

# Non-Equilibrium Kinetics and Transport Processes in a Hypersonic Flow of CO<sub>2</sub>/CO/O<sub>2</sub>/C/O Mixture

E.V. Kustova\*, E.A. Nagnibeda\*, Yu.D. Shevelev<sup>†</sup> and N.G. Syzranova<sup>†</sup>

*\*Department of Mathematics and Mechanics, Saint Petersburg State University,  
198504 Universitetskiy pr., 28, Saint Petersburg, Russia*

*<sup>†</sup>Institute of Computer Aided Design of Russian Academy of Sciences,  
123056 2d Brestskaya str., 19/18, Moscow, Russia*

**Abstract.** In this paper, non-equilibrium kinetics and transport processes in a viscous hypersonic flow of reacting CO<sub>2</sub>/CO/O<sub>2</sub>/C/O mixture are studied on the basis of the kinetic theory methods. Vibrational excitation of CO<sub>2</sub>, CO and O<sub>2</sub> molecules as well as non-equilibrium dissociation, recombination and exchange reactions are taken into account and the influence of non-equilibrium kinetics on transport properties is studied. A five-temperature model for a non-equilibrium flow suitable for applications is derived from the kinetic theory and used for the evaluation of transport properties of considered mixture under re-entry conditions. The paper presents the closed set of non-equilibrium flow equations, expressions for transport properties and results of calculations.

**Keywords:** Non-equilibrium CO<sub>2</sub> flows, multi-temperature vibrational-chemical kinetics, transport properties

**PACS:** 47.70.-n, 51.20+d, 44.20.+b, 82.20.-w

## INTRODUCTION

Theoretical modeling of non-equilibrium CO<sub>2</sub> flows is important for prediction of flow parameters near a spacecraft entering the Mars atmosphere. Accurate description of high-temperature flows containing CO<sub>2</sub> molecules requires taking into account complex vibrational and chemical kinetics and its influence on gas flow parameters and heat transfer. Existing data concerning relaxation times of various processes under re-entry conditions show that the characteristic times of kinetic and gas-dynamic processes can be comparable and, therefore, the kinetic model should be coupled to the gas-dynamic equations. An important up-to-date problem is to create a model adequately describing non-equilibrium kinetics in a flow and, at the same time, suitable for practical applications.

Several theoretical models were developed for pure carbon dioxide and for mixtures containing CO<sub>2</sub>. However, in numerical simulations of viscous supersonic CO<sub>2</sub> flows, basically, only simplified two-temperature [1, 2, 3] or one-temperature CO<sub>2</sub> kinetic models are used. These models cannot describe correctly the complex vibrational kinetics in CO<sub>2</sub>-containing mixtures. More rigorous models are based on multi-temperature distributions Refs. [4, 5, 6, 7, 8] or take into account detailed state-to-state vibrational kinetics in a flow [6, 9]. Calculations of transport properties on the basis of these models for some particular cases [8] show that the accurate state-to-state transport algorithms [9] are too complicated and time consuming especially if multi-component reacting CO<sub>2</sub>-containing mixtures are studied and many test cases should be computed. And even simpler multi-temperature models remain unused for applications due to their complexity, if the vibrational temperatures are introduced for each mode of anharmonic CO<sub>2</sub> vibrations.

Recently, a self-consistent three-temperature description of CO<sub>2</sub>/CO/O mixture was proposed in Ref. [10]. The model provides a satisfactory accuracy and, on the other hand, gives expressions for the transport coefficients suitable for applications. In Ref. [11] this model was extended for the 5-component reacting mixture CO<sub>2</sub>/CO/O<sub>2</sub>/C/O and implemented into the CFD solver for simulation of a flow in a viscous shock layer near a re-entering space craft.

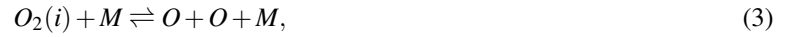
The three-temperature model [11] takes into account non-equilibrium CO<sub>2</sub> vibrational excitation, while CO and O<sub>2</sub> molecules are considered in thermal equilibrium. The objective of the present paper is to improve the model [11] by including non-equilibrium CO<sub>2</sub> vibrational excitation and that for diatomic species, which is important in a shock heated flow.

We consider the conditions typical for a high-temperature shock-layer and take into account different rates of various kinetic processes. On the basis of the kinetic theory we derive the five-temperature flow description including flow

equations and expressions for the transport and source terms. The model is applied for the evaluation of transport properties of considered five-component mixture under re-entry conditions.

## KINETIC MODEL AND BASIC EQUATIONS

There exist different channels for the vibrational relaxation in the mixture  $\text{CO}_2/\text{CO}/\text{O}_2/\text{C}/\text{O}$ : 1) the intra-mode  $\text{VV}_m$  ( $m = 1, 2, 3$ ) transitions within the each  $m$ -th vibrational mode and vibrational energy exchanges  $\text{VV}_{\text{CO}}$ ,  $\text{VV}_{\text{O}_2}$  in  $\text{CO}$ ,  $\text{O}_2$  molecules; 2) vibrational-translational transitions in  $\text{CO}_2$  (with preferential  $\text{VT}_2$  channel) and in diatomic species  $\text{VT}_{\text{CO}}$ ,  $\text{VT}_{\text{O}_2}$ ; 3)  $\text{VV}_{k-m}$  vibrational transitions between different modes of  $\text{CO}_2$  and  $\text{VV}$  exchanges between molecules of different species. Furthermore, in a high-temperature mixture, dissociation, recombination and exchange reactions



should be also included to the kinetic scheme. Here  $i, j$  are vibrational levels of  $\text{CO}$  and  $\text{O}_2$  molecules,  $i_1, i_2, i_3$  correspond to  $\text{CO}_2$  vibrational levels,  $M$  is a partner.

The analysis of the existing data on rate coefficients for considered kinetic processes [12, 13] shows that, for a wide variety of high-temperature flows, the following relation between the characteristic times holds:

$$\begin{aligned} \tau_r < \tau_{rot} < \tau_{\text{VV}_m} \sim \tau_{\text{VV}_{1-2}} \ll \tau_{\text{VV}_{1-2-3}} \sim \tau_{\text{VV}_{2-3}} \sim \tau_{\text{VV}_{3-\text{CO}}} \sim \tau_{\text{VV}_{1-2-\text{CO}}} \sim \\ \sim \tau_{\text{VV}_{1-\text{O}_2}} \sim \tau_{\text{VV}_{\text{CO}-\text{O}_2}} \sim \tau_{\text{VT}_m} < \tau_{react} \sim \theta, \quad m = 1, 2, 3, \text{CO}, \text{O}_2. \end{aligned} \quad (7)$$

Here  $\tau_r$ ,  $\tau_{rot}$  are the characteristic times of the translational and rotational relaxation;  $\tau_{\text{VV}_m}$  ( $m = 1, 2, 3, \text{CO}, \text{O}_2$ ) are the times of the intra-mode  $\text{VV}$  exchanges in  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ;  $\tau_{\text{VT}_m}$  are the times of  $\text{VT}_m$  relaxation for  $m = 2, \text{CO}, \text{O}_2$ ;  $\tau_{\text{VV}_{1-2}}$ ,  $\tau_{\text{VV}_{1-2-3}}$ ,  $\tau_{\text{VV}_{2-3}}$  correspond to the inter-mode  $\text{CO}_2$  transitions, and  $\tau_{\text{VV}_{3-\text{CO}}}$ ,  $\tau_{\text{VV}_{1-2-\text{CO}}}$ ,  $\tau_{\text{VV}_{1-\text{O}_2}}$ ,  $\tau_{\text{VV}_{\text{CO}-\text{O}_2}}$  characterize  $\text{VV}$  exchanges between different species;  $\tau_{react}$  is the characteristic time for chemical reactions;  $\theta$  is the mean time of the variation of the gas-dynamic parameters. The most probable inter-mode  $\text{CO}_2$  exchange is the near-resonant two-quantum  $\text{VV}_{1-2}$  exchange between the symmetric and bending modes due to the relation between frequencies of these modes  $\nu_1 \approx 2\nu_2$ .

Under the condition (7), relaxation processes in the considered mixture can be divided to rapid and slow stages. At the rapid stage, as a result of intra-mode  $\text{VV}$  transitions in  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ , the quasi-stationary distributions with different vibrational temperatures establish in each mode ( $m = 1, 2, 3, \text{CO}, \text{O}_2$ ). Then, the rapid  $\text{VV}_{1-2}$  exchange results in the establishment of the Boltzmann distribution with a single temperature  $T_{12}$  of the combined (symmetric + bending) mode. The slow stage of kinetic processes (at the gas-dynamic time scale  $\theta$ ), includes the  $\text{VT}$  relaxation in  $\text{CO}_2$  (with preferential channel  $\text{VT}_2$ ) and in diatomic species, energy redistribution between the asymmetric and combined modes,  $\text{VV}$  exchanges between different species and chemical reactions (1)–(6). In the present paper we use harmonic oscillator model for simulation of vibrational spectra. In the case of anharmonic vibrations quasi-stationary distributions have the form of generalized Treanor distributions [6].

On the basis of the Chapman-Enskog method modified for reacting mixtures with rapid and slow processes [10, 14], the closed flow description for the considered mixture can be obtained in terms of the number densities of chemical species  $n_c(\mathbf{r}, t)$ , flow velocity  $\mathbf{v}(\mathbf{r}, t)$ , gas temperature  $T(\mathbf{r}, t)$  and four vibrational temperatures: those of the combined (symmetric+bending), asymmetric  $\text{CO}_2$  modes  $T_{12}(\mathbf{r}, t)$ ,  $T_3(\mathbf{r}, t)$  and those of diatomic molecules  $T_{\text{VCO}}(\mathbf{r}, t)$ ,  $T_{\text{VO}_2}(\mathbf{r}, t)$ . The governing equations include the conservation equations of momentum and total energy coupled to the equations of five-temperature chemical kinetics and relaxation equations for the mean vibrational energies  $E_{12}(T_{12})$ ,  $E_3(T_3)$  of

the combined and asymmetric modes in CO<sub>2</sub> and  $E_{vibr}^c(T_{Vc})$  ( $c = \text{CO}, \text{O}_2$ ) of diatomic species:

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0, \quad (8)$$

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{react}, \quad c = \text{CO}_2, \text{O}_2, \text{CO}, \text{O}, \text{C}, \quad (9)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (10)$$

$$\rho \frac{du}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0, \quad (11)$$

$$\rho_{\text{CO}_2} \frac{dE_{12}}{dt} + \nabla \cdot \mathbf{q}_{12} = R_{12} - m_{\text{CO}_2} E_{12} R_{\text{CO}_2}^{react} + E_{12} \nabla \cdot (\rho_{\text{CO}_2} \mathbf{V}_{\text{CO}_2}), \quad (12)$$

$$\rho_{\text{CO}_2} \frac{dE_3}{dt} + \nabla \cdot \mathbf{q}_3 = R_3 - m_{\text{CO}_2} E_3 R_{\text{CO}_2}^{react} + E_3 \nabla \cdot (\rho_{\text{CO}_2} \mathbf{V}_{\text{CO}_2}), \quad (13)$$

$$\rho_c \frac{dE_{vibr}^c}{dt} + \nabla \cdot \mathbf{q}_{vibr}^c = R_c - m_c E_{vibr}^c R_c^{react} + E_{vibr}^c \nabla \cdot (\rho_c \mathbf{V}_c), \quad c = \text{O}_2, \text{CO}. \quad (14)$$

Here  $m_c$ ,  $\rho_c$  are the mass and density of species  $c$ ,  $\rho = \sum_c m_c \rho_c$  is the mixture density,  $u$  is the total energy per unit mass;  $R_c^{react}$  ( $c = \text{CO}_2, \text{CO}, \text{O}_2, \text{C}, \text{O}$ ),  $R_{12}$ ,  $R_3$ ,  $R_c$  ( $c = \text{CO}, \text{O}_2$ ) are the production terms due to chemical reactions and slow relaxation processes;  $\mathbf{P}$  is the stress tensor,  $\mathbf{V}_c$  is the diffusion velocity of species  $c$ ,  $\mathbf{q}$  is the heat flux,  $\mathbf{q}_{12}$ ,  $\mathbf{q}_3$ ,  $\mathbf{q}_{vibr}^c$  are the fluxes of vibrational energy of the combined and asymmetric CO<sub>2</sub> modes and diatomic species, respectively.

The considered five temperature model reduces to the three-temperature approach [11] if CO and O<sub>2</sub> molecules equilibrate faster than CO<sub>2</sub>. In this case vibrational distributions of diatomic species are thermal equilibrium with the gas temperature  $T = T_{V\text{CO}} = T_{V\text{O}_2}$ . In the two-temperature approximation, all three CO<sub>2</sub> modes are described with a single vibrational temperature  $T_{V\text{CO}_2} = T_{12} = T_3$ . The conditions  $T_{12} = T_3 = T_{V\text{CO}} = T_{V\text{O}_2} = T$  correspond to the one-temperature thermal equilibrium model for a chemically non-equilibrium reacting flow.

## TRANSPORT AND SOURCE TERMS

Let us consider the transport terms in the equations (9)–(14). In the zero order approximation of the modified Chapman-Enskog method,  $\mathbf{P}^{(0)} = p\mathbf{I}$ ,  $p$  is the pressure,  $\mathbf{I}$  is the unit tensor, the diffusion velocities and heat fluxes are equal to zero.

The formalism of the Chapman-Enskog method for the evaluation of the first order distribution functions and transport algorithms in the three-temperature approximation for the mixture CO<sub>2</sub>/CO/O are reported in details in Ref. [10] and generalized for the mixture CO<sub>2</sub>/CO/O<sub>2</sub>/C/O [11]. Here, we extend this method for the five-temperature model of the same mixture CO<sub>2</sub>/CO/O<sub>2</sub>/C/O.

The expression for the heat flux contains gradients of five temperatures:

$$\mathbf{q} = -\lambda \nabla T - \lambda_{v,12} \nabla T_{12} - \lambda_{v,3} \nabla T_3 - \sum_{c=\text{O}_2, \text{CO}} \lambda_{v,c} \nabla T_{Vc} - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c, \quad (15)$$

$\lambda = \lambda_{tr} + \lambda_{rot}$  is the thermal conductivity coefficient of translational and rotational degrees of freedom,  $\lambda_{12}$ ,  $\lambda_3$ ,  $\lambda_{v,c}$  ( $c = \text{CO}, \text{O}_2$ ) correspond to the vibrational thermal conductivity of the combined (symmetric+bending) and asymmetric CO<sub>2</sub> modes as well as of CO and O<sub>2</sub> molecules,  $h_c$  is the specific enthalpy of species  $c$ ,  $D_{Tc}$  are the thermal diffusion coefficients.

The fluxes of vibrational energies depend on gradients of the corresponding temperatures:

$$\mathbf{q}_{12} = -\lambda_{v,12} \nabla T_{12}, \quad \mathbf{q}_3 = -\lambda_{v,3} \nabla T_3, \quad \mathbf{q}_{vibr}^c = -\lambda_{v,c} \nabla T_{Vc}, \quad c = \text{O}_2, \text{CO}. \quad (16)$$

The pressure tensor and diffusion velocities are obtained in the form similar to the case [10, 11]:

$$\mathbf{P} = (p - p_{rel}) \mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v} \mathbf{I}, \quad (17)$$

where  $\mathbf{S}$  is the deformation rate tensor,  $\eta$  is the shear viscosity coefficient,  $\zeta$  and  $p_{rel}$  are the bulk viscosity coefficient and relaxation pressure appearing in the pressure tensor due to rapid inelastic non-resonant relaxation processes which differ from those in the case [11],

$$\mathbf{V}_c = - \sum_{d=1}^5 D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T, \quad (18)$$

where  $D_{cd}$  are the multi-component diffusion coefficients,  $\mathbf{d}_c$  are the diffusive driving forces.

If thermal and baro-diffusion processes are neglected, the equation (18) can be simplified:

$$\mathbf{V}_c = - \sum_d D_{cd} \nabla \left( \frac{n_d}{n} \right). \quad (19)$$

After further simplification, if we keep in the diffusion matrix only diagonal elements, we obtain a particular form of the Fick's law

$$\mathbf{V}_c = -D_c \nabla \left( \frac{\rho_c}{\rho} \right), \quad (20)$$

with effective diffusion coefficient  $D_c$ . The diffusion velocities calculated using the accurate and simplified expressions are compared in the next section.

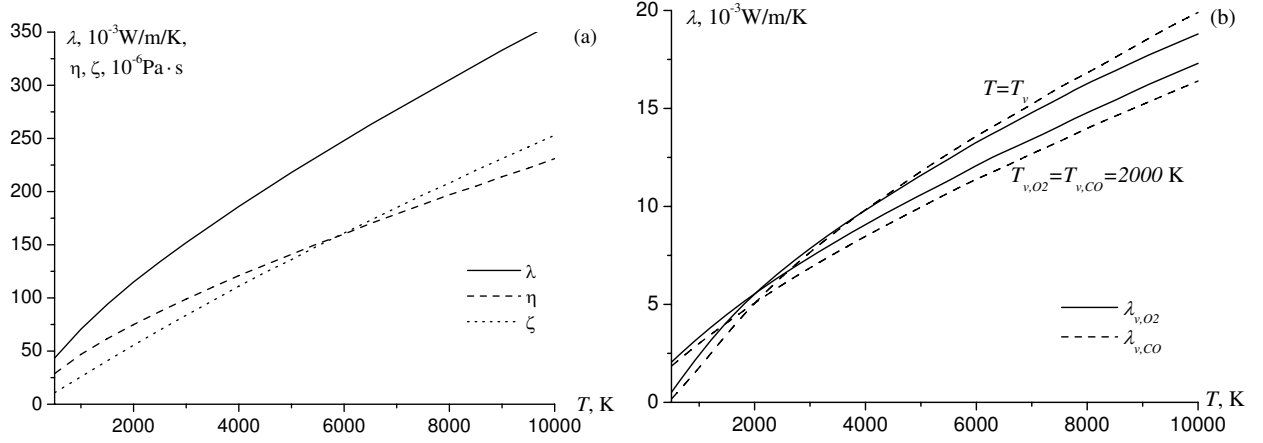
The transport coefficients are expressed in terms of the solutions of the linear transport systems following from the integral equations for the first-order correction to the distribution function derived in [14] for gases with rapid and slow processes. The coefficients of the transport systems depend on the cross sections of the most frequent collisions specifying rapid processes. As is shown in Ref. [10], neglecting anharmonicity of molecular vibrations allows to simplify considerably the transport linear systems and expressions for transport terms. Thus, relaxation pressure and bulk viscosity coefficient are determined only by the RT rotation-translation transitions because for harmonic oscillators, rapid  $VV_m$  and  $VV_{1-2}$  exchanges occur to be resonant. For anharmonic oscillators, these processes should be taken into account in the expressions for  $p_{rel}$  and  $\zeta$ . In the case of anharmonic vibrations the expressions for energy fluxes contain heat conductivity coefficients connected with rapid non-resonant vibrational transitions which come to zero if anharmonicity is neglected.

The source terms in the equations (9)–(14) describe slow processes of energy transitions and reactions. The production terms corresponding to chemical reactions contain in our case three-temperature rate coefficients for non-equilibrium  $\text{CO}_2$  dissociation (1) and exchange reactions (4), (6) involving  $\text{CO}_2$ , as well as two-temperature rate coefficients for diatomic species dissociation (2), (3) and reactions (5). Multi-temperature reaction rate coefficients are obtained by averaging state-dependent rate coefficients over quasi-stationary vibrational distributions depending on the vibrational temperatures [14]. The expressions for multi-temperature reaction rate coefficients can be written using an extension of the Treanor-Marrone model [15] for three-atomic molecules [10]. Rate coefficients of forward and backward reactions are connected by the detailed balance principle.

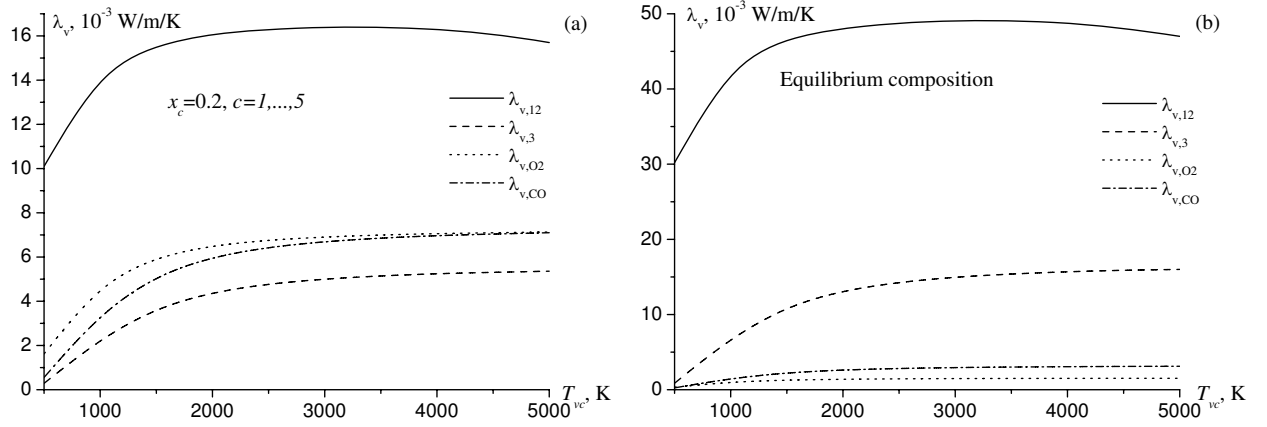
## RESULTS

In Figs. 1 and 2, the thermal conductivity and viscosity coefficients are presented as functions of temperatures. Total thermal conductivity, shear and bulk viscosity coefficients are given in Fig. 1a as functions of  $T$  at fixed vibrational temperatures and mixture composition. One can see that all coefficients increase with the temperature, the shear and bulk viscosity coefficients are of the same order of magnitude in the whole temperature range. At low temperatures, the shear viscosity coefficient exceeds that of bulk viscosity, and for  $T > 6000$  K we obtain the opposite ratio. The role of vibrational excitation of diatomic species is shown in Fig. 1b. It is seen that the vibrational thermal conductivity coefficients of  $\text{O}_2$  and  $\text{CO}$  differ for thermal equilibrium and non-equilibrium conditions. The effect of non-equilibrium vibrational excitation is more noticeable for  $\text{CO}_2$  molecules. In Fig. 2, the contributions of various vibrational modes to thermal conductivity are presented for the arbitrarily fixed and near-equilibrium mixture composition. One can notice that the vibrational thermal conductivity coefficient of the combined  $\text{CO}_2$  mode exceeds other coefficients, both  $\text{CO}_2$  coefficients  $\lambda_{12}$  and  $\lambda_3$  occur higher for near equilibrium conditions. It is seen that all thermal conductivity coefficients depend strongly on the mixture composition.

Analysis of the equations for diffusion coefficients shows that these coefficients and, correspondingly, diffusion velocities are practically independent of the species vibrational excitation whereas the mixture composition is important for their evaluation. Figs. 3(a,b) present the comparison of diffusion velocities of  $\text{CO}_2$  (a) and  $\text{CO}$  (b) calculated in



**FIGURE 1.** Transport coefficients as functions of temperature  $T$  at fixed mixture composition  $n_c/n = 0.2$ ,  $c = 1, \dots, 5$ . (a) Total thermal conductivity, shear and bulk viscosity coefficients at fixed vibrational temperatures  $T_{12} = T_3 = T_{v,O_2} = T_{v,CO} = 2500$  K; (b) Thermal conductivity coefficients of diatomic molecules.

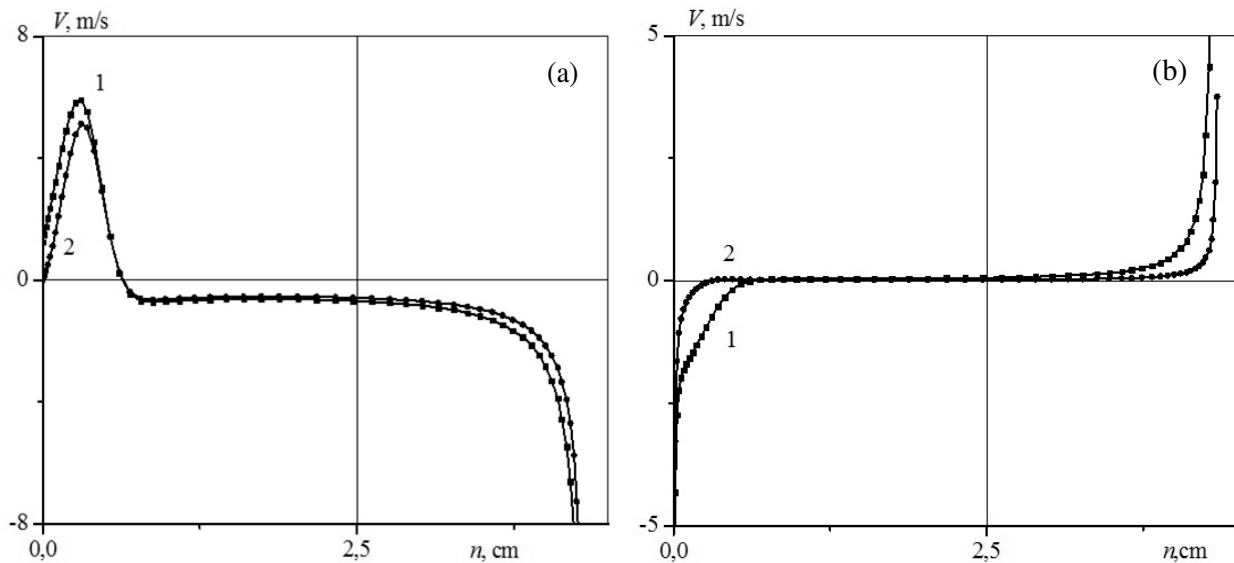


**FIGURE 2.** Thermal conductivity coefficients of different vibrational modes as functions of corresponding vibrational temperatures and fixed gas temperature  $T = 2500$  K. (a) fixed non-equilibrium mixture composition  $n_c/n = 0.2$ ,  $c = 1, \dots, 5$ . (b) near-equilibrium mixture composition.

the three-temperature approach using the expressions (19) and (20). The diffusion velocities are presented along the stagnation stream line in a viscous shock layer near a blunt body imitating the form of MSRO (Mars Sample Return Orbiter). The following test case is studied:  $V_\infty = 5687$  m/s,  $\rho_\infty = 3.141 \cdot 10^{-5}$  kg/m<sup>3</sup>,  $T_\infty = 140$  K. We can see, that the Fick's law works well only in the middle of the relaxation zone, where the rate of variation of the flow parameters is low. In the regions of high gradients (near the surface and close to the shock front), the accurate formulas of the kinetic theory are required for the correct prediction of the diffusion characteristics in a flow.

## CONCLUSIONS

In the paper, the five-temperature kinetic model for a hypersonic flow of the reacting  $\text{CO}_2/\text{CO}/\text{O}_2/\text{C}/\text{O}$  mixture is proposed. The non-equilibrium vibrational excitation of molecular species and chemical reactions are taken into account, and their influence on transport properties is studied. The results of calculations of shear and bulk viscosity and different thermal conductivity coefficients (for the translational and rotational degrees of freedom as well as for the non-equilibrium vibrational modes of  $\text{CO}_2$  (combined symmetric-bending and asymmetric ones) and diatomic species)



**FIGURE 3.** Diffusion velocity of CO<sub>2</sub> (a) and CO (b). Curves 1: formula (19) taking into account all elements of the diffusion matrix; curves 2: simplified formula (20) including only the self-diffusion coefficients.

are presented in a wide range of the gas temperature, vibrational temperatures and for various mixture compositions. The influence of chemical and vibrational non-equilibrium on the thermal conductivity coefficients is studied and the important role of mixture composition is shown. Accurate and simplified models for diffusion processes are compared and the limits of the Fick's law validity in a shock layer are found. The results show the efficiency of the proposed model and its applicability for the CFD simulations.

## REFERENCES

1. Taylor, R., and Bitterman, S., *Rev. Mod. Phys.*, **41**, 26 (1969).
2. Thomson, R., *J. Phys. D: Appl. Phys.*, **11**, 2509 (1978).
3. Brun, R., *AIAA Paper*, **88-2655** (1988).
4. Likalter, A., *Prikl. Mekh. Tekn. Fiz.*, **4**, 3 (1976), (in Russian).
5. Cenian, A., *Chem. Phys.*, **132**, 41–48 (1989).
6. Kustova, E., and Nagnibeda, E., "Nonequilibrium Distributions in CO<sub>2</sub> and their Influence on the Transport and Thermodynamic Properties," in *Rarefied Gas Dynamics 21*, CEPADUES, Toulouse, France, 1999, vol. 2, pp. 289–296.
7. Chikhaoui, A., and Kustova, E., *Chem. Phys.*, **216**, 297–315 (1997).
8. Kustova, E., Nagnibeda, E., and Chikhaoui, A., "Heat Transfer And Diffusion In Mixtures Containing CO<sub>2</sub>," in *Rarefied Gas Dynamics*, edited by A. Ketsdever and E. P. Muntz, 2003, vol. 663 of *AIP Conference Proceedings*, pp. 100–105.
9. Kustova, E., and Nagnibeda, E., "State-to-State Theory of Vibrational Kinetics and Dissociation in Three-Atomic Gases," in *Rarefied Gas Dynamics*, edited by T. Bartel and M. Gallis, 2001, vol. 585 of *AIP Conference Proceedings*, pp. 620–627.
10. Kustova, E., and Nagnibeda, E., *Chem. Phys.*, **321**, 293–310 (2006).
11. Kustova, E., Nagnibeda, E., Shevelev, Y., and Syzranova, N., "Non-Equilibrium Supersonic CO<sub>2</sub> Flows with Real Gas Effects near a Blunt Body," in *Rarefied Gas Dynamics: 26-th International Symposium*, edited by T. Abe, Kyoto, 2008.
12. Makarov, V., and Losev, S., *Khim. Fizika*, **16**, 29–43 (1997), (In Russian).
13. Losev, S., Kozlov, P., Kuznetzova, L., Makarov, V., Romanenko, Y., Surzhikov, S., and Zalogin, G., "Radiation of CO<sub>2</sub>-N<sub>2</sub>-Ar mixture in a shock wave: experiment and modeling," in *Proceedings of the Third European Symposium on Aerothermodynamics for Space Vehicles*, edited by R. Harris, ESTEC, Noordwijk, The Netherlands, ESA Publication Division, ESA SP-426, 1998, p. 437–444.
14. Nagnibeda, E., and Kustova, E., *Nonequilibrium Reacting Gas Flows. Kinetic Theory of Transport and Relaxation Processes*, Springer Verlag, Berlin, Heidelberg, 2009.
15. Marrone, P., and Treanor, C., *Phys. Fluids*, **6**, 1215 (1963).