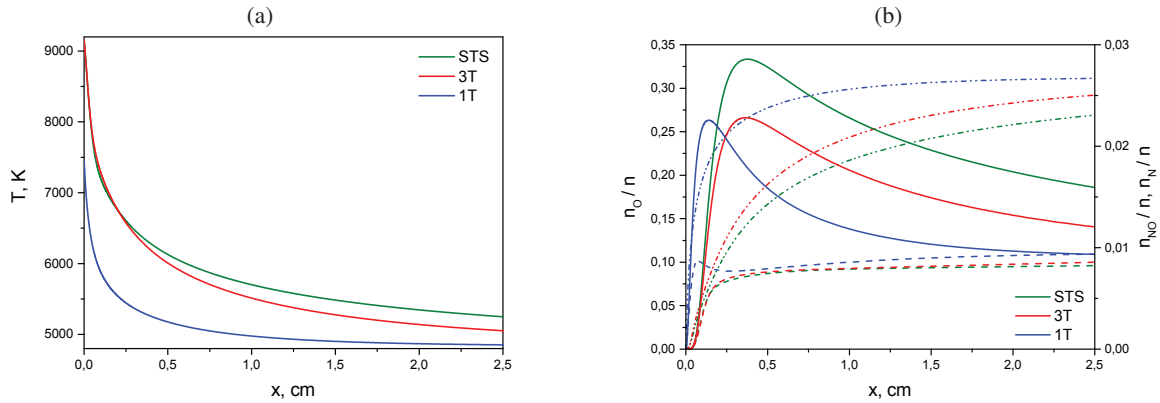


FIGURE 1. The temperature T (a) and number densities n_{NO}/n , n_N/n and n_O/n (b) behind the shock front as functions of x . Solid lines: n_{NO}/n , dash lines: n_N/n , dash-dot lines: n_O/n .

description of the vibrational excitation process in the very beginning of the relaxation zone is primarily responsible for the discrepancies between parameters obtained in three approaches. The vibrational distributions of N_2 and O_2 molecules calculated in three approaches are reproduced in Figs. 2 along the relaxation zone. It is seen that within the state-to-state and three-temperature models molecules pass through a stage of excitation and then deactivate whereas the one-temperature model overestimates the level populations in the beginning of the relaxation zone and the activation zone is absent.

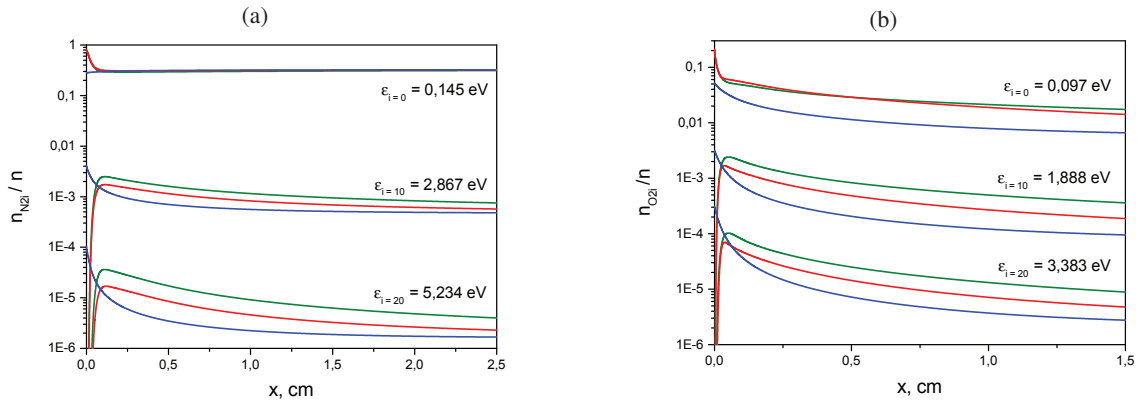


FIGURE 2. The vibrational level populations n_{N_2i}/n (a) and n_{O_2i}/n (b) as functions of x .

State-specific dissociation rate coefficients for different vibrational levels of nitrogen and oxygen molecules against temperature are presented in Fig. 3a. As we can see, the rate coefficients $k_{N_2i}^{dis}$ and $k_{O_2i}^{dis}$ rise with increased vibrational quantum number and gas temperature. Fig. 3b shows comparison of averaged rate coefficients of N_2 and O_2 dissociation in dependence of x in the air mixture. It can be easily seen for the one-temperature coefficients $k_{N_2}^{dis}$

and $k_{O_2}^{dis}$ monotonic decrease with x rising due to the gas temperature diminishing. In the very beginning of the relaxation zone these coefficients exceed the values obtained for STS and 3T approaches more than an order of magnitude. As a result, the one-temperature approach leads to overestimated values of number of free atoms and less populated vibrational levels (see Figs. 1-2). In a thin region just close to the shock front coefficients $k_{N_2}^{dis}$ and $k_{O_2}^{dis}$ increase fast, particularly coefficients of O_2 dissociation. Then coefficients change non-monotonically and decrease with x rising. Such a character of changes shows strong influence of vibrational distributions on averaged dissociation rate coefficients.

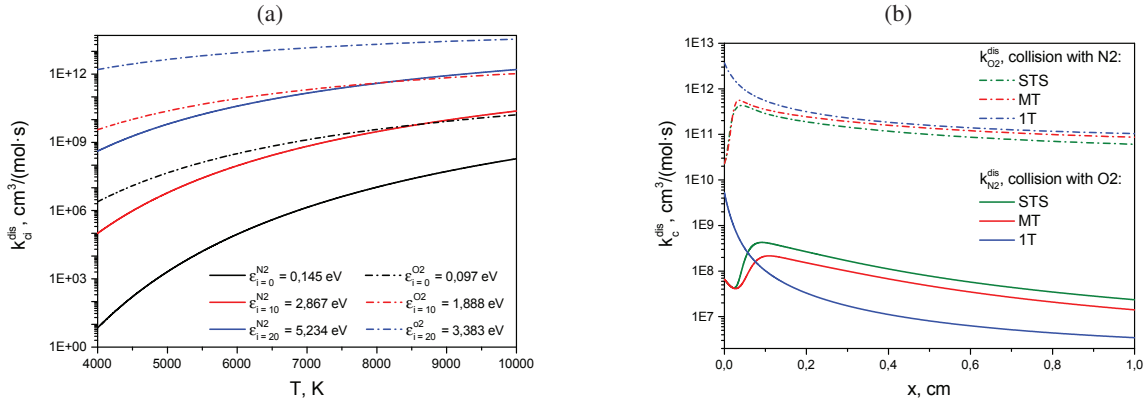


FIGURE 3. The state-dependent (a) and averaged (b) rate coefficients of N_2 and O_2 dissociation reactions at the collision N_2 - O_2 as functions of x . Solid lines: $k_{N_2i}^{dis}$ and $k_{N_2}^{dis}$, dash-dot lines: $k_{O_2i}^{dis}$ and $k_{O_2}^{dis}$.

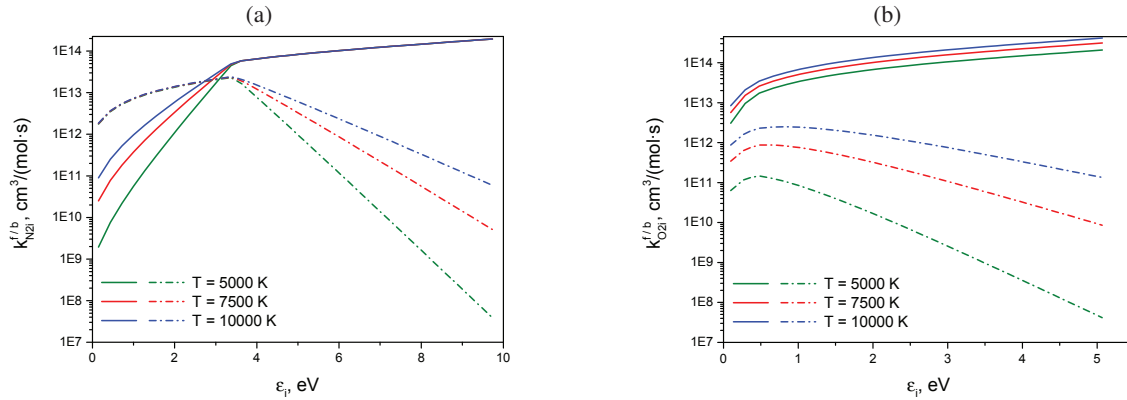


FIGURE 4. The state-dependent rate coefficients of exchange reactions $k_{N_2i}^{f/b}$ (a) and $k_{O_2i}^{f/b}$ (b) as functions of vibrational energy ϵ_i^c . Solid lines: forward reaction, dash-dot lines: backward reactions.

In Figs. 4 we compare state-dependent coefficients of forward and backward exchange reactions (4)-(5). Note that state-dependent rate coefficients on the basis of several reaction models are studied earlier in details in [19]. In the present paper coefficients are calculated with the use of the model proposed in [24]. The comparison presented in Figs. 4 shows the growth of forward reactions rate coefficients $k_{N_2i}^f$ and $k_{O_2i}^f$ with increase in the temperature and number of vibrational level. The rate coefficients of reverse exchange reactions change non-monotonically depending on the molecule vibrational energy, the highest probabilities of reverse reactions are found for $\epsilon_{i=12}^{N_2} = 3.369$ eV and $\epsilon_{i=4}^{O_2} = 0.849$ eV.

Figures 5 show averaged coefficients of forward and backward exchange reactions (4)-(5) as functions of x . Note the impact of non-monotonic variation of vibrational distributions obtained for STS and 3T approaches on averaged exchange rate coefficients of forward exchange reactions. As well as the dissociation rate coefficients, the one-temperature coefficients $k_c^{f/b}$ decrease monotonically with the distance from the shock. Rate coefficients averaged over state-to-state and two-temperature distributions change non-monotonically. Close to the shock front they grow

due to increasing of vibrational level populations and then decrease as a result of forward reactions (4) and (5). The monotonic diminishing of the rates for reverse reactions (4)-(5) connected with assumption that NO molecules remain at the ground vibrational state. In this case the rate coefficients k_c^b depend only on the behavior of the temperature. We can notice that in the very beginning of the relaxation zone the one-temperature model overestimates the probabilities of forward Zeldovich reactions more than an order of magnitude for reaction (4) and a one-half of order of magnitude for reaction (5). On the contrary, it underestimates the rates of the reverse reactions. Comparing averaged coefficients of exchange reactions presented in Figs. 5 one can see that in all three approaches reaction (4) is much more active in the backward direction whereas the forward reaction (5) occurs more active than the backward one. This is in agreement with the behavior of state-dependent coefficients of forward and backward exchange reactions (4)-(5) (see Figs. 4).

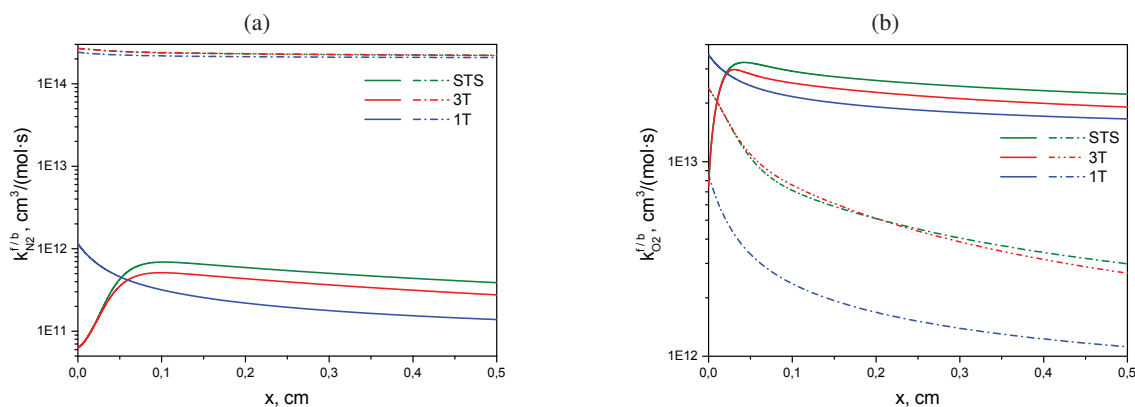


FIGURE 5. The averaged rate coefficients of exchange reactions $k_{N_2}^{f/b}$ (a) and $k_{O_2}^{f/b}$ (b) as functions of x . Solid lines: forward reaction, dash-dot lines: backward reactions.

CONCLUSIONS

Averaged rate coefficients for dissociation of N_2 and O_2 molecules along with the forward and backward Zeldovich exchange reactions in shock heated air flows are studied using the state-to-state, two-temperature Treanor distributions and thermal equilibrium Boltzmann distributions. The results show the essential influence of vibrational excitation of molecules on reaction rate coefficients. Satisfactory agreement is found for the values of rate coefficients obtained with the use of the state-to-state and Treanor vibrational distributions along the relaxation zone whereas the thermal equilibrium rate coefficients differ dramatically from the non-equilibrium ones. The one-temperature approach considerably overestimates rate coefficients for dissociation and forward exchange reactions. Non-equilibrium rate coefficients of forward chemical reactions change non-monotonically along the relaxation zone whereas thermal equilibrium coefficients decrease monotonically with the gas temperature reducing. For N_2 dissociation the one-temperature model overestimates non-equilibrium rate coefficients close to the shock front and then leads to underestimated values with x rising. For backward reactions (4)-(5) state-to-state and two-temperature rate coefficients differ slightly. The difference between coefficients found in three approaches decreases with x rising coming to the equilibrium.

ACKNOWLEDGMENTS

This study is supported by Saint Petersburg State University (grants No. 6.50.2522.2013 and No. 6.37.206.2016) and Russian Fund of Basic Research (project No. 15-01-02373).

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