

NUMERICAL MODELING OF FLOW WITH CHEMICAL REACTIONS IN A STRONG SHOCK WAVE WITH APPROXIMATE ALLOWANCE FOR TRANSLATIONAL NONEQUILIBRIUM

V. A. Gorelov, M. M. Kuznetsov, and V. L. Yumashev

UDC 533.6.011

The effect of translational nonequilibrium on the course of chemical reactions in a shock wave is studied using the “beam–gas” model extended to the case of a multicomponent gas. For Arrhenius reactions of general form with collisions between beam and gas molecules, a modified expression of reaction rate is obtained that takes into account the relative motion of the two media. A procedure for numerical solution of the problem is considered, and calculation results for a shock wave in a dissociating air at an oncoming flow velocity of 6000 m/sec are given.

Introduction. Investigation of flows with chemical reactions in strong shock waves is of practical interest and is performed by both experimental methods and numerical modeling. For numerical modeling of these processes there are many approaches which differ in complexity and adequacy.

The simplest and most widely used model is the one of an infinitely thin shock wave [1], in which the flow is considered inviscid, the jump of parameters at a shock wave corresponds to frozen flow, and physicochemical processes are considered only in the reaction layer behind the shock wave. This model allows one to introduce detailed complex schemes of physicochemical processes. However, the final shock-wave thickness due to molecular transport and the reactions proceeding in the shock wave and ahead of its front are ignored (see [2]). This limits the region of applicability of the model of a thin shock wave.

A simple way to take into account the final shock-wave thickness is to use the Navier–Stokes equations describing the flow of a viscous multicomponent gas with chemical reactions. This approach requires a more complex mathematical apparatus but allows one to introduce a scheme of physicochemical processes that is nearly as detailed as the one used in the model of a thin shock wave. In particular, calculations of a shock wave in a dissociating air in the approximation of Navier–Stokes equations [3] showed that the obtained profiles of gas-dynamic functions and species concentrations differ significantly from those for the case of a thin shock wave.

It is known, however, that the Navier–Stokes equations describe the shock-wave structure inaccurately because of the strong nonequilibrium of the statistical distribution of molecules in energy in the region of sharp change of gas parameters. This is also true for the description of the kinetics of physicochemical processes at the shock-wave front.

The most adequate method for calculating shock-wave structures is the Monte Carlo method of direct statistical modeling (see, for example, [4, 5]), which has been used in many studies of flows with nonequilibrium of a statistical nature. Direct statistical modeling has also been employed for calculation of flows with chemical reactions [6, 7]. However, in the case of high barrier reactions, the method becomes very labor-consuming because of the low probability of the reaction acts, which leads to the necessity of considerably increasing the number of particles considered.

The afore-said motivates a search for methods of approximate consideration of translational nonequilibrium in a shock wave and its effect on the chemical reaction kinetics. Thus, for solution of the Boltzmann equation for a shock wave, Velikodnyi et al. [8] and Kozlov et al. [9] use the approximate analytical expression for the Tamm–Mott-

Central Aerohydrodynamic Institute, Zhukovskii 140180. Translated from *Prikladnaya Mekhanika i Tekhnicheskaya Fizika*, Vol. 43, No. 4, pp. 75–86, July–August, 2002. Original article submitted September 20, 2001; revision submitted February 20, 2002.

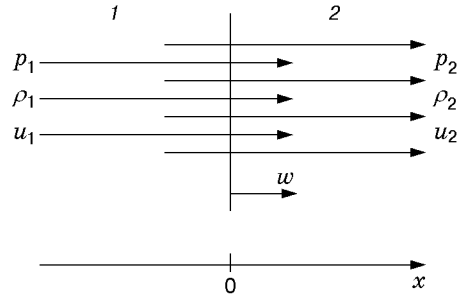


Fig. 1. Diagram of a shock wave in the “beam–gas” model: 1) oncoming flow in the form of a molecular beam; 2) single-component gas behind the shock wave.

Smith distribution function of molecules, which is a combination of two Maxwell distributions. Another approach is based on the “beam–gas” model [10, 11], in which the oncoming flow is considered a molecular beam included in the continuous medium behind the shock wave. In this model, translational nonequilibrium is determined by the first high-energy collisions of beam molecules with molecules of the continuous medium. In the original version, the “beam–gas” model is constructed for a single-component gas without chemical reactions. In the present paper, we consider an extension of this model to the case of a multicomponent gas and make corresponding changes in the chemical reaction kinetics. As a result, for a general set of reactions obeying the Arrhenius law, we obtained a modified expression for reaction rates under collisions of beam and gas molecules that takes into account the relative motion of the two media.

Numerical implementation of the model is performed by the method used previously to solve Navier–Stokes equations [3] and based on an implicit difference scheme with alternation of nodes [12, 13]. The method was validated by comparing calculation results for a shock wave in argon with Monte Carlo calculation results. Calculations of a shock wave in dissociating air for an oncoming flow velocity of 6000 m/sec were performed, whose results show significant differences in the courses of physicochemical processes in the shock wave compared to the Navier–Stokes model.

Formulation of the Problem and the Governing Equations. It is assumed that in the “beam–gas” model, shock-wave flow consists of two media. One medium is the oncoming flow, treated as a molecular beam in which particles move at constant speed and penetrate into the single-component gas behind the shock wave. The other medium is the single-component gas (continuum) behind the shock wave, whose motion is described by the Navier–Stokes equations (below it is called the gas). This flow pattern is given schematically in Fig. 1.

As $x \rightarrow -\infty$, we specify the following beam parameters: velocity, pressure, density, and the chemical composition of the oncoming flow. When the beam enters the shock-wave region, its molecules collide with the gas molecules. It is assumed that just in the first collision, a molecule of the beam passes to the gas with the corresponding transfer of mass, momentum and energy. In this case, the velocities of the remaining beam molecules (which did not participate in collisions) do not change and are equal to the oncoming flow velocity. As a result of collisions, the beam density gradually decreases to zero, so that at a certain depth in the gas, the beam practically disappears. Similarly, the gas density tends asymptotically to zero in the opposite direction.

For numerical solution of the problem, we use the time-iteration method. Therefore, all processes are considered unsteady. The equations describing the joint one-dimensional unsteady motion of the multicomponent beam and gas are written as

$$\frac{\partial}{\partial t} \begin{bmatrix} \rho_b \\ \rho_b b_j \\ \rho \\ \rho u \\ \rho(E + E_k) \\ \rho c_i \end{bmatrix} + \frac{\partial}{\partial x} \begin{bmatrix} \rho_b u_b \\ \rho_b u_b b_j \\ \rho u \\ \rho u^2 + p - f \\ \rho u(E + E_k) + up - uf - q \\ \rho u c_i - \rho d_i \end{bmatrix} = \begin{bmatrix} -G \\ -G_j \\ G \\ GJ_0 \\ GE_0 \\ r_i + g_i \end{bmatrix}, \quad (1)$$

$$u_b = \text{const} \equiv u_1, \quad i = 1, \dots, N - 1, \quad j = 1, \dots, N_b - 1.$$

Here x is the coordinate, t is time, u , p , ρ , E , and E_k are the velocity, pressure, density, internal energy, and kinetic energy of the gas, respectively, u_b and ρ_b are the velocity and density of the beam, u_1 is the velocity of the oncoming

flow, J_0 is the specific momentum of the oncoming flow, E_0 is the total energy of the oncoming flow, c_i are the mass fractions of gas species, b_j are the mass fractions of beam species, r_i are the mass rates of formation of gas species in chemical reactions, G_j are the mass rates of species transfer from the beam to the gas due to molecular collisions between the beam and the gas, g_i are the mass rates of species transfer to the gas from the beam, G is the total rate of mass transfer from the beam to the gas, f is the viscous force stress, q is the heat flux, d_i are the diffusion fluxes, i is the gas species number, j is the beam species number, N is the total number of gas species, and N_b is the total number of beam species. The number of equations for transfer of species is unity less than the number of species, by virtue of the conditions

$$c_1 + c_2 + \dots + c_N = 1, \quad b_1 + b_2 + \dots + b_{N_b} = 1.$$

It should be noted that all species available in the beam are also present in the gas, and the numbering of species for the beam and gas is identical. However, in the gas, additional species can appear as a result of chemical reactions, and, hence, $N \geq N_b$. If only ordinary reactions between gas molecules are considered and the reactions due to collisions between beam and gas molecules are ignored, the species transfer to the gas is equal to their removal from the beam, so that $g_i = G_i$ for $i \leq N_b$ (for species present in both the beam and the gas) and $g_i = 0$ for $i > N_b$ (for species present only in the gas). Allowance for the reactions between beam and gas molecules leads to more complex dependences, which will be considered below.

The following relations are valid:

$$\begin{aligned} p &= \rho T \sum_{i=1}^N c_i R_i, \quad \rho E + p = \sum_{i=1}^N c_i h_i, \quad h_i = h_{0i} + C_{pi} T + E_{vi}, \quad E_k = \frac{u^2}{2}, \\ f &= \frac{4}{3} \mu \frac{\partial u}{\partial x}, \quad q = \lambda \frac{\partial T}{\partial x} + \rho \sum_{i=1}^N h_i d_i, \quad d_i = D_i \frac{\partial c_i}{\partial x}, \quad G = \sum_{j=1}^{N_b} G_j = \sum_{i=1}^N g_i, \\ E_{vi} &= \frac{R_i \vartheta_i}{\exp(\vartheta_i/T) - 1}, \quad J_0 = u_1 + \frac{p_1}{\rho_1 u_1}, \quad E_0 = \frac{u_1^2}{2} + E_1 + \frac{p_1}{\rho_1}. \end{aligned}$$

Here T is the temperature, h_i are the enthalpies of the species, h_{0i} are the enthalpies of species formation, E_{vi} are the equilibrium vibrational energies, ϑ_i are the Debye temperatures, μ , λ , and D_i are the viscosity, thermal conductivity, and diffusion constant, respectively, and R_i and C_{pi} are the gas constants and specific heat of the species; the subscript 1 corresponds to oncoming flow parameters.

We note that unlike in [10], in the present paper, we ignore the pressure and internal energy of the oncoming flow in the general balance of momentum and energy, in order that the Hugoniot relations at the shock wave are satisfied in the same manner as in other shock-wave models with which a comparison is performed. However, in calculations of the interaction between beam and gas molecules, the rate of the natural thermal motion of beam molecules is considered negligibly small compared to the rate of their general translational motion and is assumed to be equal to zero just as in [10]. Therefore, collisions of beam molecules with each other are ignored.

Determining Source Terms. In the absence of the chemical reactions due to collisions between beam and gas molecular, the mass rate of transfer of species from the beam to the gas is determined using the hard-sphere model for elastic collision of molecules:

$$\begin{aligned} G_j &= \rho \rho_b (u_b - u) b_j \sum_{i=1}^N \sigma_{ij} \frac{c_i}{m_i}, \quad \sigma_{ij} = N_A \sqrt{\pi} \left(\frac{\delta_i + \delta_j}{2} \right)^2 F(z_{ij}), \\ F(z) &= \frac{1}{z} e^{-z} + \left(2 + \frac{1}{z^2} \right) \int_0^z e^{-x^2} dx, \quad z_{ij} = (u_b - u) \sqrt{\frac{m_i m_j}{R_0 T (m_i + m_j)}}. \end{aligned}$$

Here m_i is the molecular mass of species i , σ_{ij} is the effective collision cross section of species i and j in calculation per 1 mole, δ_i is the diameter of a molecule of sort i , N_A is the Avogadro number, and R_0 is the universal gas constant.

In the presence of chemical reactions, it is necessary to differentiate between two cases: 1) the reactions due to collisions of gas molecules with each other; 2) the reactions due to collisions between beam and gas molecules. In the first case, the molecule collision energy, which influences the reaction rate, depends only on gas temperature; the kinetics of these reactions is considered known. In the second case, the molecule collision energy depends not

only on temperature but also on the rate of motion of the beam relative to the gas. This leads to a significant change of the kinetic relations [14, 15].

We assume that between N gas species K reactions can occur, and the reaction with number k is described by the generalized formula

$$\alpha_{k1}Z_1 + \alpha_{k2}Z_2 + \dots + \alpha_{kN}Z_N = \beta_{k1}Z_1 + \beta_{k2}Z_2 + \dots + \beta_{kN}Z_N. \quad (2)$$

Here α_{ki} and β_{ki} are the stoichiometric coefficients (in practice, only some of them are different from zero) and Z_i are the gas species. We assume that the reaction rates obey to the Arrhenius law, so that the rate of formation of the i th species is written as

$$r_i = m_i \sum_{k=1}^K (\beta_{ki} - \alpha_{ki})(Q_{fk} - Q_{rk}), \quad (3)$$

$$Q_{fk} = A_{fk} T^{n_{fk}} \exp\left(-\frac{\Theta_{fk}}{T}\right) \prod_{i=1}^N \left(\frac{\rho c_i}{m_i}\right)^{\alpha_{ki}}, \quad Q_{rk} = A_{rk} T^{n_{rk}} \exp\left(-\frac{\Theta_{rk}}{T}\right) \prod_{i=1}^N \left(\frac{\rho c_i}{m_i}\right)^{\beta_{ki}}.$$

Here Q is the reaction rate and A , n , and Θ are the coefficient, exponent, and normalized activation energy in the Arrhenius law, respectively; the subscripts f and r denote the direct and reverse reactions, respectively.

A distinguishing feature of the reactions occurring during collisions between beam and gas molecules is that they involve two particles and reverse reactions are absent because there is no back transfer of the material from the gas to the beam. Therefore, from the set of reactions (2), the beam directly participate only in reactions (from the right or left sides of the formula) that involve only two species, one of which is initially contained in the beam. Formally, the reactions involving the beam form an independent set in addition to (2) and are described by a similar generalized formula

$$\alpha_{k1}Z_1 + \alpha_{k2}Z_2 + \dots + \alpha_{kN}Z_N \rightarrow \beta_{k1}Z_1 + \beta_{k2}Z_2 + \dots + \beta_{kN}Z_N. \quad (4)$$

Obviously, the beam species is always on the left side of (4) even if the initial reaction was taken from the right side of (2); in the last case, the coefficients α_{ki} and β_{ki} change places.

Let L reactions of the form of (4) occur (and L can be both smaller and larger than K). Then, the rate of decrease of the i th species of the beam due to all reactions (4) is written as

$$B_i = m_i \sum_{k=1}^L \alpha_{ki} Q_k,$$

and the rate of formation of the i th species of the gas is written as

$$s_i = m_i \sum_{k=1}^L (\beta_{ki} - \alpha_{ki}) Q_k.$$

Here the new notation s_i is introduced to differentiate between reactions with the participation of the beam from similar reactions in the gas (3).

For definiteness, let reaction with number k proceed between the i th species of the beam and the j th species of the gas. For molecular-kinetic reasons, considering the translational motion of the beam molecules, to evaluate the reaction rate Q_k , it is necessary to know the collision cross section of the molecules. As the initial data for determination of the collision cross section, we use the known rate of the same reaction in the gas: we assume that the dependence of the cross-sectional area on the relative velocity of the molecules is such that in the case of equilibrium thermal motion, it gives the Arrhenius law with known parameters A , n , and Θ . From this, by analogy with [14, 15], it is possible to obtain a modified expression for the reaction rate taking into account the relative motion of the two media. If, in addition, we assume that the rate of thermal motion of the beam molecules is negligibly small compared to the translational velocity, the reaction rate becomes

$$Q_k = A_k T^{n_k} \Phi(z, \varepsilon_k, n_k) (1 + m_j/m_i)^{-1} \rho_b \rho b_i c_j / (m_i m_j), \quad (5)$$

where

$$z = (u_b - u) \sqrt{m_j / (2R_0 T)}, \quad \varepsilon_k = \sqrt{(1 + m_j/m_i) \Theta_k / T},$$

$$\Phi(z, \varepsilon, n) = \frac{\sqrt{\pi}}{\Gamma(n + 3/2)} \int_{\varepsilon}^{\infty} \frac{\exp(-(x-z)^2) - \exp(-(x+z)^2)}{2z} (x^2 - \varepsilon^2)^{n+1/2} dx.$$

Formula (5) takes into account the effect of translational nonequilibrium, which is related to the high energy of the first collisions of molecules of the oncoming flow. Formula (5) corresponds to the limiting case of the Tamm–Mott-Smith distribution, where the temperature of one of the Maxwellian (beam) tends to zero. Under certain conditions, it yields a considerable increase in reaction rate compared to the Arrhenius law since the relative motion of the beam and gas leads to a shift of the activation barrier toward lower energies. Here the results obtained earlier for the case $n = 0.5$ [14] are extended to the case of arbitrary $n > -1.5$, which is of significance when real reaction schemes are used.

We note that the presence of reactions does not influence the rate of removal of species from the beam G_i because upon collision with a gas molecule, a beam molecule leaves the beam in any case. However, a result of the reactions is that the composition of the species entering the gas differs from the composition of the species leaving the beam. Indeed, as a result of the reactions, only part of the species leaving the beam, which is determined by the velocity $G_i - B_i$, enters the gas, but, simultaneously, part of the same species formed in other reactions, determined by the velocity s_i , is added. As a result, $g_i = G_i - B_i + s_i$ for $i \leq N_b$ and $g_i = s_i$ for $i > N_b$.

Procedure of Numerical Solution. To solve Eq. (1), one needs to formulate boundary conditions and consider a mixed problem. In choosing boundary conditions, it is necessary to take into account that the oncoming flow parameters p_1 , ρ_1 , and u_1 , the parameters of the gas at a large distance behind the shock wave p_2 , ρ_2 , and u_2 , and the shock-wave velocity w (Fig. 1) obey the system of three Hugoniot equations. Consequently, any four of these parameters can be specified separately, and the remaining three parameters are obtained from solution of the problem.

The afore-said is also valid and in the presence of chemical reactions. In this case, it is also necessary to specify the chemical composition of the oncoming flow.

In numerical integration of system (1), it is convenient to specify values of p_1 , ρ_1 , and u_1 on the left boundary and value of p_2 on the right boundary. As a result of solution, we obtained a certain value of the shock-wave velocity w (generally, $w \neq 0$). The oncoming flow velocity relative to the shock wave is equal to $u_1 - w$, which does not agree with the initial conditions of the problem.

In the case of a perfect gas, it is not difficult to predict the exact value of p_2 for which $w = 0$. However, in the case of a generalized gas model involving complex physicochemical processes, this is difficult to do. In this case, global iterations are applied: the boundary-value problem is solved for a sequence of values of p_2 , as a result of which, a sequence of values of w converging to zero is determined. In each global iteration, the boundary-value problem is solved using the time-iteration method: a certain initial flow field is specified and its evolution to the final stationary state for fixed boundary conditions is considered.

Numerical integration of system (1) is performed by the method used in [3] for shock wave calculations based on the Navier–Stokes equations. The method uses an implicit difference scheme with node alternation [12, 13], which shows unconditional stability, monotonicity, and second-order accuracy and does not introduce errors to the solution because of scheme viscosity. The solution is constructed on a movable grid which traces shock wave propagation automatically. This simplifies analysis of results because flow parameter profiles are fixed relative to the computation grid.

A distinguishing feature of the problem is that the boundary conditions at $x \rightarrow -\infty$ refer to the beam and those at $x \rightarrow +\infty$ to the gas. Let us consider opposite boundary conditions for each of the two media. The equations of motion for the beam are such that they do not require boundary conditions at $x \rightarrow +\infty$. The boundary conditions for the gas at $x \rightarrow -\infty$ are the oncoming flow velocity and the pressure and density tending asymptotically to zero with the temperature tending to the oncoming flow temperature.

In practice, the numerical solution is constructed in a region of finite dimension, and the conditions valid at $\pm\infty$ are extended to the boundaries of the finite region. The dimensions of the region are chosen such that the at the boundaries, the gradients of all parameters are negligibly small; usually, these dimensions are up to several tens of molecular free path. We note that zero boundary values of the gas pressure and density cannot be specified because this causes an error of the type of division by zero in the computational algorithm. Therefore, it is assumed that besides the molecular beam, the oncoming flow contains a small amount of a single-component gas (0.01–0.02%) at the same velocity and temperature as the beam. This amount of the gas agrees with the estimate of the asymptotic behavior of the solution of system (1) at $x \rightarrow -\infty$.

One computational difficulty of the problem considered is due to the fact that the function $\Phi(z, \varepsilon, n)$ in (5) has the form of an integral which is not expressed in terms of elementary functions convenient for evaluations, except in a few special cases. Generally, values of the integral should be obtained numerically. However, this is

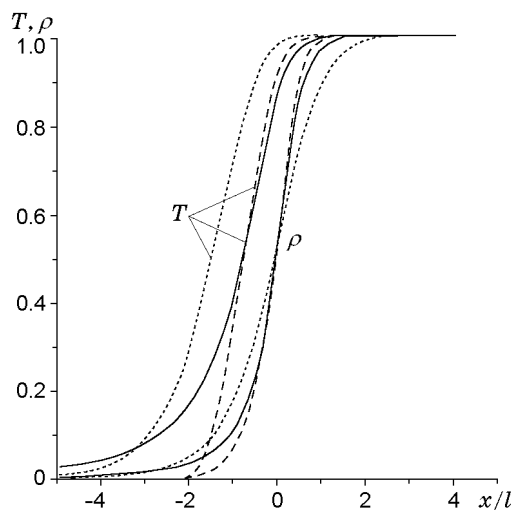


Fig. 2. Density and temperature profiles in a shock wave in argon: solid curves correspond to the “beam-gas” model, dashed curves to the Navier–Stokes model, and dotted curves to the Monte Carlo method.

TABLE 1

Species	m	h_0/R , K	ϑ , K	δ , m
O ₂	32	0	2256	$2 \cdot 10^{-10}$
O	16	29,760	—	10^{-10}
N	14	56,600	—	10^{-10}
NO	30	10,810	2710	$2 \cdot 10^{-10}$
N ₂	28	0	3354	$2 \cdot 10^{-10}$

a rather laborious procedure, which considerably increases computing expenditures in the solution of the problem as a whole. Therefore, we represent the function $\Phi(z, \varepsilon, n)$ in table form and used interpolation by tables. In constructing the tables, it is necessary to evaluate the integral for a grid of values of z, ε, n but this is done once at the beginning of the solution of the problem and increases computing expenditures only slightly.

Condition and Results of Numerical Experiment. As a test example of the formulation considered, we calculated a shock wave in an inert gas (argon) for an oncoming flow Mach number $M_\infty = 11$. In Fig. 2, solid curves show density and temperature profiles in the shock wave normalized to the interval $(0, 1)$, and the x coordinate is normalized to the molecular free path l in the oncoming flow. The dashed curves show results of calculation by the procedure of [3] using the Navier–Stokes equations, and the dotted curves show the results of Monte Carlo direct statistical modeling in [4].

As one might expect, compared with the Monte Carlo method, in the Navier–Stokes model, the gradients at the shock-wave front are overpredicted by factor of two and the upstream displacement of the temperature front relative to the density front is underpredicted by a factor of two. The “beam-gas” model underpredicts somewhat the gradients of shock-wave parameters but this is insufficient for agreement with the results of the Monte Carlo method; the upstream displacement of the temperature front does not increase. At the same time, earlier increase of the parameters ahead of the shock-wave front is observed, so that at a distance of two-four free paths upstream, the parameter values are close to those obtained by the Monte Carlo method. Thus, the “beam-gas” model improves the description of the flow ahead of the shock-wave front compared with the Navier–Stokes model, by allowing for approximately the effect of translational nonequilibrium manifested in more severe heating of the gas because of the energy exchange with the beam.

The present calculations were performed for the case of a shock wave in a dissociating air for oncoming flow parameters $u_1 = 6000$ m/sec, $\rho_1 = 1.681 \cdot 10^{-4}$ kg/m³, and $p_1 = 13.158$ Pa. It is assumed that the air consists of five species: N₂, O₂, N, O, and NO (Table 1), and the oncoming flow contains only N₂ and O₂ in a ratio of 77 : 23. The species are involved in five reactions, whose parameters are given in Table 2 (dimensions of A_f and A_r correspond

TABLE 2

Reaction	A_f	n_f	Θ_f , K	A_r	n_r	Θ_r , K
$N_2 + M = N + N + M$	$1.86 \cdot 10^{14}$	-0.5	113,200	$6.0 \cdot 10^5$	0.5	0
$O_2 + M = O + O + M$	$3.6 \cdot 10^{15}$	-1.0	59,370	$1.8 \cdot 10^7$	0	0
$NO + M = N + O + M$	$5.0 \cdot 10^{12}$	0	75,500	$8.5 \cdot 10^4$	1.0	0
$O + NO = N + O_2$	$3.2 \cdot 10^6$	1.0	19,700	$9.62 \cdot 10^8$	0.5	3600
$O + N_2 = N + NO$	$6.4 \cdot 10^{14}$	-1.0	38,370	$1.4 \cdot 10^{14}$	-1.0	620

TABLE 3

Molecules	Effectiveness ratio for particles M				
	N	O	NO	N_2	O_2
N_2	2.5	1	1	2.5	1
O_2	1.0	25	1	2.0	10
NO	22.0	22	22	1.0	1

to the SI system). In the dissociation–recombination reactions, the effectiveness ratios of various sorts of molecules considered as passive particles M (Table 3) are allowed for. It should be noted that for the same reactions, the literature gives different values of the Arrhenius law parameters, which, nevertheless yield close values of reaction rates, thus approximating real processes somehow or other. Therefore, the choice of reaction parameters is usually subjective to some extent. In our case, we chose combinations of parameters such that they did not contain large negative values of the exponent n and the above-mentioned constraint $n > -1.5$ was satisfied.

The five reactions (see Table 2) yield seven reactions between beam and gas molecules. In the reaction formulas given below, the first species on the left side correspond to the beam and the second species to the gas: $N_2 + M \rightarrow N + N + M$, $O_2 + M \rightarrow O + O + M$, $O_2 + N \rightarrow O + NO$, $M + N_2 \rightarrow N + N + M$, $M + O_2 \rightarrow O + O + M$, $N_2 + O \rightarrow N + NO$, and $M + NO \rightarrow N + O + M$.

In determining transfer coefficients, it is necessary to take into account that the interaction between beam and gas molecules is calculated by the hard-sphere model. For conceptual unity, the gas viscosity should also be determined using the hard-sphere model; otherwise a comparison of different processes and models is incorrect. The molecule sizes given in Table 1 are chosen so that the viscosity differs little from the air viscosity. In this case, the viscosity is defined by the formula $\mu = 6.24 \cdot 10^{-5}(T/273)^{0.5}$ kg/(m·sec) and differs from the air viscosity by less than 30% over the entire range of temperature. The thermal conductivity and diffusion constant are obtained by assigning Prandtl and Schmidt numbers. This is justified by the fact that the dominant species is molecular nitrogen with a mass fraction of about 0.7. Therefore, it is possible to speak of binary diffusion of the other species in nitrogen.

In Figs. 3–5, the shock-wave parameter profiles calculated for the “beam–gas” model are shown by solid curves, and those obtained for the Navier–Stokes model are shown by dashed curves. The x coordinate is normalized to the molecular free path l in the oncoming flow. The origin of x is taken to be the point of the mean pressure $p = (p_1 + p_2)/2$. We note that in the presence of chemical reactions, the position of the shock-wave front is easier to check by the pressure rather than by the density, which changes significantly in the reaction layer behind the shock wave. For the same reasons, the dimensional parameter values are plotted on the ordinates, their normalization is ineffective when the functions are nonmonotonic, and their asymptotic values are weakly related to the shock-wave processes.

The interaction between the beam and the gas can be judged by the variation of their densities, shown in Fig. 3 by curves 1 and 2, respectively. The main absorption of the beam in the gas occurs at a distance of about one free path at the shock-wave front. At the same time, a decrease in beam density and an increase in gas density begin at a rather large distance upstream. In the same region, the total density of the beam and the gas (curve 3) is somewhat larger than the density in the Navier–Stokes model (dashed curve).

It is natural to make a comparison with the Navier–Stokes model for the total parameters of the “beam–gas” mixture. Figure 4 shows profiles of the total velocity, pressure, and temperature in the shock wave. Large differences compared with the Navier–Stokes model are suggested by the slopes of the velocity and temperature profiles and their extent equal to several free paths upstream. The extension of the shock-wave region in the beam model gives a slight decrease in maximum temperature.

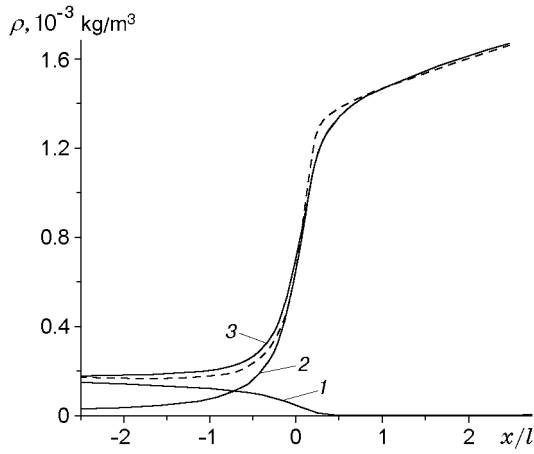


Fig. 3

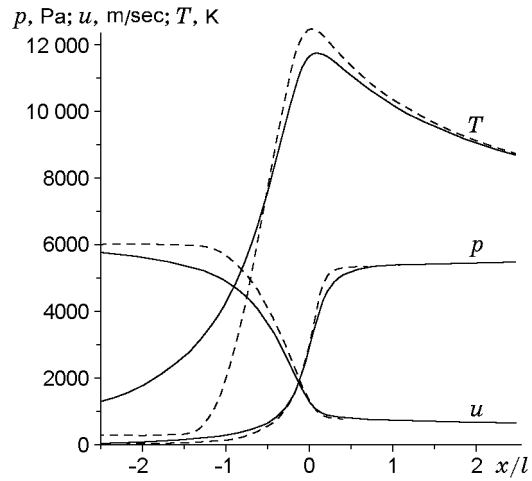


Fig. 4

Fig. 3. Density profiles in a shock wave in air for the beam (1), gas (2), "beam-gas" model (3), and Navier-Stokes model (dashed curve).

Fig. 4. Velocity, pressure, and temperature profiles in a shock wave in air for the "beam-gas" model (solid curves) and Navier-Stokes model (dashed curves).

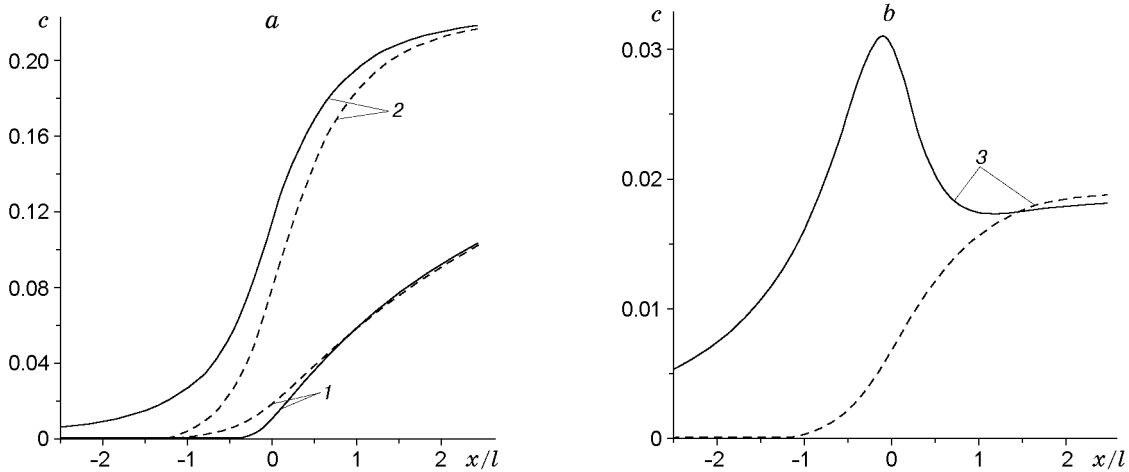


Fig. 5. Mass fractions of N (curves 1) and O (curves 2) (a) and NO (curves 3) (b) in a shock wave in air: solid curves refer to the "beam-gas" model and dashed curves to the Navier-Stokes model.

Features of reactions in the "beam-gas" model can be judged by the behavior of species concentrations. Figure 5a gives profiles of the mass fractions of atomic nitrogen and oxygen (curves 1 and 2, respectively). In the gradient region of the shock wave, profile 2 in the beam-gas model is slightly shifted upstream compared with the Navier-Stokes model. In the region upstream at a distance of several free paths there is only atomic oxygen of the beam model is present.

The behavior of atomic nitrogen profile is opposite: in the gradient region of the shock-wave, curve 1 is shifted downstream compared with the Navier-Stokes model, and upstream, the mass fraction of nitrogen is approximately equal to zero. This occurs because the entire atomic nitrogen produced by dissociation is immediately expended in the exchange reaction $O_2 + N \rightarrow O + NO$, whose efficiency increases manifold in the beam model. This is responsible for the above-mentioned increase in the amount of atomic oxygen and has the most significant effect on the behavior

of the nitrogen oxide profile (curves 3 in Fig. 5b). In the beam model, there is an abrupt maximum of profile 3 at the shock-wave front, which is not available in the Navier–Stokes model, and a considerable amount of NO is present in the region upstream. Since the excitation of NO molecules is a source of emission, this can be responsible for the glow ahead of the shock-wave front observed in the experiments of [2].

Conclusions. The “beam–gas” model is extended to the case of a multicomponent gas and is used to estimate the effect of translational nonequilibrium on the course of chemical reactions in a shock wave. For a generalized set of reactions obeying the Arrhenius law, a modified expression is obtained for reaction rates under collisions between beam and gas molecules taking into account the relative motion of the two media. A procedure for numerical solution of the problem is developed based on an implicit difference scheme with alternation of nodes and table approximation of the beam reaction rates. Calculations of a shock wave in dissociating air for an oncoming flow velocity of 6000 m/sec were performed, which show that there are significant differences in the course of physicochemical shock-wave processes between the “beam–gas” model and the Navier–Stokes model.

REFERENCES

1. E. V. Stupochenko, S. A. Losev, and A. I. Osipov, *Relaxation Processes in Shock Waves* [in Russian], Nauka, Moscow (1966).
2. V. A. Gorelov, M. K. Gladyshev, A. Yu. Kireev, et al., “Experimental and numerical study of nonequilibrium ultraviolet NO and N_2^+ emission in shock layer,” *J. Thermophys. Heat Transfer*, **12**, No. 2, 172–180 (1998).
3. A. Yu. Kireev and V. L. Yumashev, “Numerical modeling of viscous nonequilibrium air flow behind a strong shock wave,” *Zh. Vychisl. Mat. Mat. Fiz.*, **40**, No. 10, 1563–1570 (2000).
4. O. G. Byzykin, V. S. Galkin, A. I. Erofeev, and V. I. Noski, “Macroscopic model for the structure of a strong shock wave,” *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 4, 125–135 (1999).
5. S. L. Gorelov and S. V. Rusakov, “Structure of a shock wave for a gas with internal degrees of freedom,” *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 3, 121–125 (1999).
6. A. P. Genich, S. V. Kulikov, G. B. Manelis, and S. L. Cheremiev, “Translational relaxation in shock waves in gases,” Preprint, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka (1991).
7. A. B. Karlson and G. A. Bird, “Implementation of a vibrationally linked chemical reaction model for DSMC,” in: *Proc. of the 19th Int. Symp. on Rarefied Gas Dynamics* (Oxford, July 25–29, 1994), Vol. 1, Oxford Univ. Press, Oxford (1995), pp. 434–440.
8. V. Yu. Velokodnyi, A. V. Eemel’yanov, and A. V. Eremin, “Nonadiabatic excitation of iodine molecules in the region of translational nonequilibrium of a shock wave,” *Zh. Tekh. Phys.*, **69**, No. 10, 23–28 (1999).
9. P. V. Kozlov, S. A. Losev, and Yu. V. Romanenko, “Translational nonequilibrium at the shock-wave front in a mixture of argon and helium,” Preprint No. 59-2000, Inst. of Mechanics, Moscow State Univ., Russian Acad. of Sci. (2000).
10. D. L. Turcotte and I. M. Scholnick, “Structure of strong shock waves,” *Phys. Fluids*, **12**, No. 5, Part 2, 80–82 (1969).
11. A. K. Artamonov and V. N. Arkhipov, “Hypersonic rarefied flow around a sphere,” *Izv. Akad. Nauk USSR, Mekh. Zhidk. Gaza*, No. 6, 85–90 (1979).
12. I. I. Vorozhtsov and V. L. Yumashev, “Approximating properties of an implicit difference scheme for the equations of gas dynamics,” *Zh. Vychisl. Mat. Mat. Fiz.*, **30**, No. 7, 1093–1102 (1990).
13. I. I. Vorozhtsov and V. L. Yumashev, “Application of an implicit staggered grid scheme for compressible flow computations,” in: *Proc. of the 4th Int. Symp. on Comput. Fluid Dynamics* (Davis, California, Sept. 9–12, 1991), Vol. 2, Univ. of California, Davis (1991), pp. 1167–1172.
14. V. Yu. Velokodnyi, “Effect of gas flow on the kinetics of physicochemical transformations,” *Zh. Tekh. Fiz.*, **59**, No. 12, 126–129 (1989).
15. M. M. Kuznetsov, “Kinetic effects in limiting hypersonic flows of a viscous gas,” in: *Proc. of the XVth Session of Int. Scholarship on Models of Continuum Mechanics*, Institute of Chemistry, St. Petersburg Univ. (2001), pp. 33–42.