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Numerical Modeling of Hypersonic Aerodynamics and Heat Transfer Problems of the Martian Descent Modules

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Abstract

Computational fluid dynamics (CFD) is the important tool to analyze physics of fluids. Hypersonic flows over real space configurations represent a substantial problem from the point of view of the development of new and more effective mathematical models, numerical methods, and the use of computer systems. Governing equations for multi-component, multi-temperature, chemically reacting non-equilibrium radiant mixtures are the mathematical foundation for the study of vehicles entering in Martian atmosphere. Based on the kinetic equations for the distribution functions, an efficient three-temperature model suitable for Mars re-entry applications derived and used for the simulations of a non-equilibrium flow in a viscous shock layer near a space vehicle. The closed self-consistent description of a flow in terms of densities of species, macroscopic velocity, gas temperature, and three vibration temperatures are proposed. The transport properties in dissociating CO₂ flows have been evaluated. The proposed model takes into account real structure of polyatomic CO₂ molecules, non-equilibrium CO₂ vibration excitation, different rates of various energy transitions, and chemical reactions. Numerical investigations of a flow past a frontal part of Mars Sample Return Orbiter (MSRO) and MARS EXPRESS vehicles descending in an atmosphere of Mars are presented. The radiation processes taking into account of non-equilibrium character are considered.

Keywords: mechanical and aerospace engineering, aerothermophysics, thermo-chemical models, convective and radiation heat transfer

1. Introduction

A problem of non-equilibrium thermochemical processes in carbon dioxide (CO₂) mixture flows has been studied in a great number of experimental and theoretical works owing to

needs of Mars planet investigations. These works started in the 1960s. Further studies were stimulated by development of Pathfinder and other Martian entry vehicles [1–6].

There are two ways of derivation of the gas dynamics equations for a multi-component mixture: kinetic and phenomenological. The first approach is based on the kinetic theory of gases. The zero-order and the first-order distribution functions are known and expressed by means of different gradients, the diffusive driving forces, etc. [7, 8]. If potentials of interaction between particles are defined, then the equations in terms of species densities, macroscopic velocity, and gas temperature can be carried out by methods of the kinetic theory of gases [9–12]. The transport theory of polyatomic gas mixtures taking into account internal molecular structure, different rates of vibration, and non-harmonic transitions has been developed for a five component $\text{CO}_2/\text{O}_2/\text{CO}/\text{O}/\text{C}$ mixture taking vibration excitation of molecules into account. The algorithm for transport coefficients calculation has been realized as a program module.

The phenomenological approach is based on application of the basic theorems of mechanics and laws of thermodynamics for macroscopic volume of the continuous media and leads to unclosed system of the equations. For closure of this system, the additional definition of mass, momentum, and energy fluxes is necessary. Unknown values of transfer coefficients within the framework of the phenomenological approach can be defined from approximation either from experiment. The kinetic and phenomenological approaches give the same result as structure of gas dynamic equations system.

The governing equations with rigorous kinetic schemes for transport coefficients are solved numerically for a flow in a viscous shock layer near the blunt body imitating the form of the spacecraft Mars Sample Return Orbiter (MSRO) and MARS EXPRESS vehicles descending in an atmosphere of Mars for the conditions typical for the re-entering regime [9–12]. The form of considered vehicles represents spherically blunted cone with an angle 120° and radius $R = 1.0$ m (MSRO) and $R = 0.38$ m (MARS EXPRESS) joined with the cylinder (**Figure 1**).

Figure 1. Martian vehicle.

Calculations of the convective heat flux and the non-equilibrium radiation were carried out of the MSRO vehicle entering into the Martian atmosphere [7–19].

The part of results have been obtained in the framework of the INTAS Project 03-51-5204 “Numerical, Analytical and Experimental Investigation of Convective and Radiative Heating of Martian Descent Module”. This Project was elaborated jointly between institutes-participants from Russian side and European Collaborators [5].

2. Governing equations of hypersonic non-equilibrium polyatomic gas flows

The Martian atmosphere is composed mostly of carbon dioxide (96%), nitrogen (1.9%), argon (1.9%), and others. Small admixtures of nitrogen (N_2) and argon (Ar) in the Mars atmosphere do not play a significant role in the process of heat transfer to descent vehicles (at least, at moderate velocities of flight till the convective heat transfer prevails). It is possible to restrict ourselves by consideration of model atmosphere as the pure carbon dioxide. The pressure on the planet surface is taken equal to 6.0 mbar. It is 0.6% of Earth’s mean sea level pressure. The atmosphere is quite dusty.

The conditions of a flow corresponding to the last stage of flight of space vehicles in an atmosphere of Mars ($V_\infty \leq 6$ km/s, $\rho_\infty > 10^{-5}$ kg/m³, $H < 60$ km) were studied. Determining process at such velocities is a process of dissociation. Up to 75% of full gas flow energy can be spent on it.

The region where non-equilibrium physical and chemical processes realized is a significant part from all considered regions (**Figure 2**). Velocity of physical and chemical processes, as a rule, grows together with density of gas. For considered flow conditions, the degree of gas ionization is small and does not bring the appreciable contribution to internal gas energy. The translational degrees freedom becomes equilibrium on distances of several free path lengths of molecules behind front of a shock wave for considered altitude. The distribution of rotation energy also is established slightly later. Therefore, it is usually supposed that translational and vibration degrees of freedom of particles are in equilibrium. At high temperatures that observed in a shock layer, the characteristic times of a vibration energy relaxation of molecules and characteristic times of dissociation become one order. Thus the account of non-equilibrium excitation of vibration degrees of freedom of carbon dioxide molecules is necessary. The region of relaxation behind the bow shock wave has a specific structure that consists of sequential relaxation zones. The flow in shock and boundary layers are being especially non-equilibrium. It causes the energy redistribution of the internal energy.

Since the Martian atmosphere is strongly rarefied, non-equilibrium processes affect heat transfer at the more significant part of the descent trajectory. The most thermal-loaded part of the typical descent trajectory is the region of frozen chemical reactions and equilibrium-excited vibration degrees of freedom.

Figure 2. (a) The region of different flow regimes of flow for MSRO vehicle (red line) and MARS EXPRESS vehicle (blue line); (b) Mars descent vehicles.

The thermo-chemical model of the processes occurring in the shock layer includes the chemical reactions, dissociation and recombination of CO_2 molecules, dissociation and recombination of diatomic molecules, exchange reactions, processes of vibration energy exchange between various levels of molecules, influence of the vibration relaxation on the chemical reactions and vice versa (CVDV-processes), processes of excitation and deactivation of the electronic states of molecules, and spontaneous radiation processes for excited particles.

We consider a high-temperature flow of the mixture taking into account vibration excitation and the following exchange reactions, dissociation, and recombination:

where M is a molecule or an atom [10].

As known molecule of CO_2 have three vibration modes with different characteristic temperatures: symmetric, deformation (twice degenerate), and asymmetric. According to fast exchange of vibration energy between the different modes, it is assumed that molecules reach the Boltzmann distribution with a uniform temperature.

We consider the conditions typical for a high-temperature shock layer, while the translational and rotational relaxation are supposed to proceed fast as well as intra-mode VV-transitions in CO₂, O₂, CO and inter-mode VV-exchange between CO₂ symmetric and bending modes. All other vibration energy transitions, dissociation, recombination, and exchange reactions are considered to be slower with relaxation times comparable with the mean time of the gas dynamic parameters variation. Such a relation between the characteristic times makes it possible to introduce vibration temperatures for the coupled (symmetric-bending) and asymmetric CO₂ modes.

The existing experimental and theoretical data on relaxation times of different processes in mixtures containing CO₂ molecules show that in a wide range of conditions the following relations are valid:

$$\tau_{tr} < \tau_{rot} < \tau_{VV_m} \sim \tau_{VV'_{1-2}} \ll \tau_{VT_2} \sim \tau_{VV'_{1-2-3}} < \tau_{VT_3} \ll \tau_r \sim \theta, \quad m = 1, 2, 3 \quad (4)$$

Here τ_{tr} , τ_{rot} are the characteristic times of translational and rotation relaxation; τ_{VV_m} are the times of intra-mode VV exchanges; τ_{VT_2} , τ_{VT_3} are the times of VT transitions; $\tau_{VV'_{k-m}}$ correspond to inter-mode transitions; τ_r is the characteristic time of chemical reactions; and θ is the mean time of gas dynamic parameters change.

On the basis of the kinetic theory principles, the closed self-consistent three-temperature description of a flow in terms of densities of species, macroscopic velocity, gas temperature, and three vibration temperatures are obtained [7, 8]. The set of governing equations contains the conservation equations of mass, momentum, and total energy coupled to the equations of non-equilibrium three-temperature chemical kinetics as well as the relaxation equations for vibration temperatures.

Under condition (5) the set of equations are obtained in the following form:

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (5)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0 \quad (6)$$

$$\rho \frac{de}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0 \quad (7)$$

The equations of non-equilibrium chemical kinetics written in the following form

$$\frac{dn_i}{dt} + n_i \nabla \cdot \mathbf{v} + \nabla \cdot (n_i \mathbf{V}_i) = R_i^r \quad (i = \text{CO}_2, \text{CO}, \text{O}_2, \text{O}, \text{C}) \quad (8)$$

Here n_i is the number density of species i (1—CO₂, 2—CO, 3—O₂, 4—C, 5—O). Values $\rho_i = m_i n_i$ is the species density, m_i and n_i are the species mass and number density, $\rho = \sum \rho_i$ is the mixture density; $\mathbf{v}$ is the macroscopic gas velocity, e is the mixture total energy per unit mass; R_i^t , R_{12} , R_3 are the production terms due to dissociation, recombination, exchange reactions and slow processes of CO₂ vibration relaxation; $\mathbf{V}_i$ is the diffusion velocity; $\mathbf{P}$ is the pressure tensor; and $\mathbf{q}$ is the heat flux.

We consider the condition that corresponds to rapid translational and rotational relaxation, VV_m is the vibration energy exchanges within modes and VV'_{12} is the exchange between symmetric and bending CO_2 modes. In this case the vibration CO_2 distributions depend on the vibration temperatures T_{12} of the combined (symmetric + bending) mode, and T_3 of the asymmetric mode. The vibration distributions of CO and O_2 are supposed to be close to the thermal equilibrium; vibration spectra are simulated by the harmonic oscillator model. Values $E_{\text{vibr}1}(T_{12}, T_3) = E_{12}(T_{12}) + E_3(T_3)$, $E_{\text{vibr}2}(T)$, $E_{\text{vibr}3}(T)$ are the specific vibration energies of molecular species CO_2 , CO , and O_2 , respectively; thus $E_{12}(T_{12})$, $E_3(T_3)$ are the specific vibration energies of non-equilibrium CO_2 modes.

The equations of non-equilibrium vibration kinetics written in the following form

$$\rho_1 \frac{dE_{12}}{dt} + \nabla \cdot \mathbf{q}_{12} = R_{12} - m_1 E_{12} R_1' + E_{12} \nabla \cdot (\rho_1 \mathbf{V}_1) \quad (9)$$

$$\rho_1 \frac{dE_3}{dt} + \nabla \cdot \mathbf{q}_3 = R_3 - m_1 E_3 R_1' + E_3 \nabla \cdot (\rho_1 \mathbf{V}_1) \quad (10)$$

x_i is the molar fraction of species i (1— CO_2 , 2— CO , 3— O_2 , 4— C , 5— O). Values $\mathbf{q}_{12}$, $\mathbf{q}_3$ are the fluxes of vibration energy in the combined and asymmetric modes, respectively.

The vibration relaxation of molecules time of CO_2 molecules is calculated under the usual formulas by approximation of theoretical and experimental data for particles of different types.

3. Transport and source terms

The transport theory of polyatomic gas mixtures taking into account internal molecular structure, different rates of vibration transitions, and unharmonicity has been developed for a five component $\text{CO}_2/\text{O}_2/\text{CO}/\text{O}/\text{C}$ mixture taking into account vibration excitation of diatomic molecules.

The transport properties in the viscous gas approximation are determined by the first-order distribution functions. The zero-order and the first-order distribution functions are known and express by means different gradients, the diffusive driving forces, etc. [7, 8].

Pressure tensor, diffusion velocity, heat flux, and vibration energy fluxes are expressed in terms of macroscopic parameters gradients and transport coefficients.

The pressure tensor is obtained in the form:

$$\mathbf{P} = (p - p_{\text{rel}}) \mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v} \mathbf{I}. \quad (11)$$

Here $\mathbf{S}$ is the strain rate tensor, $\mathbf{I}$ is the unit tensor, η is the shear viscosity coefficients, and ζ and p_{rel} are the bulk viscosity coefficient and relaxation pressure appearing in the diagonal elements of the pressure tensor due to rapid inelastic non-resonant processes. The Navier-Stokes equation

derivation leads to the definition of two coefficients of viscosity: shear coefficient of viscosity and coefficient of bulk viscosity.

Transport coefficients (bulk and shear viscosity, heat conductivity, diffusion, pressure- and thermo-diffusion of multi-component gas mixture) are calculated according to the basic kinetic theory. The algorithms for thermal conductivity, vibration thermal conductivity, diffusion, thermal diffusion, shear, and bulk viscosity coefficients computation are developed.

These transport coefficients are defined by functions B_{cij} , F_{cij} , G_{cij} :

$$\eta = kT[B, B]/10, \quad \zeta = kT[F, F], \quad p_{rel} = kT[F, G] \quad (12)$$

Here $[A; B]$ are the bracket integrals depending on the cross sections of rapid processes (see for instance [7, 8] for definition).

The values of diffusion fluxes can be written down through thermodynamic forces (external mass forces it is neglected):

$$\mathbf{J}_i = -\rho_i \sum_j D_{ij}^* \mathbf{d}_j - \rho_i D_{Ti} \nabla \ln T \quad (13)$$

Here D_{ij}^* is the multi-component coefficients of diffusion, D_{Ti} is the coefficients of thermo-diffusion, $\mathbf{d}_j$ is the diffusion driving forces:

$$\mathbf{d}_j = \nabla \left(\frac{n_j}{n} \right) + \left(\frac{n_j}{n} - c_j \right) \nabla \ln p. \quad (14)$$

Here n_j is the number of j th mole components, n is the common mole's number. Let us take the difference between D_{ij}^* and D_{ij} , where D_{ij} is the binary diffusion coefficients.

The basic way of finding the independent transfer coefficients D_{ij}^* , D_{Ti} are connected to the kinetic theory methods. In order to define the multi-components diffusion coefficients, it is necessary to solve the system of the linear algebraic equations that in case of gas mixture have the next form

$$D_{ij} = [\mathbf{D}^i, \mathbf{D}^i]/3n, \quad D_{Ti} = [\mathbf{D}^i, \mathbf{A}^i]/3n. \quad (15)$$

Here $[\mathbf{D}^i, \mathbf{D}^i]$, $[\mathbf{D}^i, \mathbf{A}^i]$ are the bracket integrals depending on the cross sections of rapid processes. Functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{(12)}$, $\mathbf{A}_{cij}^{(3)}$, $\mathbf{A}_{cij}^{(c,1)}$, $\mathbf{B}_{cij}$, F_{cij} , F_{cij} are found from the linear integral equations for the first-order correction to the distribution function. The relaxation pressure determine by the slow non-equilibrium processes. This quantity is basically supposed to be small compared to p , and by value p_{rel} is neglected.

The total heat transfer of a multi-component mixture is defined by effects of heat conductivity of various kinds of energy and diffusion. The heat flux is given by the formula

$$\mathbf{q} = -\lambda' \nabla T - \lambda_{12} \nabla T_{12} - \lambda_3 \nabla T_3 - p \sum_{i=1}^5 D_{T_i} \mathbf{d}_i + \sum_{i=1}^5 \rho_i h_i \mathbf{V}_i \quad (16)$$

Here p is the pressure, h_i is the specific enthalpy of species i , $\lambda' = \lambda_{tr} + \lambda_r + \lambda_v$ is the thermal conductivity coefficient of all degrees of freedom which deviate weakly from local thermal equilibrium. They include the translational and rotational modes as well as CO and O₂ vibration degrees of freedom. Thus, the coefficient $\lambda_v = \lambda_{v,CO} + \lambda_{v,O_2}$. Coefficients λ_{12} , λ_3 correspond to the thermal conductivity of strongly non-equilibrium modes: combined (symmetric + bending) and asymmetric ones.

The fluxes of vibration energy in the combined and asymmetric CO₂ modes in the harmonic oscillator approach depend only on the gradient of corresponding vibration temperature:

$$\mathbf{q}_{12} = -\lambda_{12} \nabla T_{12}, \quad \mathbf{q}_3 = -\lambda_3 \nabla T_3 \quad (17)$$

The thermal conductivity coefficients are expressed in terms of bracket integrals

$$\lambda = k[\mathbf{A}, \mathbf{A}]/3, \quad \lambda_{12} = k[\mathbf{A}^{(12)}, \mathbf{A}^{(12)}]/3, \quad \lambda_3 = k[\mathbf{A}^{(3)}, \mathbf{A}^{(3)}]/3 \quad (18)$$

The algorithms of transport coefficients calculation are similar for various multi-temperature models and consist of the following steps:

1. Unknown functions A_{cij} , $A_{cij}^{(12)}$, $A_{cij}^{(3)}$, $A_{cij}^{(c,1)}$, B_{cij} , F_{cij} , F_{cij} are expanded in the series of Sonine and Waldmann-Trubenbacher polynomials; the trial functions are introduced accordingly to the right hand sides of integral equations for the first-order correction to the distribution function.
2. Transport coefficients are expressed in terms of expansion coefficients.
3. Integral equations are reduced to the linear systems of algebraic equations involving bracket integrals as coefficients.
4. Bracket integrals are simplified on the basis of some assumptions about cross sections of rapid processes; finally they are expressed in terms of the standard $\Omega_{cd}^{(l,r)}$ is the integrals and relaxation times which can be measured experimentally. The $\Omega_{cd}^{(l,r)}$ is the integrals are calculated for particular models of inter-molecular interaction potentials. In the present study, the Lennard-Jones potential is used for low and moderate temperatures whereas in the high-temperature interval the repulsive potential is applied.
5. Transport coefficients are found as solutions of transport linear systems using some numerical algorithms (for instance, the Gauss method or new iterative procedures).

For example, let us consider the bulk viscosity coefficient. In Navier-Stokes equations, the terms involving bulk viscosity multiplied by divergence of velocity and can play a significant role in flow fields with substantial dilatation. The bulk viscosity coefficient was discussed

theoretically in the literature [18] for weak and strong non-equilibrium conditions but up to now it was not evaluated in real gas flows.

The experiments and kinetic theory show that bulk viscosity can significantly influence shock wave structure for polyatomic molecules. In polyatomic gases of the deviation from local equilibrium effects itself as bulk viscosity. From the Chapman-Enskog's theory, it can be proved that for any perfect monoatomic gas, the coefficient of bulk viscosity is equal to zero. Bulk viscosity results from contributions from the several internal degrees of freedom of the gas.

The bulk viscosity coefficient is defined by rotational energy transitions of all molecular species and VT vibration energy transfer in CO and O₂ molecules and can be written as follows

$$\zeta = \zeta_r + \zeta_{v,CO} + \zeta_{v,O_2} \quad (19)$$

For harmonic oscillators, rapid inelastic VV and VV'₁₋₂ exchanges occur to be resonant and therefore do not give contribution to the coefficient ζ .

The bulk viscosity coefficient can be obtained in the form [18]:

$$\zeta = -kT \left(x_1 f_{1,10} + x_2 f_{2,10} + x_3 f_{1,10} + x_4 f_{4,1} + x_5 f_{5,1} \right), \quad (20)$$

where k is the Boltzmann constant, x_i is the molar fraction of species i (1—CO₂, 2—CO, 3—O₂, 4—C, 5—O).

Coefficients $f_{i,mn}$ are the solutions of the system

$$\mathbf{B} \times \mathbf{f} = \mathbf{s}. \quad (21)$$

Here matrix $\mathbf{B}$ is composed of the bracket integrals $\beta_{mm'nn'}^{ij}$:

$$\mathbf{B} = \begin{pmatrix} x_1 c_{tr} & x_2 c_{tr} & x_3 c_{tr} & x_4 c_{tr} & x_5 c_{tr} & x_1 c_{rot,1} & x_2 c_{int,2} & x_3 c_{int,3} \\ \beta_{11}^{2-1} & \beta_{11}^{2-2} & \beta_{11}^{2-3} & \beta_{11}^{2-4} & \beta_{11}^{2-5} & \beta_{1001}^{2-1} & \beta_{1001}^{2-2} & \beta_{1001}^{2-3} \\ \beta_{11}^{3-1} & \beta_{11}^{3-2} & \beta_{11}^{3-3} & \beta_{11}^{3-4} & \beta_{11}^{3-5} & \beta_{1001}^{3-1} & \beta_{1001}^{3-2} & \beta_{1001}^{3-3} \\ \beta_{11}^{4-1} & \beta_{11}^{4-2} & \beta_{11}^{4-3} & \beta_{11}^{4-4} & \beta_{11}^{4-5} & \beta_{1001}^{4-1} & \beta_{1001}^{4-2} & \beta_{1001}^{4-3} \\ \beta_{11}^{5-1} & \beta_{11}^{5-2} & \beta_{11}^{5-3} & \beta_{11}^{5-4} & \beta_{11}^{5-5} & \beta_{1001}^{5-1} & \beta_{1001}^{5-2} & \beta_{1001}^{5-3} \\ \beta_{0110}^{1-1} & \beta_{0110}^{1-2} & \beta_{0110}^{1-3} & \beta_{0110}^{1-4} & \beta_{0110}^{1-5} & \beta_{0011}^{1-1} & 0 & 0 \\ \beta_{0110}^{2-1} & \beta_{0110}^{2-2} & \beta_{0110}^{2-3} & \beta_{0110}^{2-4} & \beta_{0110}^{2-5} & 0 & \beta_{0011}^{2-2} & 0 \\ \beta_{0110}^{3-1} & \beta_{0110}^{3-2} & \beta_{0110}^{3-3} & \beta_{0110}^{3-4} & \beta_{0110}^{3-5} & 0 & 0 & \beta_{0011}^{3-3} \end{pmatrix} \mathbf{f} = \begin{pmatrix} f_{1,10} \\ f_{2,10} \\ f_{3,10} \\ f_{4,1} \\ f_{5,1} \\ f_{1,01} \\ f_{2,01} \\ f_{3,01} \end{pmatrix} \mathbf{s} = \begin{pmatrix} 0 \\ -x_2(c_u - c_{tr})/c_u \\ -x_3(c_u - c_{tr})/c_u \\ -x_4(c_u - c_{tr})/c_u \\ -x_5(c_u - c_{tr})/c_u \\ x_1 c_{rot,1}/c_u \\ x_2 c_{int,2}/c_u \\ x_3 c_{int,3}/c_u \end{pmatrix} \quad (22)$$

Matrix $\mathbf{B}$, vectors $\mathbf{f}$ and $\mathbf{s}$ are given above. Here c_{tr} , c_{rot} , c_{int} are specific heats of translation, rotational, internal degrees of freedom and c_u is the total specific heat. The bracket integrals

$\beta_{mm'nn'}^{ij}$ required for the evaluation of the bulk viscosity coefficient are determined by the energy variation in inelastic processes. The system (22) in this form has a unique solution.

The rates of vibration energy transitions are expressed in terms of corresponding relaxation times. The rate coefficients for non-equilibrium CO₂ dissociation were calculated using the expressions proposed in Ref. [8] as an extension of the Treanor-Marrone's model [20] for three-atomic molecules. For the recombination rate coefficients, the detailed balance principle is used. For the rate coefficients of exchange reactions and dissociation of diatomic molecules, the Arrhenius formulas are applied. The vibration relaxation of molecules time of CO₂ molecules is calculated under the usual formulas by approximation of theoretical and experimental data for particles of different types [10].

4. Results the calculation of transport coefficients

For calculation of transport coefficient of gas mixture, ones need the information how interaction between themselves and each pair of species of gas mixture is going on. It is shown that under considered conditions, the transport coefficients are defined by the collisions with translational and rotational energy changing whereas the reaction rate coefficients depend on the cross sections of slow energy transitions, dissociation, and exchange reactions.

The algorithm for the calculation of transport coefficients has been realized for the 5-temperature model as a program module in a form of Fortran 90 code. The code calls several independent modules: CONSTANT: common constants and variables definition; SPECIFIC HEAT: calculates vibration energy levels, non-equilibrium vibration partition functions, vibration specific heat capacities; OMEGA INTEGRALS: calculates integrals and their ratios using the Lennard-Jones and the Born-Meyer potentials for moderate and high-temperature ranges; BRACKET INTEGRALS: calculates bracket integrals in the transport linear systems; INVERS: solves systems of linear algebraic equations using the Gauss method.

Eqs. (6)–(11) with kinetic schemes for transport coefficients described above are solved numerically for a flow in a viscous shock layer near the blunt body imitating the form of the spacecraft MSRO (Mars Sample Return Orbiter) for the conditions typical for the re-entering regime.

In **Figure 3**, coefficients of shear and volume viscosity along a stagnation line are presented. Calculations are obtained for ideal catalytic wall having the constant temperature $T = 1500$ K and conditions of a flow of MSRO vehicle $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³ (curves T1) and $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³ (curves T2). Near surface of a body, the value of volume viscosity about value of shear, and in a shock layer surpasses it approximately in two times. It is established that the mechanism of non-equilibrium excitation of vibration degrees of freedom of molecules CO₂ does not affect on value of volume viscosity. Estimations of influence of volume viscosity on parameters of flow and a heat transfer to a surface of a space vehicle in an atmosphere of Mars are carried out. For the specified parameters of a flow, the

Figure 3. Coefficient of shear μ and volume ζ viscosity along a stagnation line. T1: $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³, T2: $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³.

influence of account of volume viscosity in the equations of flow leads to increase of a heat flux up to 10%. The similar tendency takes place and for other conditions of a flow.

In **Figure 4**, the similar data are presented for coefficient of heat conductivity.

For conditions of a MSRO vehicle, flow values of multi-component diffusion coefficient D_{ij}^* have been obtained with help of diffusion flux definition through thermodynamic forces [13].

In **Figure 5**, the distribution of self-diffusion coefficients along a stagnation line for the some component of a gas mixture is presented.

The values corresponding to diagonal elements D_{ij}^* ($i \neq j$) of a matrix diffusion, and in **Figure 6** shows non-diagonal elements D_{ij}^* ($i \neq j$). It is evident that values of the elements belonging to the main diagonal in the most part of a shock layer surpass values of non-diagonal elements. It is testifies to legitimacy of application of the Fick's law for calculation of diffusion flux. However, near surface of a body and in the field of a shock wave the values of elements (e.g. D_{11}^* and D_{1j}^* , $j \neq 1$) can be same order. It means that in these zones to use Fick's law it is incorrect.

Diffusion flux of everyone components depends on own gradient of concentration components and coefficient of self-diffusion. In **Figure 7** confirmation of this fact are presented and the diffusion velocities for component CO₂ and CO obtained by using the "exact" expression

Figure 4. Coefficient of heat conductivity along a stagnation line for MSRO vehicle. 1: model of [8], 2: model of [21, 22], 3: model of [23, 24]. $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³.

$$V_i = - \sum_j D_{ii}^* \nabla x_j \quad (23)$$

and relation

$$V_i = -D_{ii}^* \nabla x_i. \quad (24)$$

From the data of **Figure 7**, it is obtained that for considered flow conditions, it is necessary to take into account and non-diagonal elements of diffusion matrix. Influence of thermo-diffusion and pressure diffusion on parameters of a flow was considered also. As pressure across a shock layer is equal practically constant then process of pressure diffusion can be not taken into account. The temperature in a shock layer changes essentially.

The temperature gradients are observed near a body surface and near a shock wave. In **Figure 8**, distribution along a stagnation line of sizes of thermo-diffusion coefficient D_T for separate component of a gas mixture is shown. In the first case, diffusion velocity speed was calculated under the formula

$$V_i = - \sum_j D_{ij}^* \nabla x_j - D_{Ti} \nabla \ln T \quad (25)$$

Figure 5. The coefficient of self-diffusion D^*_{ii} along stagnation line. 1: D^*_{11} ($\text{CO}_2\text{--CO}_2$), 2: D^*_{22} (CO--CO), 3: D^*_{55} (O--O). $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

In the second case, without taking into account the second term in the right part of above expression. The data resulted in **Figure 8** confirm that influence of thermo-diffusion effect is small.

In **Figure 9**, the obtained values of diffusion velocities for various component of a mixture with taking in account and without of thermo-diffusion are presented. It is evident that these values basically are much lower than corresponding parameters of mass diffusion. It allows suppose that thermo-diffusion influences are negligible. However for full clearness, it is necessary to take into account change of temperature.

In **Figure 10**, comparison of effective diffusion coefficients D_i for a component of mixture CO_2 and CO is determined in two ways—with the help of binary diffusion coefficients D_{ij} and multi-component coefficients D_{ij} is shown. The data in **Figure 10** are presented along a stagnation line across a shock layer for conditions of a flow of the vehicle: $V_\infty = 5292$ m/s, $\rho_\infty = 2.5 \times 10^{-4}$ kg/m³ in a case of ideal catalytic surfaces. It is shown that the effective diffusion coefficient determined with the help of two methods is very close.

Figure 6. Coefficient self-diffusion D^*_{ij} ($i \neq j$) along stagnation line, $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

Figure 7. Diffusion velocity along the stagnation line: 1: results with taking into account of all diffusion coefficients (formula (24)); 2: results with taking into account coefficients self-diffusion (formula (25)); (a) red line—CO₂ component; (b) black line—CO component. $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

Figure 8. Distribution of thermo-diffusion coefficient D_T along the stagnation line. $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

The Schmidt number is characterized the ratio of processes of momentum and mass transfer. For multi-component gas mixtures Schmidt's, Lewis's numbers depend on temperature and species fraction. For multi-component gas mixtures, Schmidt's numbers are defined for every pair of gas mixture. In practice during numerical calculations of chemically non-equilibrium flow, Schmidt's number are chosen be equal to constant. Sometimes to all components of a mixture Schmidt's number is used as identical. In this connection, it is important to estimate the influence of this supposition on the received results. Let us remind the definition of Schmidt's number $S_{ij} = \mu / \rho D_{ij}$, $D_{ij} = C_3 C_4 / p Q_{ij}^{1,1}$, $C_3 = 8.256 \cdot 10^{-7} T^{3/2}$, $[D_{ij}] = m^2 / c$, $[p] = atm$, $Q_{ij}^{1,1} = A^{02}$.

The Schmidt's number distribution along the stagnation line are shown in **Figure 11**.

Distribution of Lewis numbers along the stagnation line ($Le = Pr / Sc$, Pr is the Prandtl's number) for one of variants resulted in **Figure 12**. We shall notice, that near the surface of the vehicle ($n = 0$), Lewis's number considerably differs from unit that testifies discrepancy of mass velocities due to heat conductivity and diffusion in this area.

Figure 9. Distribution of diffusion velocity of different mixture component along the stagnation line with influence and without thermo-diffusion. $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

Figure 10. Effective diffusion coefficient along the stagnation line for CO_2 and CO , is obtained by two methods: $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³.

Figure 11. Values of Schmidt number along the stagnation line, ideal catalytic surface, (a) $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³, (b) $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³.

Figure 12. Values of Lewis's number along the stagnation line for different component of mixture, ideal catalytic surface. $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³.

5. Boundary conditions

The solution must be found out in the region restricted by: (a) body surface; (b) inflow: surface of external flow, where the conditions are known— $V_\infty, p_\infty, \rho_\infty, c_{i\infty}$; (c) axis of symmetry:

symmetrical or anti-symmetrical reflection depending on functions; (d) outflow: some surface in down part of flow, where usually ones use so called "soft" boundary extrapolation conditions.

The boundary conditions at the thermo-chemically stable surface include no slip conditions for component of velocities. Scott's wall slip conditions applied to velocity, species mass fractions for modeling flow fields in high altitude [25].

Appropriate boundary conditions at thermally stable surface include conditions for the diffusive fluxes of element at the wall, mass balance equations for the reaction product. When the temperature of the wall is done ($T = T_\infty$), then boundary conditions at the surface include L conditions for the elemental diffusive fluxes at the wall

$$J_{jw}^* = 0, (j = 1, \dots, L) \quad (26)$$

and the mass balance equations for the reaction products

$$J_{iw} = (\rho_w c_{iw})^v K_{wi}, (i = L + 1, \dots, N), \quad (27)$$

where $K_{wi} = \gamma(kT_w/2\pi m_i)^{1/2}$ is the effective catalytic constant. Here recombination is qualitatively characterized by an effective probability $0 < \gamma < 1$ or by rate constant K_{wi} ($K_{wi} = 0$ for an non-catalytic wall, $K_{wi} = \infty$ for a perfect catalytic wall). Value v is the order of the reaction, m_i is the atomic mass. The cases of $\gamma = 1$ and 0 correspond to absolutely catalytic and absolutely non-catalytic materials. The catalytic property of the wall has an important effect on the heat transfer of reusable vehicles over the considerable interval of the trajectory. The structure of the surface (contamination, roughness, porosity, etc.) affects the rates of the atomic adsorption and de-sorption processes.

A phenomenological model for catalytic reactions used that accounts for physical and chemical absorption, the interaction between the impinging atoms and ad-atoms (adsorbed atoms), and between the ad-atoms themselves. A model of the Rideal-Eley and Langmuir-Hinshelwood layer with ideal adsorption applied. Let us consider the heterogeneous catalytic reactions on surfaces [6]:

For a surface with final catalytic properties, it is applicable the simplified boundary conditions with use of effective probabilities of heterogeneous recombination that are equal among themselves $\gamma_O = \gamma_{CO} = \gamma_w$. Diffusion fluxes on a surface for a molecule CO and atoms O can be written as follows:

$$-J_{CO} = \rho k_{wCO} c_{CO}, -J_O = \rho k_{wO} c_O, k_{wi} = \frac{2\gamma_w}{2 - \gamma_w} \sqrt{\frac{RT_w}{2\pi m_i}}, i = CO, O \quad (29)$$

And for molecules O_2 and CO_2

$$J_{O_2} = -J_O, J_{CO_2} = -J_{CO} - J_O \quad (30)$$

Above boundary condition for the mass concentration on the body surface can be expended

$$\rho D_{ij} \partial c_i / \partial y = (\rho_w c_{iw})^v K_{wi} \quad (31)$$

If surface posses by catalytic properties then surface provoke to recombine the atoms in molecules. On absolutely catalytic surface concentration of atoms, it is equal to zero: $c_A = 0$. For absolutely non-catalytic wall $-\partial c_A / \partial y = 0$.

An expression for the heat flux to the surface may be deduced (for simplicity, relaxation is considered to be already completed at the wall), that is.

$$J_{qw} = -\lambda \partial T / \partial y - \sum_{k=L+1}^N h_k J_k \quad (32)$$

The heat flux depends essentially on the boundary conditions for the species concentrations at the wall. Thus at $K_{wi} = 0$, we obtain

$$J_{qw} = -\lambda \partial T / \partial y \quad (33)$$

For reusable vehicles, the catalyze quality of heat-protective coverings become very important. The heat flux increases as the diffusion contributes to the maximum total heat flux. Since homogenous recombination and neutralization occur slowly at high altitudes, exothermic heterogeneous processes at the body surface become crucial to the magnitude of the convection heat flux.

Next equation may be used to find the temperature with the boundary condition of heat balance at the wall between flux to surface and reflection. The energy equation yields

$$J_{qw} = \varepsilon \sigma T_w^4 \quad (34)$$

where ε is a measure of the surface blackness and σ is the Stefan-Boltzmann constant.

Rotational temperatures of molecules are equal to the translational temperature of heavy atomic particles due to a fast translational-rotational energy exchange requiring only several collisions to establish the Boltzmann distribution. In the free stream, CO_2 molecules have almost zero vibration energy, therefore, for them in a shock layer, there is an area with non-equilibrium vibration. Vibration temperatures of all the electronically exited molecules are considered to be equal to the translation temperature of heavy atomic particles.

6. Mathematical models and numerical methods

Hypersonic flows over real space configurations represent a substantial problem from the point of view of the development of new and more effective mathematical models, numerical algorithms and the use of modern computer systems.

During the past decade, a large number of computational codes have been developed that differ in the grid generation methods and numerical algorithms used. For numerical simulation of external flow fields, past real form bodies are necessary to construct the geometry, to design a discrete set-grid, to provide the mathematical model of the initial value problem, to approximate the governing equation by numerical ones, to design a computational algorithm, to realize the flow field, to establish a feed-back of obtained results with experiment, analytical and benchmark problems, and so on.

As mathematical model, the Navier-Stokes equations and the various sub-models obtained in frameworks of the asymptotic analysis sub- and supersonic flow past blunted bodies in various statements and in a wide range of numbers of Reynolds are used.

Traditional asymptotic analysis of Navier-Stokes equations for different regimes of viscous compressible flow depending on small parameter $1/Re$ make it possible to decouple the different types of gas flows. The next methods were used: Navier-Stokes equations in so-called approximation of a viscous shock layer and full Navier-Stokes (N-S) equations. For solution of governing equations, the implicit finite-difference monotone schemes of the second order are used [15, 16]. Generalized Rankine-Hugoniot's conditions are imposed in the shock wave. Special method of high stiffness resolution of non-equilibrium phenomena is applied [16].

The Navier-Stokes equations are written in a conservative form for arbitrary coordinate system. The implicit iterative scheme is based on a variant of Lower-Upper Symmetric Gauss-Seidel (LU-SGS) scheme. At high altitudes (low Reynolds numbers) where the bow shock has a finite thickness, a shock capturing approach is used. So inflow boundary conditions are specified in the free stream. At lower altitudes, a shock fitting scheme is employed with the modified Rankine-Hugoniot conditions specified at the bow shock. Besides the Navier-Stokes equations at lower altitudes, the viscous shock layer equations are also solved. This implicit scheme leads to the scalar diagonal manipulation for a case of non-reacting perfect gas flow and does not require any time-consuming matrix inversion. In more details, the numerical methods is described in [26–28] for the shock layer equations.

7. Results of numerical investigation of hypersonic flow past space vehicle in Martian atmosphere

The investigations of a hypersonic flow past a frontal part of MSRO (Mars Sample Return Orbiter) and MARS EXPRESS vehicles descending in an atmosphere of Mars are shown below. The hypersonic Mach number means that appreciable quantity of molecules in high-temperature region began to dissociate. For an Earth atmosphere such numbers is equal to $M_\infty \geq 6$. For an atmosphere of Mars in which main component is carbon dioxide as hypersonic numbers, the values $M_\infty \geq 10$ are considered. The typical regimes of the entry in a Martian atmosphere are considered (**Figure 2**). The conditions of a flow corresponding to the last stage of flight of space vehicles in an atmosphere of Mars ($V_\infty \leq 6$ km/s, $\rho_\infty \approx 10^{-5}$ kg/m³, $H < 60$ km)

were studied. Determining process at such velocities is a process of dissociation. Up to 75% of full gas flow, energy can be spent on it [29].

The region where non-equilibrium physical and chemical processes realized is a significant part from all considered regions. Velocity of physical and chemical processes, as a rule, grows together with density of gas. As the density of an atmosphere of Mars is much less than in atmosphere of the Earth, the equilibrium flows for bodies of the moderate sizes are observed at smaller altitude: $H < 10\text{--}20\text{ km}$ —for an atmosphere of Mars, $H \leq 30\text{ km}$ —for an atmosphere of the Earth.

At high temperatures that observed in a shock layer, the characteristic times of a vibration energy relaxation of molecules and characteristic times of dissociation become one order. Thus the account of non-equilibrium excitation of vibration degrees of freedom of carbon dioxide molecules is necessary.

7.1. Some features of a reacting gas mixtures flow

At a supersonic flow, the main features of reacting gas mixture can be evidently shown by change of flow parameters across shock layer. The distribution of pressure, velocities in a shock layer depends on physical and chemical processes weakly. The pressure with high degree of accuracy is estimated in limits between values $p = \rho_\infty V_\infty^2 (1 - k)$ behind a direct shock wave and $p = \rho_\infty V_\infty^2 (1 - 0.5 \cdot k)$ in a stagnation point [29]. Here value $k = \rho_\infty / \rho_s$ is the characteristic value of gas compression in the shock layer equal the ratio of density in an external flow and density behind a direct shock wave. For flow parameters of MARS EXPRESS vehicles presented in **Table 1**, the pressure in a stagnation point equals to values 0.95–0.96 of a high-speed pressure $\rho_\infty V_\infty^2$. We shall notice that for the perfect gas with a parameter of an adiabatic ratio $\gamma = 1.4$ at the given velocities, the pressure in a stagnation point takes ~ 0.92 from a high-speed pressure.

Main results are shown: (1) in shock layer across of stagnation line; (2) along of surface body for heat transfer; and (3) in shock layer along body. We used the orthogonal system of coordinates (ξ, ζ) . One coordinate ξ directs from a forward stagnation point along a streamline contour along the surface. The coordinate ζ is a normal to wall.

The change of specific heat capacity ratio $\gamma = c_p / c_v$ (c_p is the specific heat capacity at constant pressure and c_v is the specific heat capacity at constant volume) is shown in **Figure 13**.

$H, \text{ km}$	$V_\infty, \text{ m/s}$	$\rho_\infty, \text{ kg/m}^3$	$T_\infty, \text{ K}$	Re_∞	$P_0 / (\rho_\infty V_\infty^2)$
52.59	5923	7.61×10^{-5}	140	1.7×10^4	0.96
43.01	5292	2.51×10^{-4}	149	5.0×10^4	0.96
36.16	4259	5.58×10^{-4}	158	9.1×10^4	0.95
32.42	3433	8.45×10^{-4}	163	1.1×10^5	0.96

Table 1. Trajectory parameters of MARS-EXPRESS.

Figure 13. Changing ratio of specific heat capacity for flows past MSRO.

The ratio is always greater than 1 and its value is an important indication of the atomicity of the gas. The laminar-to-turbulent transition of flow on the frontal surface proceeds at the altitude below 20 km. Thus the taking into account of the boundary layer transition does not affect on the results of heating the thermal protection. In **Figure 14**, distributions of shock layer temperature along a stagnation line near spherically blunted body (radius $R = 1$ m) under various conditions of a flow are shown. It includes the regimes from completely viscous shock layer until flow with a thin boundary layer. Parameters of flow in a shock layer is obtained in approach of a viscous shock layer by numerical computation and with help of the physical and chemical models submitted in work [10]. Thus Reynolds's number— Re_∞ varied (due to change of density of an external flow) from 5×10^3 to 1.5×10^5 . In the shock layer, the pressure determined by the velocity and density of the external flow equal to $p = 0.22$ atm ($Re_\infty = 1.5 \times 10^5$) and in the most part of a shock layer close to equilibrium value (a curve 4).

With reduction of pressure and also Reynolds's numbers the length of non-equilibrium region increases and at $p = 0.007$ atm character of flow in a shock layer becomes closer to frozen (curve 1). For comparison in **Figure 14**, the structure of temperature on a stagnation line of a flow without taking into account physical and chemical transformations is shown also (curve 5). This calculation is carried out under condition of laws of the perfect gas. It is visible that behind a boundary layer, the temperature leaves on "slop" and its value in some times higher than in case of a flow with chemical reactions. The estimations show that in case of chemical reactions under the given conditions up to 75% of full energy of an external flow it can be spent on dissociation molecules. As a result, the temperature in a shock layer essentially goes down and the density of gas increases. Thus the share of kinetic energy spent on realization of

Figure 14. Distribution of temperature along stagnation line for two points MARS EXPRESS vehicle. 1: model of [30], 2: model of [31], 3: model of [32–34].

physical and chemical processes in a shock layer is essential that affects distribution of temperature and does inapplicable many results of gas dynamics of the perfect gas.

7.2. Influence of various models of chemical kinetics on a hypersonic flow past bodies

One of the most important problems of a hypersonic flow is the account of the real physical and chemical transformations in a shock layer. In theoretical works, the different authors used models of the chemical reactions essentially differing by reaction rate constants. Let us carry out comparison of the basic models used for calculation of chemical reaction rate constants in a high-temperature flow of carbon dioxide gas. We can estimate the influence of these models on character of a flow and heat transfer to the wall. The basic models of chemical reactions have essentially different reaction rate constants in a high-temperature flow of carbon dioxide gas. The corresponding dissociation reaction rate constants in a considered range of temperatures can differ up to two orders in dependence on used models [30–35].

In works [10, 13, 17–19], numerical research of a non-equilibrium flow of the bodies modeling the form of Martian vehicles MARS EXPRESS and MSRO with use of these models is carried out. The surface of the vehicles was considered or as ideal catalytic (the maximal velocities heterogeneous recombination a component of dissociated carbon dioxide gas), or non-catalytic (velocities of heterogeneous recombination of component is equal to zero). We shall consider some results of numerical researches.

As an example of the distribution of CO₂ concentration in **Figure 15** in shock layer for two type of cone; (a) $\theta = 60^\circ$, (b) $\theta = 10^\circ$; $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³ is shown.

In **Figure 16**, structures of mass concentration component CO₂ and CO obtained in case of use one-temperature ($T_v = T$) and two-temperature [36] reaction rate constants of chemical reactions. It is evident that for considered flow conditions an influence of non-equilibrium vibration on dissociation process is insignificant: structures of mass concentration CO₂ and CO coincide almost in all region of a shock layer. The small divergence is observed near a shock wave. From data, it is followed that process vibration non-equilibrium does not affect on parameters of flow near a body.

With use of these models, chemically non-equilibrium flow is considered and their influence on parameters of flow and heat exchange is established. The significant differences in distributions of temperature, concentration of a component of a gas mixture in a shock layer is observed at a variation of model chemical kinetics.

From the data shown in **Figure 17**, it is evident that for conditions of flight $H = 43$ km, the significant differences of values of mass concentration of carbon dioxide and an withdrawal of the shock wave from a surface is observed. For $H = 32$ km, corresponding values practically coincide. This fact can be explained at an altitude $H = 43$ km, the mode of flow in a shock layer is far from chemical equilibrium. In this case, the parameters of flow depend on reaction rate constants of direct and reverse chemical reactions. For different models under these conditions of a flow, it differs essentially. Therefore in considered case, if you used models of Park then the dissociation reaction CO₂ in the disturbed region goes with much more rate than it is proposed by another two models. The chemical components in a shock layer affects on distributions of temperature and also on size of a withdrawal of a shock wave from a surface of a body.

Figure 15. Distribution of CO₂ concentration in shock layer for two type of cone; (a) $\theta = 60^\circ$, (b) $\theta = 10^\circ$; $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³.

Figure 16. Distribution of mass concentration CO_2 and CO along the stagnation line, 1—with, 2—without taking into account the influence of vibration relaxation on process dissociation, $V_\infty = 5223 \text{ m/s}$, $\rho_\infty = 2.93 \times 10^{-4} \text{ kg/m}^3$.

Figure 17. Profile of mass concentration of CO_2 along the stagnation line for two point of trajectories MARS EXPRESS vehicle. 1: model of [30], 2: model of [31], 3: model of [32–34].

With reduction of velocity flight, it corresponds with an increase of density in a shock layer and flows more close to equilibrium case. The parameters of flow and structure of a gas mixture are defined by conditions of chemical equilibrium. The reaction rate constants in equilibrium will be the same for all used models. In this connection, corresponding structures of temperature and concentration, and also value of a withdrawal of a shock wave from a surface received for different models under conditions of a flow at height $H = 32$ km well enough coincide.

Influence of chemical models on flow parameters and heat exchange is determined in a wide range of parameters of a flow of MSRO vehicle in cases ideally catalytic and non-catalytic wall. In **Figures 18** and **19**, mass concentrations of component CO_2 and CO along stagnation line for different models and types of condition on wall are submitted. The data are resulted for conditions of flow $V_\infty = 5687$ m/s, $\rho_\infty = 3.14 \times 10^{-5}$ kg/m³ that corresponds approximately to altitude of flight $H \approx 60$ km; the temperature of a surface equal to $T_w = 1500$ K.

Comparing the data of **Figures 18** and **19**, it is possible to notice that influence of catalytic surface properties affects profiles of concentration basically near to a wall. In these figures, the significant divergence in the distributions of concentration the components obtained for different models is observed. It is evident that it is greater for degree CO_2 dissociation in a shock layer when it used of model of Park [31], and is smaller—when the model of Kenzie-Arnold [30] used. The model of Research Institute of Mechanics (NIIMekh) of Moscow State University [32–34] gives the intermediate results. It is established that change of reaction rates practically does not influence on value of a heat flux to ideal catalytic wall of the vehicle. In a

Figure 18. Profiles of mass concentration CO_2 (—) and CO (- - -) along stagnation line MSRO vehicle, ideal-catalytic wall, 1: model of [30], 2: model of [31], 3: model of [32–34].

case non-catalytic surfaces the difference in values of the heat fluxes received for different models can be essential up to 30%.

In **Figure 20**, for two points of a trajectory of MARS EXPRESS vehicle (altitude of flight equal to $H = 43$ km and $H = 32$ km) the distributions of temperature obtained with the help of model

Figure 19. Profiles of mass concentration CO_2 (—) and CO (---) along stagnation line MSRO vehicle, non-catalytic wall, 1: model of [30], 2: model of [31], 3: model of [32–34].

Figure 20. The temperature along the stagnation line for sphere $R = 1$ m in Mars atmosphere. 1: pressure $p = 0.007$ atm, $\text{Re}_\infty = 5 \times 10^3$; 2: 'frozen' flow: $p = 0.07$ atm, $\text{Re}_\infty = 5 \times 10^4$; 3: $p = 0.22$ atm, $\text{Re}_\infty = 1.5 \times 10^5$; 4: $p = 0.22$ atm, $\text{Re}_\infty = 1.5 \times 10^5$, equilibrium case; 5: $p = 0.065$ atm, $\text{Re}_\infty = 1.3 \times 10^5$, perfect CO_2 gas.

of Park [31], models of Kenzie-Arnold [30] and the model developed in Research Institute of Mechanics (NIIMekh) of Moscow State University [32–34] are shown. The data are resulted along a stagnation line. The surface of the vehicle it is an ideal—catalytic wall with the constant temperature.

Figure 21 shows the density distribution along the stagnation line for three conditions of a flow of MSRO vehicle in an atmosphere of Mars. In case of non-equilibrium flows, the density along stagnation line considerably changes.

7.3. Influence of non-equilibrium vibration kinetics on parameters of a flow

Let us consider results of numerical calculation of a non-equilibrium flow from point of view of different vibration relaxation models. The influence of non-equilibrium excitation of vibration degrees of freedom of carbon dioxide was investigated on a basis of three-temperature kinetic model and two simplified case: in two-temperature approach when it introduced uniform vibration temperature for all types of vibration of CO_2 molecule and in one temperature approach when translational and vibration temperature was the same [10, 36].

Structures of two specific vibration energy E_{12} and E_3 for conditions of a flow past MSRO vehicle $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³ (altitude of flight ~40 km) along the stagnation line in shock layer obtained with use of three-temperature model of a vibration relaxation and presented in **Figure 22**.

These profiles are characterized by significant flow gradients in relaxation region near a shock wave and their behavior reflects of features of considered vibration relaxation model of molecules CO_2 which is taking into account internal structure of molecules CO_2 and extra mode exchanges by vibration energy.

Figure 21. Density distribution along the stagnation line for different condition of flow past MSRO vehicle. 1: $V_\infty = 5223$ m/s, $\rho_\infty = 2.933 \times 10^{-4}$ kg/m³; 2: $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-4}$ kg/m³; 3: $V_\infty = 3536$ m/s, $\rho_\infty = 2.819 \times 10^{-5}$ kg/m³.

In **Figure 23**, comparison of total rotation energy $E_v = E_{12} + E_3$ and the vibration energy E_v obtained with the help of three-temperature [10] and two-temperature models [36] for two conditions of a flow of the vehicle is carried out: $V_\infty = 5223$ m/s (altitude of flight $H \sim 40$ km) and $V_\infty = 5687$ km/s ($H \sim 60$ km).

The vibration energy difference near a shock wave in relaxation zone is visible. The structures received with the help of two-temperature model have more “smearing” type than the structures

Figure 22. Distribution of vibration energy component along stagnation line MSRO vehicle, three-temperature model [10], 1: E_{12} , 2: E_3 . $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³.

Figure 23. Distribution of vibration energy along stagnation line MSRO vehicle; 1: $E_v = E_{12} + E_3$, three-temperature model of [10]; 2: E_v , model of [37]; (a) $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³; (b) $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³.

received with use of more rigorous three-temperature approach. You can see also that the maximum values of vibration energy obtained with the help of three-temperature model on 15–20% surpass corresponding values of two-temperature model. In the most part of a shock layer, conditions of thermodynamic equilibrium are realized and both models give identical result.

It is possible to estimate the non-equilibrium vibration zone value considering the structures translational and vibration temperatures T_{12} , T_3 . The various modes received with help of three-temperature model and for two variants of a flow are displayed in **Figure 24**. It is visible that the size of this zone is more for the second variant of a flow ($V_\infty = 5687$ m/s) corresponding to altitude ~ 60 km.

Comparison of values of translational temperature for two conditions of a flow in the assumption of a weak deviation from thermal equilibrium at $Tv = T$ (a curve 1) and in non-equilibrium gas (curves 2, 3) along a stagnation line is presented in **Figure 25(a)** and **(b)**. Corresponding to relaxation models profiles of temperature (curves 2 and 3) for these conditions practically coincide, a divergence no more than 5%.

It is visible that the account of non-equilibrium excitation of vibration degrees of freedom of molecules CO_2 leads to insignificant increase in a withdrawal of a shock wave from a surface of a body and to essential increase ($\sim$ on 25–30%) translational temperature in the field of a shock wave in comparison with thermally equilibrium case. It does not influence on a gas mixture temperature near to a body surface. The fact of translational temperature increase in relaxation zone is connected with transition of internal degrees energy of freedom of molecules CO_2 in translational energy of others components.

7.4. Processes of heat transfer in the multi-component mixture

Comparison of a heat transfer in the assumption thermally equilibrium (curves 1) and non-equilibrium gas (curves 2, 3) in cases ideal catalytic (**Figures 26** and **27**) and non-catalytic

Figure 24. Profiles translational (T) and vibration (T_{12} , T_3) temperature for MSRO vehicle, three-temperature model of [10]; (a) $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³; (b) $V_\infty = 5687$ m/s, $\rho_\infty = 3.141 \times 10^{-5}$ kg/m³.

Figure 25. The translational temperature along the stagnation line for MSRO vehicle, 1: equilibrium flow, 2: non-equilibrium flow, three-temperature model of [10], 3: non-equilibrium flow, two-temperature model [38], (a) $V_{\infty} = 5223$ m/s, $\rho_{\infty} = 2.93 \times 10^{-4}$ kg/m³, (b) $V_{\infty} = 5687$ m/s, $\rho_{\infty} = 3.14 \times 10^{-5}$ kg/m³.

surfaces (**Figure 27**) is carried out. It is visible that the thermal flux from point of view of non-equilibrium excitation of vibration degrees of freedom of molecules CO₂ can surpass on 10% a flux for thermally equilibrium gas.

Comparing the data in **Figures 26** and **27** for the same conditions of a flow, we shall notice that the heat transfer to ideal-catalytic surface in 3–4 times surpasses a corresponding flux to non-catalytic wall.

This fact can be explained by that in a case when on a surface the maximal rates of heterogeneous recombination of a component of carbon dioxide gas is observed (ideal catalytic), the chemical energy spent on dissociation is allocated and transferred to a surface. If recombination does not occurs (low catalytic activity), gas components pass down flow, carrying away with itself the dissociation energy and the additional heat transfer does not occur.

As it was already observed, the heat transfer to ideal catalytic wall does not depend on used model of chemical reaction rates that the curves show in **Figure 26**. For non-catalytic walls, the heat transfer to a surface with using of Kenzie-Arnold model [30] approximately on 30% exceeds a heat transfer obtained with help of model of Park [31]. It shows that at non-catalytic surfaces of the vehicle does not occur of recombination of a component. In this case, reactions go only in one direction, and with different velocities for different models. As result for considered models, the different chemical composition of a gas mixture near surfaces (**Figure 29**) obtained. Also divergences in values of a heat transfer are observed. Besides the recombination reactions on a surface of additional body heating does not occur. Therefore value of a heat transfer for non-catalytic walls in 3–3.5 times less than corresponding values for ideal catalytic surfaces (**Figure 27**). A heat transfer distribution of along a frontal surface of MARS EXPRESS vehicle (it is ideal catalytic surface) with use of three models chemical kinetics is resulted in **Figure 29**. In spite of various rates of reactions, the good correlation of results observed for a heat transfer to a surface for considered models. Really in a case, ideally catalytic wall last plays a role of the catalyst. It is promotes the reactions of recombination and as a result the

Figure 26. Heat transfer to MSRO vehicle surface in case of ideal catalytic wall; 1: equilibrium flow, 2: non-equilibrium flow for three-temperature model [10], 3: non-equilibrium flow for two-temperature model [38]. $V_{\infty} = 5223 \text{ m/s}$, $\rho_{\infty} = 2.93 \times 10^{-4} \text{ kg/m}^3$.

chemical energy spent on dissociation is transferred to wall. This process is determined mainly by conditions of equilibrium of reactions.

Influence of non-equilibrium excitation of vibration degrees of freedom of molecules CO_2 on distribution of a heat flux along a surface of a body is displayed in **Figures 26–29**.

In **Figure 29** for comparison (a triangular marker) the results of works [6] in which Navier-Stokes equations solved by method of finite volume are submitted also. In this case, the model of chemical reactions [32–34] was used. For some conditions of a flow the discrepancy reached (up to 20%) for the obtained values of heat fluxes. The corresponding data of [6] obtained for different boundary conditions: in Ref. [6] the condition conservation of heat balance used on a surface, and in our case—a condition of a constant of surface temperature is considered.

Figure 27. Heat transfer to MSRO vehicle surface in case of non-catalytic wall; 1: equilibrium flow, 2: non-equilibrium flow for three-temperature model [10], 3: non-equilibrium flow for two-temperature model [38]. $V_{\infty} = 5223$ m/s, $\rho_{\infty} = 2.93 \times 10^{-4}$ kg/m³.

Figure 28. Heat transfer to MSRO vehicle surface in case of ideal catalytic wall; 1: equilibrium flow, 2: non-equilibrium flow for three-temperature model [10], 3: non-equilibrium flow for two-temperature model [38]. $V_{\infty} = 5687$ m/s, $\rho_{\infty} = 3.141 \times 10^{-5}$ kg/m³.

Figure 29. Heat transfer to MARS EXPRESS vehicle surface in case of non-catalytic (a) and ideal catalytic wall (b); 1: model [30], 2: model of [31], 3: model of [32–34], ▲: data of [6].

Catalytic surface have selectively but significant effect on species and reactions on the surfaces. During entry in Martian atmosphere molecule of carbon dioxide (CO_2) dissociated on CO and O. The most part of energy of flow ($\frac{3}{4}$) spends on dissociation. For high catalytic surface kw (surface assist to recombination the atoms to molecules), chemical reactions that spend on dissociation transfer (partially or fully) their energy back to the surface and produce on an additional heating. For low catalytic surface, recombination does not occurs and atoms move downstream and take away the energy of dissociation and additional heating does not happen. It is possible to diminish temperature of surface on 300–500 K when temperature of flow is about 1800–2000 K.

In **Figure 30**, the heat transfer to ideal catalytic and non-catalytic surface of the vehicle for conditions of flow MSRO $V_\infty = 5687 \text{ m/s}$, $\rho_\infty = 3.14 \times 10^{-5} \text{ kg/m}^3$ and $T_w = 1500 \text{ K}$ are displayed.

In **Figure 31**, the heat transfer to non-catalytic wall of the vehicle obtained for conditions of flow $V_\infty = 3998 \text{ m/s}$, $\rho_\infty = 3.0 \times 10^{-4} \text{ kg/m}^3$. In **Figure 31**, the distinction between data of corresponding curves pick up to 15%. In this case, the flow in a shock layer is characterized by smaller temperatures (velocity in an external flow was less) than the regime which correspond to curves of **Figure 30**.

Therefore, it is marked a smaller divergence in values of reaction rate constants and as consequence at values of a heat fluxes for different models.

In **Figure 32**, the heat flux to non-catalytic wall for numbers $Sc = 0.45$; 0.65 and two conditions of a flow are shown. It is evident that for non-catalytic surfaces the value of Schmidt's number practically does not take an influence on the heat transfer. The heat flux is determined basically just by heat conductivity. In this case near the surface of a body there are not recombination reactions. The products of dissociation are carrying out with themselves the energy of dissociation. As a result of additional heating, the body caused by diffusion processes it does not occur.

In **Figure 33**, the heat transfer to non-catalytic wall is shown (conditions of flow $V_\infty = 5223$ m/s, $\rho_\infty = 2.9 \times 10^{-4}$ kg/m³) for different values of Prandtl's number: $Pr = 0.66$ and $Pr = 0.75$. In a case

Figure 30. Heat transfer to MSRO vehicle surface in case (—) ideal catalytic wall; (---) non-catalytic wall; $V_\infty = 5687$ m/s, $\rho_\infty = 3.14 \times 10^{-5}$ kg/m³; 1: model of [30], 2: model of [31], 3: model of [32–34].

Figure 31. Heat transfer to MSRO vehicle surface; non-catalytic surface $V_\infty = 3998$ m/s, $\rho_\infty = 3.0 \times 10^{-4}$ kg/m³. 1: model of [30], 2: model of [31], 3: model of [32–34].

of non-catalytic wall, a leading role has another dimensionless factor—Prandtl’s number. You can see that the increase in value of Prandtl’s number from 0.66 till 0.75 leads to reduction of a heat flux value approximately on 10%.

Figure 32. Heat transfer to vehicle surface; T1: $V_{\infty} = 5223$ m/s, $\rho_{\infty} = 2.93 \times 10^{-4}$ kg/m³; T2: $V_{\infty} = 5687$ m/s, $\rho_{\infty} = 3.14 \times 10^{-5}$ kg/m³.

Figure 33. Heat transfer to non-catalytic wall for different Prandtl’s number; $V_{\infty} = 5223$ m/s, $\rho_{\infty} = 2.9 \times 10^{-4}$ kg/m³.

7.5. Influence of catalytic wall on a heat transfer

The heat flux to a surface of the vehicle without taking into account radiation effect in one-temperature approach is determined as:

$$\mathbf{q} = -\lambda \nabla T + \sum_{i=1}^N h_i \mathbf{J}_i - p \sum_{i=1}^N D_{T_i} \mathbf{d}_i \quad (35)$$

where h_i is the enthalpy of i th components of a mixture, λ is the coefficient of heat conductivity of all degrees of freedom which are taking place in a condition of local thermal balance. The second component with in the right part (5) defines the diffusion component of a heat flux and the third term characterizes influence of thermo-diffusion on heat exchange.

As show results of calculations the contribution of the third component on value of a total heat transfer makes less than 1%. It means that influence of thermo-diffusion on heat exchange is small. The mass transfer processes play the important role in definition of a heat transfer to a surface. Really diffusion component for a heat transfer for the considered conditions of a flow makes a significant part (50–75%) from value of a full heat flux. In this connection, the correct account of diffusion processes has great importance.

As already it has been shown that the main factors influencing heat transfer to a surface of the vehicle, it is heterogeneous recombination of component in dependence on catalytic properties of a surface. We try to explain the influence of chemical reactions on parameters of flow in a shock layer and value of a heat transfer for MSRO vehicle in a case of non-catalytic surfaces. And then it is compared with received results with the corresponding data for ideal catalytic surface.

For calculation, diffusion fluxes were used: Fick's law with the adjusting amendment; Fick's law in standard form in which effective diffusion coefficients are calculated through binary diffusion coefficients and concentrations from point of view of the formula; and Fick's law in the usual form in which Schmidt's number was considered equal to all a component and to be constants.

Depending on the manner of representation of diffusion, the heat transfer can differ essentially up to 30%. Let us notice that more correct way of the diffusion definition that is used for the Fick's law with the amendment gives the values of a heat transfer exceeding on 10% corresponding values received from point of view of Fick's law in the standard form. It is evident that the variant with Schmidt's number $Sc = 0.45$ results most close to corresponding data that it is obtained at a correct way of the diffusion account [38, 39].

For non-catalytic surface, main effect will be play another parameter—Prandtl's number. In **Figure 34**, you can see the heat transfer to non-catalytic surface ($V_\infty = 5223$ m/s, $\rho_\infty = 2.9 \times 10^{-4}$ kg/m³) for different Prandtl's number: $Pr = 0.66$ and $Pr = 0.75$. Increase of Prandtl's number from 0.66 until 0.75 leads to decreasing heat transfer on 10%.

In **Figure 35**, the heat flux for two types of a surface and two flow conditions is shown. You can see that value of a heat transfer to non-catalytic surfaces is approximately 3–4 times less than corresponding value of a heat transfer in a case ideal catalytic surface.

Figure 36 shows values of a heat flux to a surface having various catalytic property. The curve 2 (a variant of a surface with final catalytic) is obtained for the following parameters:

Figure 34. Heat transfer to vehicle surface. Black line—total heat flux; red line—diffusion part; (a) $V_\infty = 5687$ m/s, (b) $V_\infty = 5223$ m/s.

Figure 35. Heat transfer to MSRO vehicle surface. 1: $V_\infty = 5223$ m/s, $H = 40$ km; 2: $V_\infty = 5687$ m/s, $H = 60$ km.

Figure 36. Heat transfer to MSRO vehicle surface. 1: Ideal catalytic wall, 2: finite catalytic, $k_{wco} = 0.77$ m/s, $k_{wo} = 1$ m/s, 3: non-catalytic wall, $V_{\infty} = 5223$ m/s, $H = 40$ km.

probability of recombination reactions— $\gamma_w = 2.7 \times 10^{-3}$; catalytic constants— $k_{wo} = 1$ m/s, $k_{wco} = 0.77$ m/s (see the formula 30). From the presented data, you can see that due to use low catalytic coverings it is possible to lower a heat transfer to a surface of the vehicle on a significant part of a trajectory in some times.

The submitted data show an insignificant influence of processes of vibration relaxation on a heat transfer to a surface of MSRO vehicle. It is also possible to note that taking into account of complex internal structure of molecules CO_2 and exchanges of vibration energy between modes does not take an influence on a heat transfer to a surface. It testifies to legitimacy of application of the simplified models of vibration kinetics at the solution of the given class of problems. The fact of weak influence of a vibration relaxation on a heat transfer to a surface of the vehicle is possible to explain for considered conditions of a flow and the considered form of a surface intensive process dissociation molecules of carbon dioxide gas in a shock layer is observed, and also by fast process of an vibration relaxation of molecules CO_2 as a result of which thermodynamic equilibrium is present almost in all shock layer.

We would like to consider the influence of the form of the blunted body on parameters of a non-equilibrium flow in modeling an atmosphere of Mars a flow of carbon dioxide gas. Let us consider the heat transfer along surface of spherically blunted cones with various half opening angles.

In a vicinity of the stagnation point on a spherical part of cone surface with various angle of opening, the solution practically coincides. On a conic surface, the size of parameters of a flow essentially depends on an angle of opening a cone that affects on value of a heat flux to a surface (Figure 37).

Figure 37. Heat transfer to the surface of blunted cones with different opening angle θ for Mars atmosphere; 1: $\theta = 60^\circ$, 2: 50° , 3: 40° , 4: 30° , 5: 20° , 6: 10° . $V_\infty = 5223$ m/s, $\rho_\infty = 2.93 \times 10^{-4}$ kg/m³.

As a result of the carried out researches, it is received (calculations were carried out with help of two-temperature model of a vibration relaxation) that for conditions of flows in an atmosphere of Mars corresponding to velocities 4–6 km/s and to altitude $H < 60$ km flight, the vibration relaxation of molecules on a spherical part of a body occurs quickly and thermodynamic equilibrium is present almost in all cross section of a shock layer.

As show numerical calculations for altitude of flight $H \leq 60$ km the blunted bodies in an atmosphere of Mars the increase of a heat transfer to a surface taking in account the mechanism of an vibration relaxation makes no more than 20%.

7.6. The role of non-equilibrium radiation

The role of radiation is rather insignificant for descent space vehicle in an atmosphere of Mars with the characteristic sizes 1–2 m and at entrance velocity of $U_\infty \approx 5 - 6$ km/s. On vehicles which sizes will be at 5–10 times more, the radiant flux can be comparable with convective. The pilot and automatic expeditions with use of diving is perspective due to aerodynamic braking devices in the top layers of Mars atmosphere with U 6–8 km/s up to 3.3 km/s with the subsequent exit into basic orbits around of Mars. In this case the radiant flux is determined by non-equilibrium radiation as the vehicle penetrates an atmosphere of Mars at heights $H > 30$ km in which physical and chemical processes in a shock layer is essentially non-equilibrium. At $H < 30$ km, the radiation flux to space vehicle is determined by equilibrium radiation and its level is insignificant. At hyperbolic velocities of an entrance of flight, the

radiation flux can be strong that play an essential role at a stage of a choice of the of descent trajectory and heat protection system of space vehicle.

Thermo-chemical model of the $\text{CO}_2\text{-N}_2$ mixtures for the calculation of the non-equilibrium ultra-violet (UV) molecular band radiation in the high-temperature shock layer around the capsule during an entry is considered [19].

In the frontal part of a thin shock layer radiation, absorption is small enough. Thus, the gas is assumed to be transparent to radiation in the relaxation zone of the shock layer. Radiation intensity is calculated in the approximation of volume luminescence. Radiation processes involving excited particles are considered as spontaneous radiating transitions, excitation and deactivation of the electronic states of the molecules, impacts of electron and heavy particles, etc. [40, 41]. Corresponding equation of excitation and deactivation of the electronic states determine a concentration of each component. Flow parameters across the shock layer are calculated and the spectral structure of radiation is obtained. For the analysis of the non-equilibrium radiation, the results of some theoretical and experimental studies behind shock waves in $\text{CO}_2\text{-N}_2$ mixtures used. In the relaxation zone of the vehicle shock layer, the Boltzmann distribution of the electronically excited states of atoms and molecules does not exist under the considered Martian entry conditions. It leads to a significant deviation of the radiation intensity from local equilibrium especially for low gas density.

The suggested thermo-chemical model of the $\text{CO}_2 + \text{N}_2$ mixture contains 10 neutral chemical species: CO_2 , CO , CN , NO , N_2 , O_2 , C_2 , C , N , O , 4 molecular ions and free electrons: CO^+ , NO^+ , N_2^+ , O_2^+ , e^- , and 12 electronically excited states of diatomic molecules: $\text{CO}(\text{A}^1\Pi)$, $\text{CO}(\text{b}^3\Sigma^+)$, $\text{CN}(\text{B}^2\Sigma^+)$, $\text{CN}(\text{A}^2\Pi)$, $\text{NO}(\text{B}^2\Pi)$, $\text{NO}(\text{A}^2\Sigma^+)$, $\text{NO}(\text{C}^2\Pi)$, $\text{NO}(\text{D}^2\Sigma^+)$, $\text{N}_2(\text{A}^3\Sigma_u^+)$, $\text{N}_2(\text{B}^3\Pi_g)$, $\text{O}_2(\text{B}^2\Sigma_u^-)$, $\text{C}_2(\text{d}^3\Pi_g)$.

The thermo-physical properties of chemical species are taken from Ref. [42]. Thus, 19 chemical reactions and 33 reactions of the excitation of the electronic states of molecules are taken into account. The reactions with the participation of the neutral and charged particles in a high-temperature Martian atmosphere are considered. The rate constants of the basic chemical reactions have been collected from the literature [29, 31–34, 43].

Practically, it is convenient to use simplified radiation models that are capable to estimate radiation emission with sufficient accuracy. The estimations have shown that the gas is transparent to UV molecular radiation in the shock layer under the considered conditions. And it is possible to calculate radiation intensity with the approximation of volume luminescence. The “just overlapping line model” model is used to calculate spectral distribution of non-equilibrium molecular band radiation. The model considers a spectrum consisting of only one branch of rotational lines. The shock layer is optically thin for spectral range considered so the process of light absorption is not taken into account. It is shown that the depletion of electronically excited states of molecules due to spontaneous radiation transitions has a great effect on excited state populations and must be necessarily accounted for under the MSRO trajectory conditions. Spontaneous radiation emission leads to violation of Boltzmann approximation for excited state populations. The molecular band radiation results obtained in the local equilibrium approximation (i.e. the supposition of the Boltzmann distribution of molecules on

electronic states) strongly overestimates non-equilibrium radiation values and cannot be used even for preliminary predictions.

Calculations of the convective heat flux and the non-equilibrium radiation were carried out for the MSRO vehicle entering into the Martian atmosphere. The wall is assumed non-catalytic. Trajectory parameters are presented in **Table 2**.

In **Figure 38a**, distributions of temperature along the stagnation line are shown. In all cases, it follows from a result the model viscous shock layer is realized. Boundary layer thickness takes approximately 1/4 from the shock layer thickness.

The main contribution to a radiation in the shock layer is produced by the bands of the molecular systems as found from theory and experiments. Main source of the shock layer radiation are the molecules that form as a result of chemical reactions.

Molecules CO, O₂, CN, C₂ are formed only as a result of the chemical reactions and the information about vibration states of these molecules are absent. For these molecules, their vibration modes are in thermal equilibrium. Besides, there is a significant amount of oxygen atoms due to the fast dissociation of the molecules CO₂ behind shock wave. Oxygen atoms have large enough cross sections for V-T processes energy exchange. In the free stream, CO₂ and N₂ molecules have almost zero vibration energy, therefore, for them in a shock layer there is an area with non-equilibrium vibration.

V, m/s	T _{oof} K	ρ _{oof} kg/m ³
3536	140	2.82 × 10 ⁻⁵
3998	140	3.07 × 10 ⁻⁴
5223	140	2.93 × 10 ⁻⁴
5687	140	3.125 × 10 ⁻⁵

Table 2. Trajectory parameters.

Figure 38. Translational temperature (a) and mass concentrations, $V = 5687$ m/s, (b) along stagnation line.

The radiation intensities are obtained for the 11 strongest systems of molecular bands: 3rd and 4th positive band of CO molecule, the red and violet band of CN molecule, the Schuman-Runge system of O₂ molecule, the β , γ , δ , ϵ systems NO molecule, the Swan band of the C₂ molecule, 1st positive band of N₂ molecule.

In **Figure 38b**, distributions of mass concentrations of neutral chemical species along the stagnation line are shown for 5687 m/s. Note a maximum of concentration CN in the relaxation zone behind the shock wave. With increasing velocity, the degree of dissociation of the molecules CO₂ increases and concentration of CN molecules become larger.

In **Figure 39**, distributions of volume concentration of the electronically excited states along the stagnation line are shown. Continuous lines show the values obtained with non-equilibrium approach, while dotted lines correspond to the local equilibrium approximation. Practically, all the excited levels, except O₂(B), reach a maximum near the shock wave. Such a fact is due to the larger values of the temperature in this region. Populations of the molecules containing carbon, except CN (A) and CO (d3) are essentially smaller (approximately in 100 times), the corresponding Boltzmann distributions. Thus, in the relaxation zone of the shock layer, the Boltzmann distribution of atoms and molecules on the electronically excited states is violated. It leads to a significant deviation of the radiation intensity from that corresponding to local equilibrium case especially for low gas density.

For the molecules forming behind the shock waves, the populations of NO (D), NO (C) states are close to equilibrium. The populations of the rest electronic states differ from their equilibrium values but in a less degree than for the molecules containing carbon.

Intensity of radiation strongly decreases near the body surface. Thus for rather low value of temperature across the boundary layer, it does not bring an appreciable contribution to the radiation heat transfer. Boundary conditions on the surface of the body, in particular, the catalytic condition does not affect value of radiation heat transfer.

Figure 39. Populations of electronically excited states along stagnation line, $V = 3998$ m/s.

Spectral distributions of radiation intensity from ultra-violet up to near infra-red are estimated. The data of non-equilibrium radiating processes and the local equilibrium approach are compared. Use of the local equilibrium modifies drastically the spectral distribution of radiation intensity.

In **Figure 40**, the convective heat fluxes for different trajectory points are shown. It is possible to divide the distribution of the convective heat flux along the surface in three distinct regions. The maximum heat transfer occurs at the stagnation point. Then, along the spherical part, the heat transfer decreases as the pressure drops. The heat transfer along the conic part is almost constant. At last, there is a local increase of the heat transfer in the shoulder region connected with an increase of the velocity gradient.

In **Figure 41**, convective and radiation heat transfer values are compared for different trajectory points. Convective heat flux is predominant compared to the non-equilibrium radiation flux. With account of non-equilibrium character of collision-radiation processes in the shock layer values of radiation heat transfer are several orders (from 10^2 to 10^7 times) below convective ones for the considered trajectory points. For a correct prediction of heat transfer and surface temperatures near space vehicle at entry conditions in the Martian atmosphere, the careful examination of theoretical and experimental catalytic properties results of a of thermal protection covering are required.

However, for the local equilibrium approach, the radiation flux is close to the convective value only for the trajectory point ($V = 5687$ km/s, $\rho_\infty = 3.125 \times 10^{-5}$ kg/m³). The non-equilibrium radiation flux is one order of magnitude smaller less than the flux obtained under the local equilibrium assumption.

To assess the influence of the catalytic wall on heat transfer and radiation equilibrium temperature of the surface thermal protection calculations for 120 degree cone blunted on sphere of radius $R = 0.7$ m at speed $V = 6150$ km/s considering a pure CO₂ atmosphere at an altitude of 40 km have been carried out. Calculations were made for four values of the recombination

Figure 40. Convective heat flux distributions.

Figure 41. Heat flux at the stagnation point along trajectory, 1: convective, 2: local equilibrium radiation, 3: non-equilibrium radiation.

γ	K_w m/s	Q_w kW/m ²	T_w K
10^{-4}	0.035	281	1530
10^{-3}	0.37	380	1650
10^{-2}	4	692	1915
10^{-1}	40	897	2045

Table 3

probability that are typical for heat-shielding materials of different types. Results of calculations are presented in **Table 3**.

According to the results, the ratio between the lowest heat flux and largest one is close to three. The equilibrium surface temperatures when blackness of a surface $\varepsilon = 0.9$ can differ more than 500 K. For a correct prediction of heat transfer and surface temperatures, careful experimental researches about the catalytic properties of the thermal protection covering are required.

8. Conclusions

Non-equilibrium flows of the reacting mixture $\text{CO}_2/\text{CO}/\text{O}_2/\text{C}/\text{O}$ in a viscous shock layer near a spacecraft entering the Mars atmosphere are studied using the accurate three-temperature model developed on the basis of the kinetic theory methods. Gas dynamic parameters, transport coefficients in a shock layer, and heat fluxes to the body surface are calculated for non-catalytic

and fully catalytic surfaces. The results are compared with the ones obtained in the simplified two-temperature approximation and in the one-temperature approach for weak deviations from thermal equilibrium. A considerable influence of CO₂ vibration excitation on the flow parameters and transport properties in a shock layer is found. The difference between the results obtained using the accurate and simplified vibration non-equilibrium models are weak under conditions considered in the paper. This justifies the validity of the approximate two-temperature model under the re-entry conditions. It is shown that difference in reaction rate constants practically has small influence on value of a heat transfer to ideal catalytic surfaces of the vehicle. In a case of non-catalytic surfaces difference in value of the heat transfer obtained by different models can be essential up to 30%. The effect of bulk viscosity in a shock layer is studied. Including this coefficient to the fluid dynamics equations improves the accuracy of the heat flux calculation up to 10%.

The heat flux to ideal catalytic surface for the considered conditions of a flow can up to four times surpasses a heat transfer to non-catalytic wall.

The influence of the different chemical reactions models: (1) Mc. Kenzie and Arnold chemistry model, (2) Park's model, and (3) model of S. Losev and others, on component concentrations and heat flux are presented. Numerical calculations of the coefficients of viscosity and heat conductivity give the close result for the heat flux for different models comparing with results obtained by exact kinetic theory. The diffusion parameters affects on the magnitude of the heat flux especially in the case of a catalytic wall. The pressure- and thermo-diffusion influence on heat flux are small. The different models of the vibration relaxation of CO₂ considered. They give approximately the same values of main properties of the flow. The catalytic properties of the surface are most important for a valid determination of the heat flux to the wall. The insertion of bulk viscosity into the equations leads to the small increase of the heat fluxes.

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