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.
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:

\[
CO_2 + M \leftrightarrow CO + O + M, \tag{1}
\]
\[
O_2 + M \leftrightarrow O + O + M, \tag{2}
\]
\[
CO + M \leftrightarrow C + O + M, \tag{3}
\]
\[
M = CO_2, CO, O_2, O, C, \tag{4}
\]
\[
CO_2 + O \leftrightarrow CO + O_2, \tag{5}
\]
\[
CO + O \leftrightarrow C + O_2, \tag{6}
\]
\[
CO + CO \leftrightarrow CO_2 + C. \tag{7}
\]

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 ($VV_{O_2}, VV_{CO}$); $VT_m$, $VT_{O_2}$, $VTCO$ 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]:

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

here $\theta$ 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]):

\[
n_{i_1i_2i_3}(T_{12}, T_3) = \frac{n_{CO_2}(i_2 + 1)}{Z_{vibr}^{CO_2}(T_{12}, T_3)} \exp \left( - \frac{i_1 \varepsilon_{100} + i_2 \varepsilon_{010}}{kT_{12}} - \frac{i_3 \varepsilon_{001}}{kT_3} \right).
\] (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:

\[
n_c^i(T) = \frac{n_c}{Z_c^{vibr}(T)} \exp \left( - \frac{\varepsilon_c^i}{kT} \right),
\]

where \( Z_c^{vibr}(T) \) is the vibrational partition function of species \( c \), \( \varepsilon_c^i = ih\nu_c \) is the vibrational energy of diatomic molecule \( c \) in the case of harmonic oscillations, \( \nu_c \) 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:

\[
\frac{dn_c}{dt} = R_c^{react},
\]

\[
c = CO_2, CO, O_2, O, C, \]

\[
\rho CO_2 \frac{dE_{12}}{dt} = R_{12} - m_{CO_2}E_{12}R_{CO_2}^{react},
\]

\[
\rho CO_2 \frac{dE_3}{dt} = R_3 - m_{CO_2}E_3R_{CO_2}^{react},
\]

\[
\frac{3}{2} n kT + (n_{CO_2} + n_{CO} + n_{O_2}) kT + \rho CO_2 E_{vibr}^{CO_2}(T_{12}, T_3) + \rho CO E_{vibr}^{CO}(T) +
\]

\[
+ \rho O_2 E_{vibr}^{O_2}(T) + n_{CO_2} \varepsilon_{CO_2} + n_{CO} \varepsilon_{CO} + n_{O_2} \varepsilon_{O_2} + n_O \varepsilon_O + n_c \varepsilon_c = \text{const}.
\]

Here \( n = n_{CO_2} + n_{CO} + n_{O_2} + n_O + n_C \) is the total numeric density, \( \varepsilon_c \) is the formation energy, \( E_{12}, E_3 \) are the vibrational energies of the coupled and asymmetric CO\(_2\) modes:

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

\[
\rho CO_2 E_3(T_3) = \frac{n_{CO_2}}{Z_3(T_3)} \sum_{i_3} i_3 \varepsilon_{001} \exp \left( - \frac{i_3 \varepsilon_{001}}{kT_3} \right),
\] (14)

where \( Z_{12}(T_{12}), Z_3(T_3) \) are the vibrational partition function of the coupled and asymmetric CO\(_2\) modes.
Let us consider right hand part of equation (9):

3. Reaction rate coefficients

contains equations of chemical kinetics (9) with reaction rate coefficients depending only on the

n

distributions. The set of equations for macroscopic parameters chemical reactions are simulated on the basis of maintaining thermal equilibrium vibrational levels populations are described by

T

shorter than the mean time of chemical reactions, vibrational level populations are described by

(16) with

\[ T \]

is the composition due to chemical reactions and changing of vibrational energies

\[ \text{CO} \]

Dissociation-recombination processes are described by the following expressions:

In (12) \( E_{\text{CO}_2}^{\text{vib}}(T_1, T_3), E_{\text{CO}}^{\text{vib}}(T), E_{\text{O}_2}^{\text{vib}}(T) \) are the vibrational energies of molecules \( \text{CO}_2, \text{CO}, \text{O}_2 \) per the unit mass:

\[
\rho_{\text{CO}_2} E_{\text{vib}}^{\text{CO}_2}(T_1, T_3) = \frac{n_{\text{CO}_2}}{Z_{\text{CO}_2}^{\text{vib}}(T_1, T_3)} \sum_{i_1, i_2, i_3} (i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001})(i_2 + 1),
\]

\[
\cdot \exp \left( - \frac{i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001}}{kT_1} - \frac{i_3 \varepsilon_{001}}{kT_3} \right),
\]

\[
\rho_c E_{\text{vib}}^c(T) = \frac{h \nu_c}{\exp \left( \frac{h \nu_c}{kT} \right) - 1}, \quad c = \text{CO}, \text{O}_2.
\]

Production terms \( R_{\text{react}}^c, R_{\text{diss}}, R_3 \) 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 \( \text{CO}_2 \) modes proceed faster than \( VT_m \) transitions and chemical reactions the total vibrational temperature \( T_v = T_{12} = T_3 \) for \( \text{CO}_2 \) molecules may be introduced and vibrational distributions (8) take the form:

\[
n_{i_1, i_2, i_3}(T_v) = \frac{n_{\text{CO}_2}(i_2 + 1)}{Z_{\text{CO}_2}^{\text{vib}}(T_v)} \exp \left( - \frac{i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001}}{kT_v} \right).
\]

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

\[
\rho_{\text{CO}_2} \frac{dE_{\text{vib}}^{\text{CO}_2}(T_v)}{dt} = R_{\text{CO}_2} - m_{\text{CO}_2} E_{\text{CO}_2}^{\text{vib}}(T_v) R_{\text{CO}_2}^{\text{react}},
\]

where

\[
\rho_{\text{CO}_2} E_{\text{vib}}^{\text{CO}_2}(T_v) = \frac{n_{\text{CO}_2}}{Z_{\text{CO}_2}^{\text{vib}}(T_v)} \sum_{i_1, i_2, i_3} (i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001})(i_2 + 1) \exp \left( - \frac{i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001}}{kT_v} \right)
\]

is the vibrational energy of \( \text{CO}_2 \) 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 \( n_{\text{CO}_2}, n_{\text{CO}}, n_{\text{O}_2}, n_{\text{O}}, n_{\text{C}}, T \) 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):

\[
R_{\text{c}}^{\text{react}} = R_{\text{c}}^{\text{diss}} + R_{\text{c}}^{\text{exch}}, \quad c = \text{CO}_2, \text{CO}, \text{O}_2, \text{O}, \text{C}.
\]

Dissociation-recombination processes are described by the following expressions:

\[
R_{\text{CO}_2}^{\text{diss}} = \sum_M n_M \left( k_{\text{rec}, \text{CO}_2}(T)n_{\text{CO}}n_{\text{O}} - k_{\text{diss}, \text{CO}_2}(T_1, T_3) n_{\text{CO}_2} \right),
\]

\[
R_{\text{CO}}^{\text{diss}} = \sum_M n_M \left( k_{\text{rec}, \text{CO}}(T)n_{\text{CO}}n_{\text{C}} - k_{\text{diss}, \text{CO}}(T)n_{\text{CO}} \right),
\]

\[
R_{\text{O}_2}^{\text{diss}} = \sum_M n_M \left( k_{\text{rec}, \text{O}_2}(T)n_{\text{O}}^2 - k_{\text{diss}, \text{O}_2}(T)n_{\text{O}_2} \right),
\]
here $k_{\text{diss,c},c}^M$, $k_{\text{rec,c}}^M$ 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]:

$$k_{\text{diss,CO}_2}^M(T; T_{12}, T_3) = k_{\text{diss,CO}_2}^{eq,M}(T) \frac{Z_{\text{vibr}}^{\text{CO}_2}(T)}{Z_{\text{vibr}}^{\text{CO}_2}(T; T_{12}, T_3)} \sum_{i_1,i_2,i_3} (i_2 + 1) \cdot \exp \left( \frac{i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001}}{k} \left( \frac{1}{T} - \frac{1}{T_{12}} \right) + \frac{i_3 \varepsilon_{001}}{k} \left( \frac{1}{T} - \frac{1}{T_3} \right) + \frac{i_1 i_2 i_3}{kU} \right),$$

(17)

here $\varepsilon_{i_1i_2i_3} = i_1 \varepsilon_{100} + i_2 \varepsilon_{010} + i_3 \varepsilon_{001}$, $k_{\text{diss,CO}_2}^{eq,M}(T)$ is the equilibrium dissociation rate coefficient defined by the Arrhenius 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 Arrhenius law as well as $\text{CO}_2$ 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 $k_{\text{diss,CO}_2}^{eq,M}(T)$. 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]:

$$k_{\text{rec,CO}_2}^M(T) = k_{\text{diss,CO}_2}^{eq,M}(T),$$

$$k_{\text{rec,CO}}^M(T) = k_{\text{diss,CO}}^{eq,M}(T),$$

$$k_{\text{rec,O}_2}^M(T) = k_{\text{diss,O}_2}^{eq,M}(T) \left( \frac{2}{m_c} \right)^{3/2} (2\pi kT)^{-3/2} h^3 Z_{\text{vibr}}^{\text{CO}_2}(T) Z_{\text{rot}}^{\text{CO}_2}(T) \exp \left( -\frac{\varepsilon_{\text{CO}_2} - \varepsilon_{\text{O}} - \varepsilon_C}{kT} \right),$$

$$k_{\text{rec,CO}}^M(T) = k_{\text{diss,CO}}^{eq,M}(T) \left( \frac{m_c}{m_{\text{CO}} m_{\text{O}}} \right)^{3/2} (2\pi kT)^{-3/2} h^3 Z_{\text{vibr}}^{\text{CO}}(T) Z_{\text{rot}}^{\text{CO}}(T) \exp \left( -\frac{\varepsilon_{\text{CO}} - \varepsilon_{\text{O}} - \varepsilon_C}{kT} \right),$$

$$k_{\text{rec,O}_2}^M(T) = k_{\text{diss,O}_2}^{eq,M}(T) \left( \frac{2}{m_c} \right)^{3/2} (2\pi kT)^{-3/2} h^3 Z_{\text{vibr}}^{\text{O}_2}(T) Z_{\text{rot}}^{\text{O}_2}(T) \exp \left( \frac{2\varepsilon_{\text{O}}}{kT} \right),$$

here $m_c$ is the mass of species $c$, $Z_{\text{rot}}^{\text{CO}_2}(T)$, $Z_{\text{rot}}^{\text{CO}}(T)$, $Z_{\text{rot}}^{\text{O}_2}(T)$ are the rotational partition functions of $\text{CO}_2$, $\text{CO}$ and $\text{O}_2$ 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 $\text{CO}_2$ modes are not available in the literature. Therefore in the present paper we consider the classical expression for $R_{\text{exch}}^c$ with one-temperature rate coefficients:

$$R_{\text{exch}}^{c} = \sum_{d \neq d'} \left( k_{c \rightarrow d}^{d \rightarrow c}(T) n_c n_d^* - k_{c \rightarrow d}^{d \rightarrow c}(T) n_c n_d \right).$$

Rate coefficients for the backward reactions are found using the detailed balance principle:
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 $T_1 = 6000$ 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 $T < T_1 = 3000$ K and overestimated values of this coefficient for $T > T_3 = 6000$ K in comparison with the more accurate three-temperature coefficients $k_{diss,CO_2}(T, T_1, T_3)$. 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:

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

(18)
\[ R_3 - m_{CO_2}R_{CO_2}^{react} = \rho_{CO_2} \sum_{\gamma} \frac{E_3^\gamma(T) - E_3(T_3)}{\tau_\gamma}, \]  

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.

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 $CO_2, CO, O$ 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](image1.png)  
**Figure 4.** The gas temperature in dependence on $t$.

![Figure 5](image2.png)  
**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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