

Multi-temperature kinetics and thermodynamic properties behind shock waves in reacting air components

K.I. Karakulko and E.A. Nagnibeda

Mathematics and Mechanics Dept., Saint Petersburg University, 198904, Saint Petersburg, Russia

Abstract. Non-equilibrium kinetics, gas dynamic parameters and thermodynamic properties in gas flows of air species behind shock waves are studied under different free stream conditions. The influence of shock wave intensity and chemical reactions on macroscopic parameters is shown. A comparison of the results obtained in the quasi-stationary two-temperature approximations with the one-temperature approximations is presented.

Keywords: Multi-temperature kinetics, non-equilibrium distributions, dissociation

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INTRODUCTION

The paper presents the results of investigations into non-equilibrium kinetics, gas dynamic parameters and thermodynamic properties in gas flows of air species behind shock waves under different conditions in a free stream. The problem was studied by many authors using different models of non-equilibrium kinetics. The most rigorous approach is the state-to-state one [1], based on the solution of the equations for vibrational level populations. This approach has been successfully developed in recent years and permitted to obtain new results and reach good accuracy in prediction of gas dynamic parameters and distributions in different gas flows [1]. However the state-to-state model is rather numerically expensive for applications: indeed, many equations for vibrational level populations of all molecular species in considered mixtures should be coupled to gas dynamic equations. Therefore implementation of the state-to-state model to CFD codes consumes a lot of computational time particularly if many practical cases should be considered. Simpler models are based on quasi-stationary distributions. These models contain much smaller number of equations of non-equilibrium kinetics and consequently their realization requires less computer resources. Multi-temperature quasi-stationary models are used in many applications, most of them are based on non-equilibrium Boltzmann vibrational distributions with a vibrational temperature different from the gas temperature. However such a distribution is valid only for harmonic oscillators and is not sufficiently rigorous as a model for high-temperature gas. In the present paper for the prediction of distributions, gas dynamic parameters, and thermodynamic properties in shock heated reacting gas mixtures a more accurate multi-temperature approximation based on Treanor [2] two-temperature distributions of anharmonic oscillators is used. The equations for number densities of molecules and atoms, gas velocity and temperature, and vibrational temperatures of the first levels of molecular species [1] have been solved numerically for many cases of free stream conditions in air components. The paper describes the evolution of gas dynamic parameters, specific heats, vibrational distributions and two-temperature reaction rates in the relaxation zone behind a shock. The influence of shock wave intensity on temperatures, distributions, and thermodynamic properties is demonstrated. Simultaneously the same problem has been solved using one-temperature thermal equilibrium distribution. The comparison of the results showed the influence of different distributions on gas dynamic parameters, thermodynamic properties and global reaction rates behind a shock. For validation of the considered multi-temperature model the comparison of the results with ones obtained in the state-to-state approximation for several cases [1], [3], and experimental data [4] has been used.

MAIN EQUATIONS

We consider one-dimensional stationary flows of reacting air components mixtures (N_2, N) , (O_2, O) , (NO, N, O) . The relation between the relaxation times of different processes in reacting mixture:

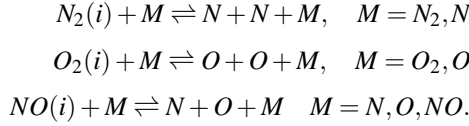
$$\tau_{tr} \leq \tau_{rot} \leq \tau_{VV} \ll \tau_{VT} \leq \tau_{react} \sim \theta. \quad (1)$$

Here $\tau_{tr}, \tau_{rot}, \tau_{VV}, \tau_{VT}, \tau_{react}$ are, respectively, the mean times between collisions with translational, rotational energy transfer, VV energy exchange, VT relaxation and those with chemical reactions, θ is the macroscopic relaxation time. For describing populations of the vibrational levels the Treanor vibrational distribution has been used [2]:

$$n_i = \frac{n_{mol}}{Z_{vibr}(T, T_1)} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), \quad (2)$$

where $Z_{vibr}(T, T_1)$ is the non-equilibrium vibrational partition function, T is the gas temperature, T_1 is the temperature of the first vibrational level, n_{mol} is the molar fraction, k is the Boltzmann constant, ε_i is the vibrational energy of the i -th vibrational level of an anharmonic oscillator. In the case of thermal equilibrium n_i are described by the Boltzmann distribution with the gas temperature T .

The reaction system is the following:



For the stationary one-dimensional flow in two-components mixture behind a plane shock wave the system of equations has the form [1]:

$$\begin{aligned} \frac{d(n_{mol}v)}{dx} &= R^{diss-rec}, \\ \frac{d(n_{at}v)}{dx} &= R_a, \\ \rho v \frac{dv}{dx} &= -\frac{dp}{dx}, \\ v \frac{dE}{dx} + (p + E) \frac{dv}{dx} &= 0, \\ \frac{d(Wv)}{dx} &= R_w. \end{aligned} \quad (3)$$

Here n_{mol} and n_{at} are the number densities of molecules and atoms, $\rho = n_{mol}m_{mol} + n_{at}m_{at}$ is the gas density, m_{mol} , m_{at} are the masses of a molecule and an atom respectively, v is the velocity, $p = (n_{mol} + n_{at})kT$ is the pressure, E is the energy per unit volume:

$$E(n_{mol}, n_{at}, T, T_1) = \frac{5}{2}n_{mol}kT + \frac{3}{2}n_{at}kT + E_{vibr}(T, T_1, n_{mol}) + E_f,$$

where

$$E_{vibr}(T, T_1, n_{mol}) = \sum_{i=0}^L \varepsilon_i n_i(T, T_1, n_{mol}), \quad E_f = \frac{1}{2}n_{at}D,$$

D is the dissociation energy of a molecule. In the case of three-components mixture we have n_{at_1} and n_{at_2} and, respectively, two equations for number densities of atoms in Eqs. (3); in the equations for p and E we have $n_{at} = n_{at_1} + n_{at_2}$ and $E_f = e_{fmol}n_{mol} + e_{fat_1}n_{at_1} + e_{fat_2}n_{at_2}$. Here $e_{fmol}, e_{fat_1}, e_{fat_2}$ are the energies of formation of molecule and atoms.

In the case of binary mixture production terms of Eqs. (3) are the following [1]:

$$\begin{aligned} R^{diss-rec} &= R^{diss} + R^{rec}, \\ R^{diss} &= -n_{mol}(n_{at}k_{diss}^{at} + n_{mol}k_{diss}^{mol}), \\ R^{rec} &= n_{at}^2(n_{at}k_{rec}^{at} + n_{mol}k_{rec}^{mol}), \\ R_w &= R_w^{vibr} + R_w^{diss-rec}, \\ R_w^{vibr} &= \sum_{i=0}^L i(R_i^{VT(mol)} + R_i^{VT(at)}), \\ R_w^{diss-rec} &= R_w^{diss} + R_w^{rec}. \end{aligned} \quad (4)$$

In the case of three-components mixture production terms of Eqs. (3) have the form:

$$\begin{aligned}
R^{diss-rec} &= R^{diss} + R^{rec}, \\
R^{diss} &= -n_{mol}(n_{at_1}k_{diss}^{at_1} + n_{at_2}k_{diss}^{at_2} + n_{mol}k_{diss}^{mol}), \\
R^{rec} &= n_{at_1}n_{at_2}(n_{at_1}k_{rec}^{at_1} + n_{at_2}k_{rec}^{at_2} + n_{mol}k_{rec}^{mol}), \\
R_w^{vibr} &= \sum_{i=0}^L i(R_i^{VT(mol)} + R_i^{VT(at_2)} + R_i^{VT(at_1)}).
\end{aligned} \tag{5}$$

Here $k_{diss}^{(M)}(T, T_1)$ is the two-temperature rate coefficient of the dissociation, it has been obtained by averaging of state-to-state rate coefficients with Treanor two-temperature distribution [6], recombination rate coefficient $k_{rec}^{(M)}(T)$ has been calculated using the detailed balance principle [1]. Detailed expressions for R_w^{vibr} and $R_w^{diss-rec}$ are given in [1]. For the calculation of the rate coefficients of vibrational energy transitions we use approximate formulas of Capitelli [7]. Thermal equilibrium rate coefficient $k_{diss}^{(eq,M)}(T)$ is calculated using the generalized Arrhenius law. According to [1] we have the following expressions for $k_{diss}^{(M)}(T, T_1)$:

$$\begin{aligned}
k_{diss}^{(M)}(T, T_1) &= Z^{(M)}(T, T_1, U)k_{diss}^{(eq,M)}(T), \\
Z^{(M)}(T, T_1, U) &= \frac{1}{n_{mol}} \sum_i n_i Z_i^{(M)}(T, U), \\
Z_i^{(M)}(T) &= \frac{Z_{vibr}(T)}{Z_{vibr}(-U)} \exp\left(\frac{\epsilon_i}{k} \left(\frac{1}{U} + \frac{1}{T}\right)\right),
\end{aligned}$$

where $Z_{vibr}(T)$ is the equilibrium partition function, U is the parameter of the dissociation model, a partner M can be a molecule or atom. In order to estimate thermodynamic properties of the gas flow we have defined nonequilibrium specific heats as follows:

$$C_v^T(T, T_1) = \frac{\partial E_{vibr}(T, T_1)}{\partial T}, \quad C_v^{T_1}(T, T_1) = \frac{\partial E_{vibr}(T, T_1)}{\partial T_1}, \quad C_v^{T,eq}(T) = \frac{\partial E_{vibr}(T)}{\partial T}.$$

RESULTS AND DISCUSSION

State-to-state nonequilibrium factor $Z_i(T, U)$ as a function of i is presented in Fig. 1a. Different values of the parameter U were used for calculation. It is seen that $Z_i^{NO}(T)$ and $Z_i^{O_2}(T)$ have similar plots; in the cases of $U = 3T$ and $U = D/6k$ we have similar values of $Z_i^{NO}(T)$ for all vibrational levels but in O_2 we have it only for high levels ($i > 20$); in the case of $U = \infty$ we have higher values of Z_i for low levels and smaller values of Z_i for high levels than in the case of using other values of U . The comparison of the values $Z(T, T_1, U)$ in N_2 , O_2 and NO is shown in Fig. 1b. Fixed vibrational temperature $T_1 = 3000$ K and $U = D/6k$ are used.

The temperature dependence of $k_{diss}^{(M)}(T, T_1)$ is seen from Fig. 2a, the thermal equilibrium dissociation rate coefficient $k_{diss}^{(eq,M)}$ is also plotted in Fig. 2a. (NO, N, O) mixture and different values of U are considered. One can notice that $U = \infty$ and one-temperature model give overestimated values of dissociation rate coefficients in the case of $T > T_1$. Fig. 2b plots temperature dependence of the vibrational specific heats $c_v^{T,eq}/(k/m)$. The results for N_2 , O_2 and NO are presented.

Equations (3) have been solved numerically at the following free stream conditions: $T_0 = 293$ K, $p_0 = 100$ Pa, $n_{at,0} = 0.2n$, $n_{mol,0} = 0.8n$ (in the case of three-components mixture $n_{N_0} = n_{O_0} = 0.1n$), $M = 10$ and $M = 5$. The vibrational distributions in a free stream are assumed to be equilibrium Boltzmann distributions with gas temperature T_0 .

Figs. 3a and 3b plot the gas temperature and the vibrational temperature T_1 behind a shock. One can notice that the one-temperature model underestimates the gas temperature, especially in the beginning of a relaxation zone. Increase of Mach number in a free stream leads to higher vibrational temperature T_1 in a relaxation zone.

Fig. 4 gives the number densities of atoms and molecules as functions of x . The results show weak influence of the vibrational distributions due to rapid vibrational relaxation of NO , the maximum deviation does not exceed 5%.

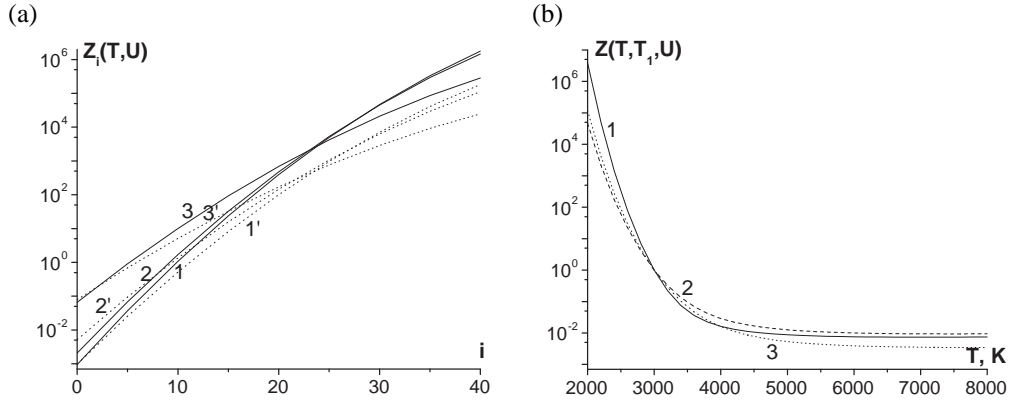


FIGURE 1. (a) State-to-state nonequilibrium factor $Z_i(T, U)$ as a function of i , $T = 5000$ K, NO and O_2 . 1, 1' — $U = D/6k$, 2, 2' — $U = 3T$, 3, 3' — $U = \infty$. Solid lines — NO , dashed lines — O_2 . (b) Averaged nonequilibrium factor $Z(T, T_1, U)$ as a function of T , $T_1 = 3000$ K. 1 — $Z^{N_2}(T, T_1, U)$, 2 — $Z^{NO}(T, T_1, U)$, 3 — $Z^{O_2}(T, T_1, U)$.

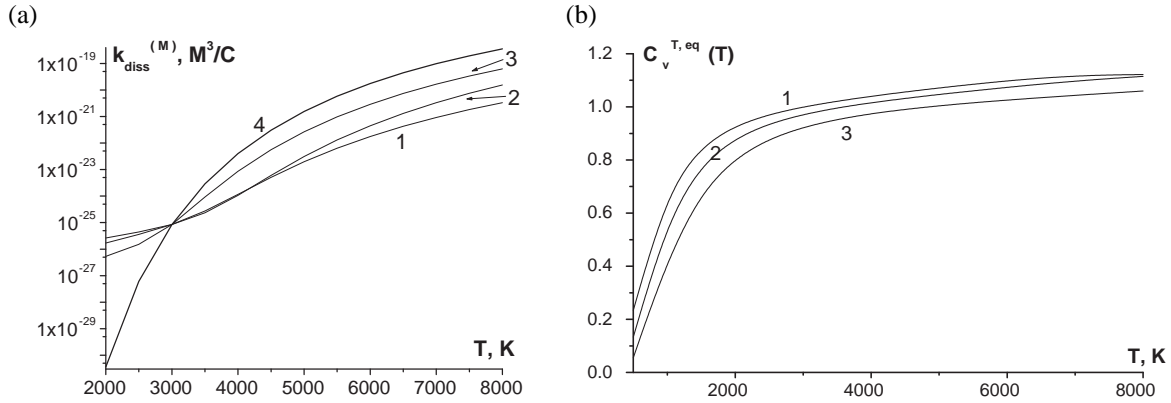


FIGURE 2. (a) Dissociation rate coefficient $k_{diss,NO}^N$ as a function of temperature, $T_1 = 3000$ K. 1 — $U = D/6k$, 2 — $U = 3T$, 3 — $U = \infty$, 4 — thermal equilibrium rate coefficient. (b) Dimensionless vibrational specific heats $c_v^{T,eq}/(k/m)$ as a function of T . 1 — O_2 , 2 — NO , 3 — N_2

As it has been pointed above in considered cases the results of calculations have shown weak influence of recombination on macroscopic parameters behind shock wave. The maximum influence of recombination is found to be about 4%.

Fig. 5a plots the dissociation rate coefficient as a function of x behind shock wave. It can be seen that the one-temperature approach gives the unreal high dissociation rate in the beginning of a relaxation zone. Comparison of two-temperature and Arrhenius dissociation rates shows that the latter ones give strong overestimation of dissociation rates in the beginning of a relaxation zone in all cases considered and their underestimation in near-equilibrium regime. Dimensionless vibrational specific heats $c_v^{T,eq}/(k/m)$ as a function of x are plotted in Fig. 5b. A comparison between (N_2, N) and (O_2, O) mixtures is shown.

CONCLUSIONS

Non-equilibrium kinetics, gas dynamic parameters and thermodynamic properties are studied in gas flows of air species behind shock waves. The comparison of the results showed the influence of different vibrational distributions on

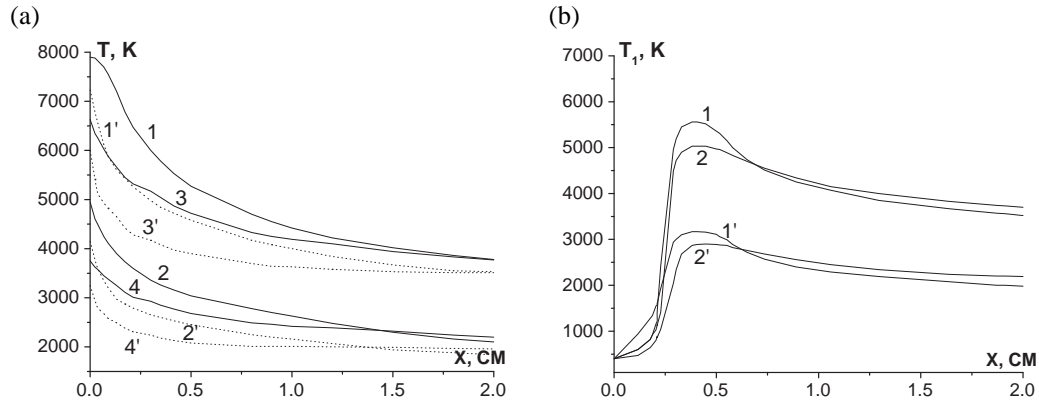


FIGURE 3. (a) Gas temperature as a function of x , (N_2, N) and (O_2, O). 1, 1', 2, 2' — (N_2, N), 3, 3', 4, 4' — (O_2, O); 1, 1', 3, 3' — $M = 10$, 2, 2', 4, 4' — $M = 5$. Solid lines — two-temperature approach, dashed lines — one-temperature approach. (b) Vibrational temperature T_1 as a function of x . 1, 1' — N_2 , $M = 10$, $M = 5$; 2, 2' — O_2 , $M = 10$, $M = 5$.

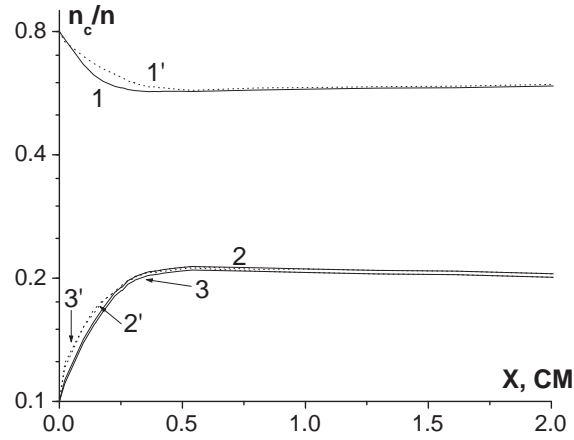


FIGURE 4. Number densities of atoms and molecules as functions of x , $M = 5$, (NO, N, O), 1, 2, 3 — two-temperature approach, 1', 2', 3' — one-temperature approach. 1, 1' — n_{NO} , 2, 2' — n_O , 3, 3' — n_N .

gas dynamic parameters, thermodynamic properties and global reaction rates behind a shock. Thus, one-temperature approximation gives an underestimation of the gas temperature behind a shock wave and does not describe the delay of dissociation, especially in the beginning of the relaxation zone. In considered cases the results of calculations have shown weak influence of recombination on macroscopic parameters behind shock wave and prevalence of dissociation process. The increase of intensity of a shock wave in a free stream gives higher values of the vibrational temperature in the relaxation zone. The proposed multi-temperature model can be recommended for applications for shock heated gases due to its simplicity and satisfactory accuracy.

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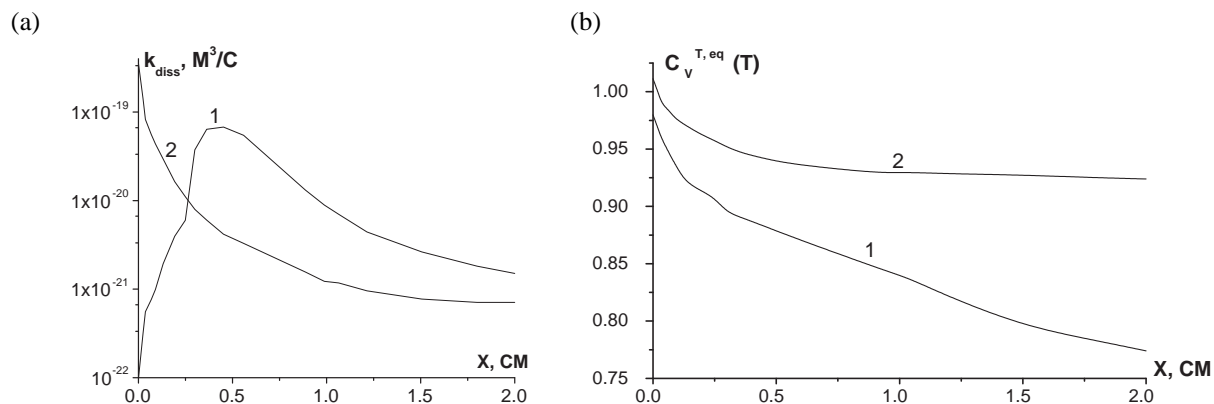


FIGURE 5. (a) Dissociation rate coefficient $k_{diss}^{O_2}$ as a function of x . 1 — two-temperature approach, 2 — one-temperature approach. (b) Dimensionless vibrational specific heats $c_v^{T,eq}/(k/m)$ as a function of x . 1 — (N_2, N) , 2 — (O_2, O) , $M = 5$.

REFERENCES

1. Nagnibeda E.A., Kustova E.V. Kinetic theory of transport processes and relaxation in non-equilibrium reacting flows // St. Petersburg University Press, St. Petersburg, 2003, p. 270
2. Treanor C.E., Rich J.W., Rehm R.G. Vibrational relaxation of anharmonic oscillators with exchange dominated collisions. — J. Chem. Phys. 1968. Vol. 48. P. 1798-1807.
3. Capitelli M., Ferreira C.M., Gordiets B.F. and Osipov A.I. Plasma kinetics in atmospheric gases, Berlin: Springer-Verlag, Berlin, 2000. 302p.
4. E.A. Kovach, S.A. Losev, and A.L. Sergievskaya Chem. Phys. Rep., 14, 1357-1387, (1995).
5. Karakulko K. I., Nagnibeda E. A. Aerodynamics, St. Petersburg University Press, St. Petersburg, 2004, pp. 32-46
6. Marrone P.V. and Treanor C.E. Chemical relaxation with preferential dissociation from excited vibrational levels. — J. Phys. Fluids. 1963. Vol. 6. P. 1215-1221.
7. Capitelli M., Armenise I., Gorse C. State-to-state approach in the kinetics of air components under re-entry conditions. — J. Thermophys. Heat Transfer. 1997. Vol. 11. No. 4. P. 570-578.
8. Chikhaoui A., Dudon J.P., Genieys S., Kustova E.V., and Nagnibeda E.A. Multi-temperature kinetic model for heat transfer in reacting gas mixture. — J. Phys. Fluids. 2000. Vol. 12. No. 1. P. 220-232.