Vibrational-Chemical Coupling in mixtures $CO_2/CO/O$ and $CO_2/CO/O_2/O/C$

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Abstract. The paper deals with modeling of vibration-chemical coupling in mixtures containing CO_2 molecules. The temporal vibrational and chemical relaxation in the five-component and three-component space-homogeneous mixtures $CO_2/CO/O_2/C/O$ and $CO_2/CO/O$ is studied taking into account vibrational energy transitions, dissociation, recombination and exchange chemical reactions. The vibrational-chemical coupling in considered mixtures is studied on the basis of three-temperature, two-temperature and one-temperature vibrational CO_2 distributions. Governing equations for macroscopic mixture parameters in the three-temperature, two-temperature and one-temperature approximations are solved numerically for different initial conditions. Comparison of the results obtained in three approaches showed the influence of non-equilibrium vibrational distributions on chemical reaction rates and on the temporal variation of the gas temperature, mixture composition and vibrational temperatures in two considered mixtures. The role of exchange chemical reactions in relaxation processes is also discussed in the paper.

1. Introduction

Modeling of non-equilibrium processes in mixtures containing CO_2 molecules is important for prediction of gas parameters near bodies moving in the Mars or Venus atmosphere [1, 2], in laser physics [3, 4, 5, 6, 7], chemical technology problems and other applications. During several last decades different models for non-equilibrium vibration-dissociation kinetics in CO_2 flows were elaborated. First of these models were proposed introducing a single vibrational temperature for three modes of a CO_2 molecule vibrations [8, 3, 9], then more accurate two-temperature CO_2 vibrational distributions were derived using the kinetic theory methods [10] and applied for simulations of a flow in a shock layer near a spacecraft Mars Sample Return Orbiter (MSRO) entering the Mars atmosphere [11]. In the present time, advances in numerical modeling made it possible to study the detailed vibrational CO_2 kinetics in the frame of the most accurate state-to-state approach [12, 13] solving the equations for populations of vibrational levels of all three (symmetric, bending and asymmetric) CO_2 modes. However, a practical use of the state-to-state kinetic model for prediction of CO_2 flow parameters calls some difficulties. First, practical realization of this model for mixtures containing CO_2 molecules requires to solve a huge number of equations for populations of vibrational levels of all three CO_2 modes. Another problem is connected with a lack of data for state dependent rate coefficients for vibrational energy transitions within three CO_2 modes and between different modes. Therefore simplified CO_2 kinetic models based on multi-temperature vibrational distributions remain attractive for practical applications.

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In the present paper we study the vibrational-chemical coupling in the space-homogeneous five-component mixture $CO_2/CO/O_2/O/C$ with the use of three models proposed in [11], [10]. Within the first model, non-equilibrium vibrational distributions of CO_2 molecules are expressed in terms of two vibrational temperatures for combined symmetric-bending and asymmetric modes. In the second case the total vibrational temperature different from the gas temperature is introduced for all three CO_2 modes whereas the third model corresponds to the thermal equilibrium vibrational CO_2 distributions depending only on the gas temperature. Temporal relaxation of the considered mixture for different initial conditions is studied taking into account vibrational energy transitions of CO_2 molecules as well as dissociation, recombination and exchange reactions and the influence of CO_2 vibrational distributions on reaction rate coefficients and variation of macroscopic mixture parameters with time is analyzed. Calculations have been done also for a simplified case of vibration-dissociation relaxation in the three-component mixture $CO_2/CO/O$. The comparison of the results obtained for two considered mixtures showed a role of a chemical kinetics scheme in relaxation processes.

2. Vibrational distributions and basic equations

We consider vibrational-chemical kinetics in the high-temperature five-component mixture $CO_2/CO/O_2/O/C$ taking into account dissociation of CO_2, O_2 and CO molecules, recombination and exchange reactions:

$$CO_2 + M \leftrightarrow CO + O + M, \tag{1}$$

$$O_2 + M \leftrightarrow O + O + M, \tag{2}$$

$$CO + M \leftrightarrow C + O + M, \tag{3}$$

$$M = CO_2, CO, O_2, O, C,$$

$$CO_2 + O \leftrightarrow CO + O_2, \tag{4}$$

$$CO + O \leftrightarrow C + O_2, \tag{5}$$

$$CO + CO \leftrightarrow CO_2 + C. \tag{6}$$

Internal energy relaxation includes different processes. It is well known that the translational and rotational energy relaxation proceeds much faster comparable to vibrational relaxation, therefore we consider equilibrium distributions over translational and rotational energy with the gas temperature. The vibrational kinetics in the considered mixture includes the following channels [11]: intra-mode VV_m vibrational energy exchanges within the each CO_2 mode ($m = 1, 2, 3$) and in O_2 and CO molecules (VV_{O_2}, VV_{CO}); VT_m, VT_{O_2}, VT_{CO} vibrational- translational energy transitions of different CO_2 modes and of O_2 and CO molecules; VV vibrational exchanges between molecules of various species VV_{3-CO}, VV_{1-2-CO}, VV_{1-2-O_2}, VV_{CO-O_2}. Existing experimental data on relaxation times of different processes in mixtures containing CO_2 molecules [14, 15] show that under wide conditions intra-mode VV_m transitions and VV_{1-2} exchanges between the bending and symmetric modes in CO_2 molecules occur much faster than all other energy VV exchanges between two or three modes, $VT_m (m = 1, 2, 3, CO, O_2)$ exchanges of translation and vibrational energies and chemical reactions. In this case the following relation between relaxation times of various processes can be written [11]:

$$\tau_{tr} < \tau_{rot} < \tau_{VV_m} \sim \tau_{VV_{1-2}} \ll \tau_{VT_2} \sim \tau_{VV_{2-3}} \sim \tau_{VV_{1-2-3}} \sim \tau_{VT_3} \sim \tau_{react} \sim \theta, \quad m = 1, 2, 3, \tag{7}$$

here θ is the mean time of variation of macroscopic mixture parameters.

Rapid energy exchanges between bending and symmetric modes and within the asymmetric mode makes it possible to introduce the vibrational temperature T_{12} for combine symmetric-bending mode and T_3 for the asymmetric mode of CO_2 molecules. In this case vibrational level populations of two-temperature vibrational distributions take the form (see [16, 17]):

$$n_{i_1 i_2 i_3}(T_{12}, T_3) = \frac{n_{CO_2}(i_2+1)}{Z_{vibr}^{CO_2}(T_{12}, T_3)} \exp\left(-\frac{i_1\varepsilon_{100} + i_2\varepsilon_{010}}{kT_{12}} - \frac{i_3\varepsilon_{001}}{kT_3}\right). \tag{8}$$

Here n_{CO_2} is the CO_2 number densities, k is the Boltzmann constant, $Z_{vibr}^{CO_2}(T, T_{12}, T_3)$ is the non-equilibrium CO_2 vibrational partition function.

Following [11] we also suppose that CO and O_2 molecules equilibrate faster than CO_2 and therefore vibrational level populations of these molecules may be described by the thermal equilibrium Boltzmann distributions:

$$n_i^c(T) = \frac{n_c}{Z_{vibr}^c(T)} \exp\left(-\frac{\varepsilon_i^c}{kT}\right),$$

where $Z_{vibr}^c(T)$ is the vibrational partition function of spicies c, $\varepsilon_i^c = ih\nu_c$ is the vibrational energy of diatomic molecule c in the case of harmonic oscillations, ν_c is the frequencies of vibrations molecules c, h is the Plank constant. All distributions hereafter are considered for the harmonic oscillator model.

Under the conditions (7) closed description of vibrational-chemical relaxation in the space-homogeneous mixture $CO_2/CO/O_2/O/C$ is given by the set of macroscopic parameters including number densities of chemical species $n_{CO_2}, n_{CO}, n_{O_2}, n_O, n_C$, gas temperature T and two vibrational temperatures T_{12}, T_3 of coupled symmetric-bending and asymmetric CO_2 modes.

The system of equations for these macroscopic parameters includes equations of non-equilibrium vibrational-chemical kinetics coupled to the conservation equation for the total mixture energy:

$$\frac{dn_c}{dt} = R_c^{react}, \tag{9}$$
$$c = CO_2, CO, O_2, O, C,$$
$$\rho_{CO_2}\frac{dE_{12}}{dt} = R_{12} - m_{CO_2}E_{12}R_{CO_2}^{react}, \tag{10}$$
$$\rho_{CO_2}\frac{dE_3}{dt} = R_3 - m_{CO_2}E_3R_{CO_2}^{react}, \tag{11}$$
$$\frac{3}{2}nkT + (n_{CO_2} + n_{CO} + n_{O_2})kT + \rho_{CO_2}E_{vibr}^{CO_2}(T_{12}, T_3) + \rho_{CO}E_{vibr}^{CO}(T) + \tag{12}$$
$$+ \rho_{O_2}E_{vibr}^{O_2}(T) + n_{CO_2}\varepsilon_{CO_2} + n_{CO}\varepsilon_{CO} + n_{O_2}\varepsilon_{O_2} + n_O\varepsilon_O + n_C\varepsilon_C = const.$$

Here $n = n_{CO_2} + n_{CO} + n_{O_2} + n_O + n_C$ is the total numeric density, ε_c is the formation energy, E_{12}, E_3 are the vibrational energies of the coupled and asymmetric CO_2 modes:

$$\rho_{CO_2}E_{12}(T_{12}) = \frac{n_{CO_2}}{Z_{12}(T_{12})}\sum_{i_1,i_2}(i_1\varepsilon_{100} + i_2\varepsilon_{010})(i_2+1)\exp\left(-\frac{i_1\varepsilon_{100} + i_2\varepsilon_{010}}{kT_{12}}\right), \tag{13}$$

$$\rho_{CO_2}E_3(T_3) = \frac{n_{CO_2}}{Z_3(T_3)}\sum_{i_3} i_3\varepsilon_{001}\exp\left(-\frac{i_3\varepsilon_{001}}{kT_3}\right), \tag{14}$$

where $Z_{12}(T_{12})$, $Z_3(T_3)$ are the vibrational partition function of the coupled and asymmetric CO_2 modes.

In (12) $E_{vibr}^{CO_2}(T_{12},T_3)$, $E_{vibr}^{CO}(T)$, $E_{vibr}^{O_2}(T)$ are the vibrational energies of molecules CO_2, CO, O_2 per the unit mass:

$$\rho_{CO_2}E_{vibr}^{CO_2}(T_{12},T_3)=\frac{n_{CO_2}}{Z_{vibr}^{CO_2}(T_{12},T_3)}\sum_{i_1,i_2,i_3}(i_1\varepsilon_{100}+i_2\varepsilon_{010}+i_3\varepsilon_{001})(i_2+1)\cdot \tag{15}$$

$$\cdot\exp\left(-\frac{i_1\varepsilon_{100}+i_2\varepsilon_{010}}{kT_{12}}-\frac{i_3\varepsilon_{001}}{kT_3}\right),$$

$$\rho_c E_{vibr}^{c}(T)=n_c\frac{h\nu_c}{\exp\left(\frac{h\nu_c}{kT}\right)-1},\quad c=CO,O_2.$$

Production terms R_{react}^{c}, R_{12}, R_3 in equations (9) – (11) describe variation of mixture composition due to chemical reactions and changing of vibrational energies E_{12}, E_3.

If all VV vibrational energy exchanges within and between three CO_2 modes proceed faster than VT_m transitions and chemical reactions the total vibrational temperature $T_v=T_{12}=T_3$ for CO_2 molecules may be introduced and vibrational distributions (8) take the form:

$$n_{i_1i_2i_3}(T_v)=\frac{n_{CO_2}(i_2+1)}{Z_{vibr}^{CO_2}(T_v)}\exp\left(-\frac{i_1\varepsilon_{100}+i_2\varepsilon_{010}+i_3\varepsilon_{001}}{kT_v}\right). \tag{16}$$

In this case the system of governing equations contains, instead of two equations (10), (11), only one equation which follows from (15) if $T_{12}=T_3=T_v$:

$$\rho_{CO_2}\frac{dE_{CO_2}^{vibr}(T_v)}{dt}=R_{CO_2}-m_{CO_2}E_{CO_2}^{vibr}(T_v)R_{CO_2}^{react},$$

where

$$\rho_{CO_2}E_{CO_2}^{vibr}(T_v)=\frac{n_{CO_2}}{Z_{vibr}^{CO_2}(T_v)}\sum_{i_1,i_2,i_3}(i_1\varepsilon_{100}+i_2\varepsilon_{010}+i_3\varepsilon_{001})\,(i_2{+}1)\exp\left(-\frac{i_1\varepsilon_{100}+i_2\varepsilon_{010}+i_3\varepsilon_{001}}{kT_v}\right)$$

is the vibrational energy of CO_2 molecules.

If the relaxation time of all internal energy modes of mixture components occurs considerably shorter than the mean time of chemical reactions, vibrational level populations are described by the Boltzmann thermal equilibrium distributions (16) with $T_v=T$. In this case non-equilibrium chemical reactions are simulated on the basis of maintaining thermal equilibrium vibrational distributions. The set of equations for macroscopic parameters n_{CO_2}, n_{CO}, n_{O_2}, n_O, n_C, T contains equations of chemical kinetics (9) with reaction rate coefficients depending only on the gas temperature and the energy conservation equation.

3. Reaction rate coefficients

Let us consider right hand part of equation (9):

$$R_c^{react}=R_c^{diss}+R_c^{exch},c=CO_2,CO,O_2,O,C.$$

Dissociation-recombination processes are described by the following expressions:

$$R_{CO_2}^{diss}=\sum_M n_M\left(k_{rec,CO_2}^M(T)n_{CO}n_O-k_{diss,CO_2}^M(T,T_{12},T_3)n_{CO_2}\right),$$

$$R_{CO}^{diss}=\sum_M n_M\left(k_{rec,CO}^M(T)n_O n_C-k_{diss,CO}^M(T)n_{CO}\right),$$

$$R_{O_2}^{diss}=\sum_M n_M\left(k_{rec,O_2}^M(T)n_O^2-k_{diss,O_2}^M(T)n_{O_2}\right),$$

here $k^M_{diss,c}$, $k^M_{rec,c}$ are the coefficients of dissociation and recombination ratea of spicies c, M is the collision partner.

The dissociation rate coefficient for carbon dioxide in the three-temperature approximation may be written in the form of the generalized Treanor-Marrone model for multiatomic molecules [10]:

$$k^M_{diss,CO_2}(T,T_{12},T_3) = k^{eq,M}_{diss,CO_2}(T)\frac{Z^{CO_2}_{vibr}(T)}{Z^{CO_2}_{vibr}(-U)Z^{CO_2}_{vibr}(T_{12},T_3)}\sum_{i_1,i_2,i_3}(i_2+1)\cdot \tag{17}$$
$$\cdot\exp\left(\left(\frac{i_1\varepsilon_{100}+i_2\varepsilon_{010}}{k}\right)\left(\frac{1}{T}-\frac{1}{T_{12}}\right)+\frac{i_3\varepsilon_{001}}{k}\left(\frac{1}{T}-\frac{1}{T_3}\right)+\frac{\varepsilon_{i_1i_2i_3}}{kU}\right),$$

here $\varepsilon_{i_1i_2i_3} = i_1\varepsilon_{100}+i_2\varepsilon_{010}+i_3\varepsilon_{001}$, $k^{eq,M}_{diss,CO_2}(T)$ is the equilibrium dissociation rate coefficient defined by the Arrenius law, U is a model parameter, in calculations we had $U = D/6k$. The dissociation of diatomic molecules is assumed equilibrium and dissociation rate coefficients are calculated according to the Arrenius law as well as CO_2 dissociation in the one-temperature approach. The dissociation rate coefficients in two-temperature approach take the form (17) under conditions $T_{12} = T_3 = T_v$ and the dissociation rate coefficients in one-temperature approach are equilibrium $k^{eq,M}_{diss,CO_2}(T)$. For calculation of rate coefficients in the paper used the Park model [1].

Recombination rate coefficients are determined on the basis of detailed balance principle [10]:

$$k^M_{rec,CO_2}(T) = k^{eq,M}_{diss,CO_2}(T)\cdot$$
$$\cdot\left(\frac{m_{CO_2}}{m_{CO}m_O}\right)^{3/2}(2\pi kT)^{-3/2}h^3\frac{Z^{CO_2}_{vibr}(T)Z^{CO_2}_{rot}(T)}{Z^{CO}_{vibr}(T)Z^{CO}_{rot}(T)}\exp\left(-\frac{\varepsilon_{CO_2}-\varepsilon_{CO}-\varepsilon_O}{kT}\right),$$

$$k^M_{rec,CO}(T) = k^{eq,M}_{diss,CO}(T)\cdot$$
$$\cdot\left(\frac{m_{CO}}{m_Cm_O}\right)^{3/2}(2\pi kT)^{-3/2}h^3Z^{CO}_{vibr}(T)Z^{CO}_{rot}(T)\exp\left(-\frac{\varepsilon_{CO}-\varepsilon_O-\varepsilon_C}{kT}\right),$$

$$k^M_{rec,O_2}(T) = k^{eq,M}_{diss,O_2}(T)\left(\frac{2}{m_O}\right)^{3/2}(2\pi kT)^{-3/2}h^3Z^{O_2}_{vibr}(T)Z^{O_2}_{rot}(T)\exp\left(\frac{2\varepsilon_O}{kT}\right),$$

here m_c is the mass of species c, $Z^{CO_2}_{rot}(T)$, $Z^{CO}_{rot}(T)$, $Z^{O_2}_{rot}(T)$ are the rotational partition functions of CO_2, CO and O_2 molecules.

For accurate determination of exchange reaction rate coefficients state-dependent coefficients for rates of these reactions should be averaged over non-equilibrium vibrational distributions. However at present time analytical expressions for rate coefficients depending on vibrational levels of CO_2 modes are not available in the literature. Therefore in the present paper we consider the classical expression for R^{exch}_c with one-temperature rate coefficients:

$$R^{exch}_c = \sum_{dc'd'}\left(k^{d'\to d}_{c'\to c}(T)n_{c'}n_{d'} - k^{d\to d'}_{c\to c'}(T)n_cn_d\right).$$

Rate coefficients for the backward reactions are found using the detailed balance principle:

$$k_{C\to CO}^{CO_2\to CO}(T) = k_{CO\to C}^{CO\to CO_2}(T)\left(\frac{m_{CO}^2}{m_{CO_2}m_c}\right)^{3/2}\frac{\left(Z_{vibr}^{CO}(T)Z_{rot}^{CO}(T)\right)^2}{Z_{vibr}^{CO_2}(T)Z_{rot}^{CO_2}(T)}\exp\left(\frac{-D_{CO_2}+2D_{CO}}{kT}\right),$$

$$k_{O_2\to O}^{CO\to CO_2}(T) = k_{O\to O_2}^{CO_2\to CO}(T)\left(\frac{m_{CO_2}m_O}{m_{CO}m_{O_2}}\right)^{3/2}\frac{Z_{vibr}^{CO_2}(T)Z_{rot}^{CO_2}(T)}{Z_{vibr}^{CO}(T)Z_{rot}^{CO}(T)Z_{vibr}^{O_2}(T)Z_{rot}^{O_2}(T)}\cdot$$
$$\cdot\exp\left(\frac{-D_{CO}-D_{O_2}+D_{CO_2}}{kT}\right),$$

$$k_{O_2\to O}^{C\to CO}(T) = k_{O\to O_2}^{CO\to C}(T)\left(\frac{m_{CO}m_O}{m_Cm_{O_2}}\right)^{3/2}\frac{Z_{vibr}^{CO}(T)Z_{rot}^{CO}(T)}{Z_{vibr}^{O_2}(T)Z_{rot}^{O_2}(T)}\exp\left(\frac{-D_{O_2}+D_{CO}}{kT}\right),$$

where D_{CO_2}, D_{CO}, D_{O_2} are the dissociation energies.

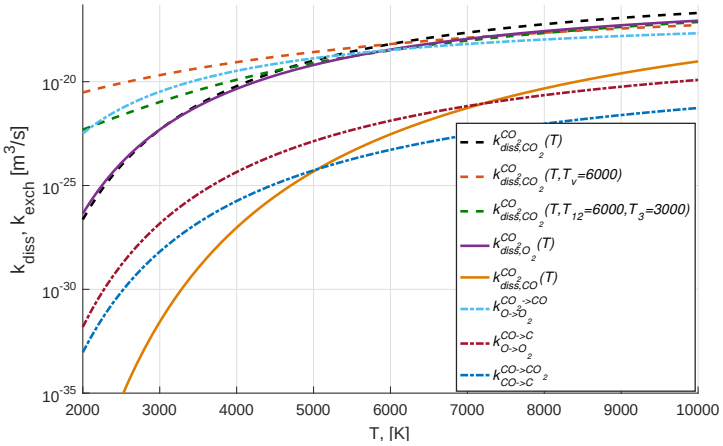


Figure 1. Reaction rate coefficients in dependence on the gas temperature T.

In figure 1 CO_2 dissociation rate coefficients calculated within three-temperature, two-temperature and one-temperature approaches are presented as well as one-temperature rate coefficients for dissociation of diatomic species (2), (3) and exchange reactions (4)-(6). Three-temperature and two-temperature coefficients are presented for fixed vibrational temperatures $T_{12} = 6000\ K$, $T_3 = 3000\ K$ and $T_v = 6000\ K$. It may be noticed that the one-temperature coefficients for CO_2 and O_2 dissociation (1), (2) as well as the forward exchange reaction (4) noticeably exceed coefficients for CO dissociation (3) and reactions (5), (6). In addition, comparing CO_2 dissociation rate coefficients calculated under considered conditions in three approaches one can conclude that one-temperature description provides underestimated values of coefficient $k_{diss,CO_2}(T)$ for the condition $T < T_{12} = 3000\ K$ and overestimated values of this coefficient for $T > T_3 = 6000\ K$ in comparison with the more accurate three-temperature coefficients $k_{diss,CO_2}(T, T_{12}, T_3)$. Similarly, we can notice that the one-temperature model leads to lower values of the coefficient $k_{diss,CO_2}(T)$ for $T < T_v = 6000\ K$ and higher its values for $T > T_v = 6000\ K$ in comparison with the two-temperature coefficient $k_{diss,CO_2}(T, T_v)$.

Now we consider the right hand parts of equations (10), (11) which describe changing of vibrational energies E_{12} and E_3 due to vibrational energy transitions. Following [18] we use approximate expressions of these parts via relaxation times:

$$R_{12} - m_{CO_2}R_{CO_2}^{react} = \rho_{CO_2}\sum_{\gamma}\frac{E_{12}^{eq}(T) - E_{12}(T_{12})}{\tau_\gamma}, \tag{18}$$

$$R_3 - m_{CO_2} R^{react}_{CO_2} = \rho_{CO_2} \sum_{\gamma} \frac{E_3^{eq}(T) - E_3(T_3)}{\tau_\gamma}, \tag{19}$$

where $\tau_\gamma, \gamma = VT_2, VV_{2-3}, VV_{1-2-3}$ were calculated on the basis of analytical approximations of experimental data [3, 14].

4. Results and discussion

In this section we present the results of numerical solutions of equations for number densities of species n_{CO_2}, n_{CO}, n_{O_2}, n_O, n_C, vibrational temperatures T_{12}, T_3, T_v and translation temperature T obtained for space-homogeneous five-component mixture in the three-temperature, two-temperature and one-temperature approaches. Calculations were done for the following initial conditions for temperatures and mixture composition: $T = 12000\ K$, $T_{12} = 6000\ K$, $T_3 = 3000\ K$, $T_v = 6000\ K$, $n_{CO_2} = 100\%$, $n_{CO} = n_{O_2} = n_O = n_C = 0$, $p = 1\ atm$. To solve stiff systems of ordinary differential equations we used the Gear method with a variable time step.

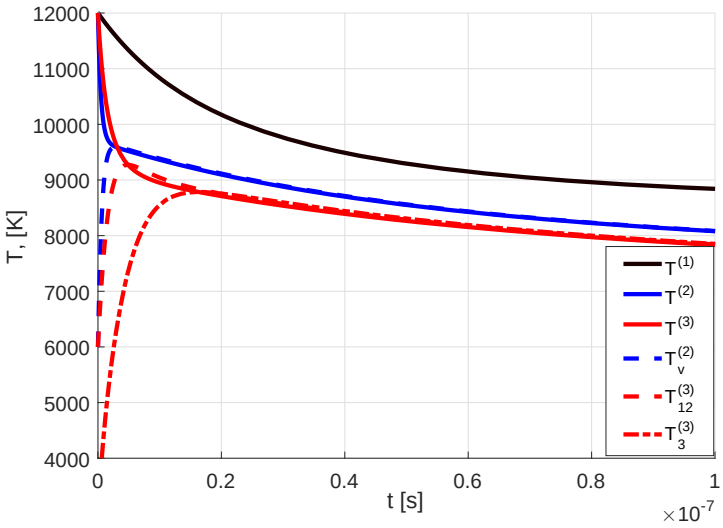


Figure 2. The gas temperature T and the vibrational temperature T_{12}, T_3, T_v in dependence on t; 1 – one-temperature, 2 – two-temperature, 3 – three-temperature approach.

In figure 2 temporal variation of the gas temperature T and vibrational temperatures T_{12}, T_3, T_v is shown whereas changing of the mixture composition in time for three approaches is demonstrated by figures 3 (a, b, c, d). It can be noticed that under considered conditions the use of the one-temperature approach provides noticeably overrated the gas temperature values than more accurate two-temperature and three-temperature kinetic models because in the one-temperature approach the mixture is considered in the thermal equilibrium and translation-vibrational energy transitions are not taken into account. The maximum difference between temperature values obtained in the three-temperature and one-temperature approaches reaches 12% whereas the two-temperature approach provides better consistency with T values obtained within the three-temperature model: the maximum discrepancy does not exceed 3%. In the considered cases of high initial values of the gas temperature vibrational relaxation proceeds much faster than chemical reactions which lead to chemical equilibrium establishing. The difference between parameters found in the frame of different kinetic schemes diminishes with time rising approaching to the equilibrium. Vibrational excitation of CO_2 molecules due to translational-vibrational energy transitions is seen in a short time interval (close to the initial moment of time) in the three-temperature and two-temperature approximations. Under

considered conditions this process is found more fast within the two-temperature description, whereas in the frame of the three-temperature model increasing of the vibrational temperature of the combined symmetric-bending mode proceeds more rapid than increasing of the vibrational temperature of the asymmetric mode.

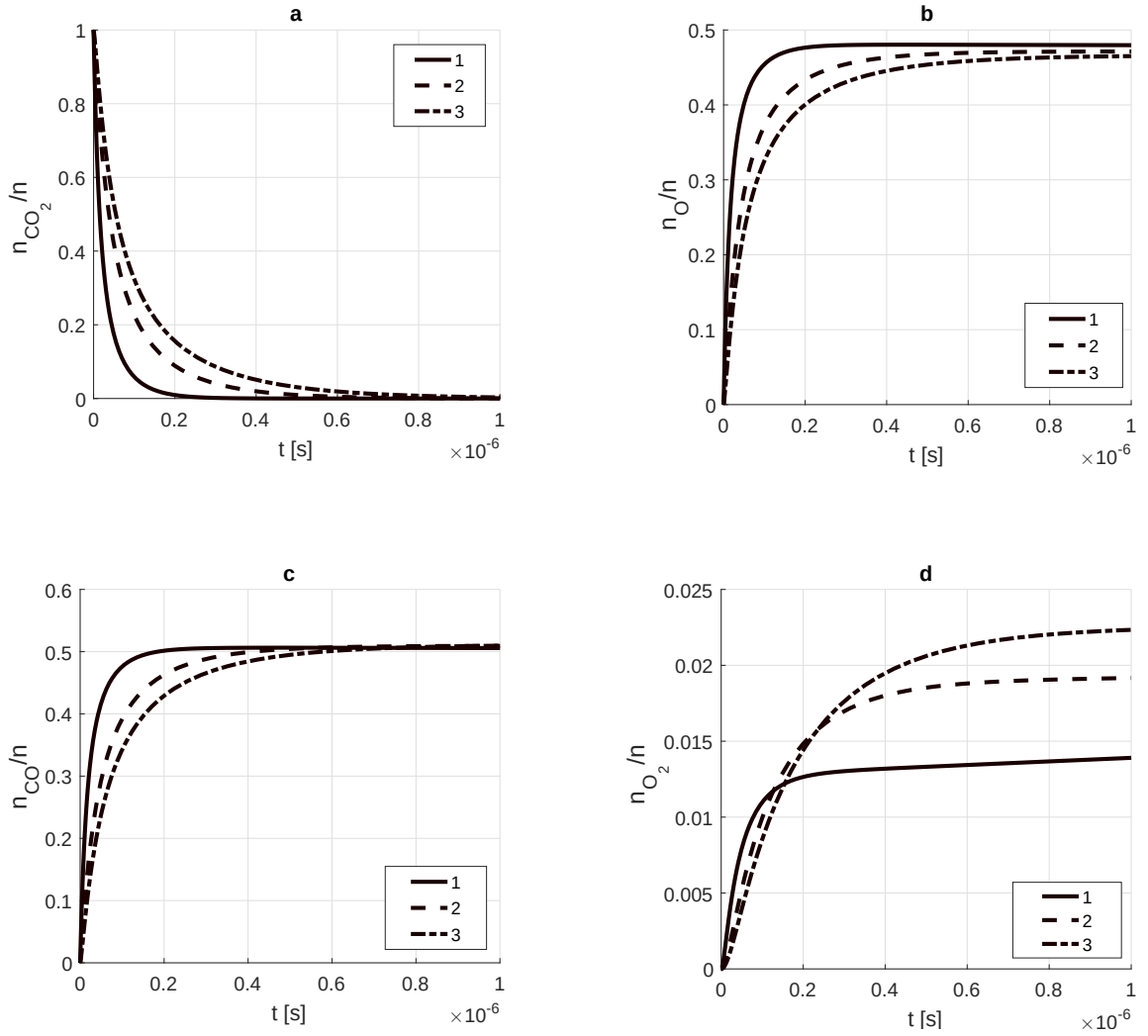


Figure 3. The relative number density of CO_2 (a), O (b), CO (c), O_2 (d) in dependence on t; 1 – one-temperature, 2 – two-temperature, 3 – three-temperature approach.

Figures 3 (a, b, c, d) show variation of number densities of mixture components CO_2 (a), O (b), CO (c), O_2 (d) with time. Again, the difference between parameters found within the non-equilibrium two-temperature and three-temperature CO_2 models occurs smaller than a discrepancy between the values obtained for thermal equilibrium and non-equilibrium CO_2 description. The values of number densities n_{CO_2}/n and n_{O_2}/n found in the three-temperature approach exceed equilibrium values more than in three times whereas the difference between the values found in the three-temperature and two-temperature approaches reaches 50%.

Rapid decreasing of CO_2 number densities due to dissociation reaction (1) (figure 3 a) resulting in increasing of number densities of O atoms (figure 3 b) and CO molecules (figure 3 c) is best seen in the one-temperature approach. Slower CO_2 dissociation within the two-temperature and three-temperature models than in the frame of one-temperature description is

explained by a delay of dissociation for vibrational CO_2 excitation for small t values in a short time interval.

It is interesting that though diatomic species are considered in this paper in the thermal equilibrium, one can see a noticeable influence of CO_2 kinetic models on number densities of CO molecules and oxygen atoms. As it is seen in figures 3 (b, c) densities of these species are rather high because they form mainly as a result of CO_2 dissociation with high reaction rate coefficients as it is seen in figure 1. Oxygen molecules are formed in result of the active exchange reaction (4) with the high rate coefficient (see figure 1), however the density of O_2 molecules decreases fast due to active O_2 dissociation as it is also shown in figure 1. The impact of CO_2 kinetics on variation of O_2 molecules (figure 3 d) and C atoms is not so important because densities of these species are rather low.

Now let us discuss the influence of a mixture composition on variation of the gas temperature and number densities of species. For this purpose we compare the results presented above for the five-component mixture $CO_2/CO/O_2/O/C$ with ones obtained for the three-component mixture $CO_2/CO/O$ under the same initial conditions. The dissociation reaction (1) is taken into account with $M = CO_2, CO, O$, whereas dissociation of CO molecules is not included to the kinetic scheme. Vibration-dissociation relaxation of this mixture was studied numerically in [19] on the basis of the equations for number densities of molecules CO_2, CO, atoms O and the total energy conservation equation. In the present paper calculations of the gas temperature and three-component mixture composition were carried out for the same initial conditions and using the same models for CO_2 dissociation and vibrational energy transitions as were applied for the five-component mixture. Below we present the comparison of the results obtained in the most accurate three temperature approach for two mixtures.

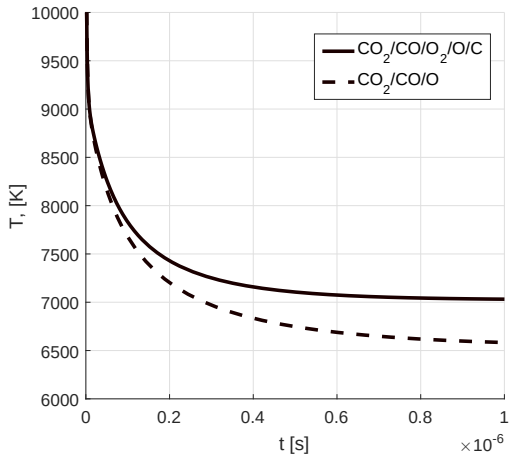


Figure 4. The gas temperature in dependence on t.

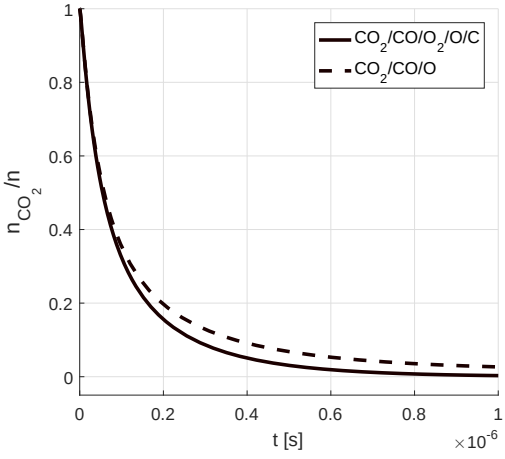


Figure 5. The relative number density n_{CO_2}/n, in dependence on t.

Figures 4, 5, 6 (a, b) plot the gas temperature T (figure 4) and number densities of species CO_2 (figure 5), CO (figure 6 a), O (figure 6 b) as functions of time for two considered mixtures. It may be noticed that in the beginning of the process, close to the initial moment of time, values of the gas temperature and number densities of species are found very close for both mixtures. It is explained by different characteristic times for vibrational and chemical relaxation. For small time values chemical reactions in both mixtures are frozen and the main process is the vibrational excitation of CO_2 molecules due to translational energy transitions to the vibrational energy. This process proceeds similarly in two mixtures and leads to close values of mixture parameters

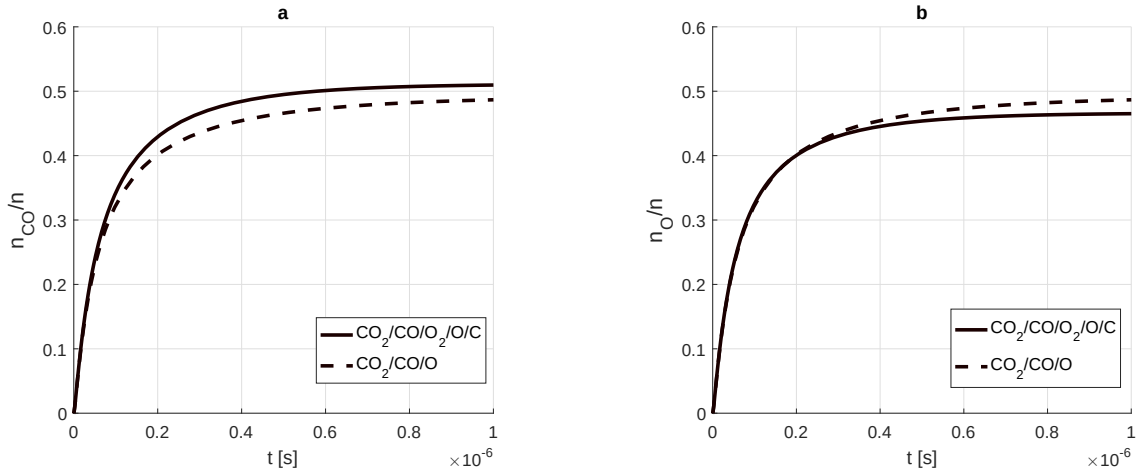


Figure 6. The relative number density n_{CO}/n (a), n_O/n (b) in dependence on t.

during a short time interval. Chemical relaxation and establishing of chemical equilibrium proceed differently in two mixtures. Calculations show higher temperature values in the five-component mixture (figure 4) and consequently more rapid dissociation and chemical reactions in this case than in the three-component mixture. Fast dissociation reaction (1) provides more intensive decrease of CO_2 number densities (figure 5) and increase of CO densities (figure 6 a) in the five-component mixture. Oxygen atoms form in result of the same dissociation reaction (1) in both mixtures. However values of n_O/n in the mixture $CO_2/CO/O_2/O/C$ (figure 6 b) are found lower than in the three-component mixture. It is explained by active O_2 dissociation reaction (2) in the five-component mixture.

5. Conclusion

In this paper vibrational-chemical kinetics in the high-temperature five-component mixture $CO_2/CO/O_2/O/C$ is numerically studied taking into account dissociation of molecular species, recombination, exchange reactions and vibrational energy transitions of CO_2 molecules. Calculations were carried out with the use of three-temperature, two-temperature and one-temperature description of CO_2 vibrational relaxation. Comparison of the results obtained in the frame of three CO_2 kinetic models showed the influence of CO_2 vibrational distributions on temporal variation of the gas temperature and mixture composition. The difference between mixture parameters obtained in the frame of the three-temperature and two-temperature models is found less than deviations from the data found using the thermal equilibrium one-temperature distributions. Calculations show that thermal equilibrium distributions establish under considered conditions much faster than the chemical equilibrium.

The results obtained for the mixture $CO_2/CO/O_2/O/C$ are compared with the data found for the three-component mixture $CO_2/CO/O$ taking into account vibration-dissociation CO_2 kinetics. The comparison showed the influence of a mixture composition on CO_2 vibration-dissociation relaxation, number densities of species CO_2, CO, O and the gas temperature.

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References

[1] Park C, Howe J and Jaffe R 1994 *J. Thermophys. Heat Transfer* **8 (1)** 9-23

[2] Shevelev Yu D and Syzranova N G 2007 *Fiz.-Khim. Kinet. Gaz. Dinam.* **5** URL http://www.chemphys.edu.ru/Media/Files/2007-12-17-001.pdf [in Russian]
[3] Taylor R L and Bitterman S 1969 *Rev. Mod. Phys.* **41 (1)** 26-47
[4] Gordiets B F, Osipov A I and Shelepin L A 1980 *Nauka. Moscow* 512
[5] Likalter A A 1975 *Kvant. Elektron.* **5 (11)** 1307-1309 [in Russian]
[6] Kozak T and Bogaerts A 2015 *Plasma Sources Sci. Technol.* **24** 015024
[7] Aerts R, Martens T and Bogaerts A 2012 *J. Phys. Chem. C.* **116** 23257-23273
[8] Thomson R 1978 *J. Phys. D Appl. Phys.* **11** 2509-2516
[9] Brun R 1988 *AIAA paper* **88** 2655.
[10] Kustova E V and Nagnibeda E A 2006 *Chem. Phys.* **321** 293-310
[11] Kustova E, Nagnibeda E, Shevelev Yu and Syzranova N 2011 *Shock Waves* **21 (3)** 273-287
[12] Armenise I and Kustova E 2013 *Chem. Phys.* **415** 269-281
[13] Kustova E and Nagnibeda E 2001 State-to-state theory of vibrational kinetics and dissociation in three-atomic gases *22nd International Symposium on Rarefied Gas Dynamics, July 2001* AIP Conference Proceedings **585** 620-627
[14] Losev S A, Kozlov P V, Kuznezova L A, Makarov V N, Romanenko Yu V, Surzhikov S T and Zalogin G N 1988 Radiation of $CO_2 - N_2 - Ar$ mixture in a shock wave: experiment and modeling Proceeding of the Third European Symposium on Aerothermodynamics for Space Vehicles *ESTEC, Noordwiik, ESA* **426** 437-444
[15] Makarov V and Losev S 1997 *Khim. Phizika* **16 (5)** 29-43 [in Russian]
[16] Likalter A A 1976 *Zh. Prikl. Mekh. Tekh. Fiz* **4** 3-10 [in Russian]
[17] Kustova E and Nagnibeda E 1999 *Rarefied Gas Dynamics* **2** 289-296
[18] Kustova E and Nagnibeda E 2012 *Chem. Phys.* **398 (1)** 111-117
[19] Kosareva A A and Nagnibeda E A 2016 *Vestnik of Saint Petersburg University. Series 1. Mathematics. Mechanics. Astronomy* **3 (61)** 468-480 [in Russian]