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EFFECT OF TRANSITIONAL NONEQUILIBRIUM ON THE MOLECULAR-DISSOCIATION RATE IN A HYPERSONIC SHOCK WAVE

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The problem of the influence of a nonequilibrium (non-Maxwellian) distribution of translational energy over the degrees of freedom of molecules on the rate of their dissociation in a hypersonic shock wave is considered. An approximate "beam"–continuous medium model, which was previously applied to describe a hypersonic flow of a perfect gas, was used to study translational nonequilibrium. The degree of dissociation of diatomic molecules inside the shock-wave front, which is caused by the nonequilibrium distribution over the translational degrees of freedom, is evaluated. It is shown that the efficiency of the first inelastic collisions is determined by the dissociation rate exponentially depending on the difference in the kinetic energy of "beam" molecules and dissociation barrier.

Introduction. Theoretical and experimental investigations [1–3] showed that the flow in a shock wave is nonequilibrium in terms of translational degrees of freedom. The consequence of translational nonequilibrium is a significant increase in chemical-reaction rates [2, 3] and other relaxation processes due to increasing efficiency of inelastic collisions in shock waves.

The effect considered may affect thermophysical parameters of hypersonic low-density gas flow in regimes where the shock-wave thickness is comparable with its stand-off distance from the body surface. In this case, direct numerical simulation based on the Monte Carlo method is used instead of the continuum model based on Navier–Stokes equations. However, the use of the method of direct numerical simulation for hypersonic flow computations taking into account complex chemical processes, ionization, and radiation in the viscous shock layer requires great resources of memory and a high speed of computers used [4]. Nevertheless, it is possible to find some problems of practical importance, where it is necessary to take into account translational nonequilibrium in the shock-wave front in the continuum flow, with the Navier–Stokes model applicable to numerical simulation of the processes in the shock layer except for the shock-wave front region. One of these problems is the determination of intensity of nonequilibrium radiation of the shock layer at the entrance to the atmosphere of the Earth and other planets at altitudes corresponding to the maximum heat flux to the spacecraft surface.

Figure 1 shows the measured intensity of nonequilibrium radiation I behind the front of a hypersonic shock wave of a CO molecule in the ultraviolet range (system of molecular emission bands of CO^{4+}), which contains the major part of the radiative heat flux to the surface of a spacecraft entering the Martian atmosphere. The radiation was registered in an electric-discharge shock tube of the Central Aerohydrodynamic Institute [5]. The gas mixture in the tube channel simulated the Martian atmosphere (97% CO_2 and 3% N_2). The initial gas pressure was $p_1 = 26.3$ Pa. The shock-wave velocity was $V^S = 7.15$ km/sec. The radiation intensity and the time from the moment of radiation registration in an examined cross section of the shock-tube

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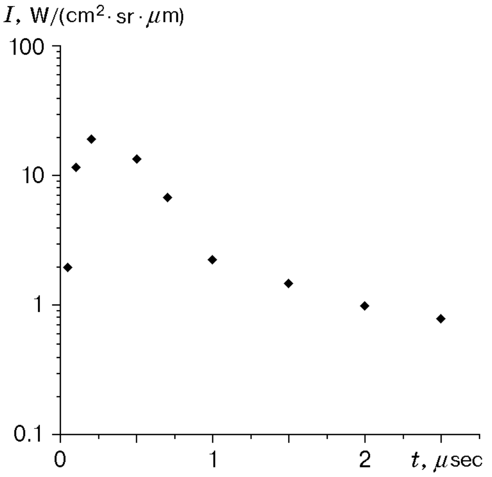

Fig. 1. Experimental dependence of the radiation intensity of a CO molecule (system of emission from CO^{4+}) on time behind the front of a strong shock wave [$\lambda = (200 \pm 3.4)$ nm].

channel are laid on the ordinate and abscissa axes, respectively. It is seen that the maximum of radiation in the system of CO^{4+} bands is observed for $t \leqslant 0.25$ μsec, which corresponds to the distance $\bar{x} = x/\lambda_\infty \leqslant 10$ from the "beginning" of the shock-wave front (λ_∞ is the mean free path of molecules ahead of the shock wave).

Thus, it follows from the experiment that the maximum intensity of nonequilibrium radiation is located in the region of shock-wave "formation." Therefore, for a correct numerical calculation of the intensity of a nonequilibrium heat flux to the spacecraft surface, one should take into account the effects of translational nonequilibrium in the bow shock-wave front, whereas the convective component of the heat flux may be determined using the Navier–Stokes solver. The example presented shows that it is reasonable to develop an approximate method for taking into account the effects of translational nonequilibrium within the Navier–Stokes hypersonic viscous flow model.

A simple physical model "beam"–continuous medium was developed in [6–8]. This model effectively takes into account the elevated concentration of high-energy molecules in the shock wave by introducing a high-energy medium ("beam") which interacts by means of collisions with randomly moving molecules having the Maxwell–Boltzmann distribution with the Navier–Stokes allowance for dissipation. In the process of elastic collisions, molecules of the "beam" are irreversibly transformed into "random" molecules; therefore, the "beam"-molecule concentration decreases from the free-stream value to zero. The concentration of "random" molecules increases from zero in the free stream up a maximum value at the back front of the shock wave.

It should be noted that the "beam"–continuous medium model is actually a simplified version of the model proposed by Tamm and Mott-Smith, which takes into account the strong asymmetry of the molecular distribution function in a hypersonic shock wave. From the physical point of view, the strong asymmetry allows one to take into account the role of the "first" high-energy collisions, which lead to excitation of internal degrees of freedom and chemical reactions. Being used for hypersonic gas flow calculations [6–9], this model in the first approximation eliminated many drawbacks inherent in the Navier–Stokes description of shock-wave processes and made it possible to take into account the basic kinetic effects, which result in an increase in the shock-wave width, a more intense increase in the mean local temperature, and an excess of the so-called longitudinal temperature over the mean local temperature [9].

In the present paper, the "beam"–continuous medium model is extended to the case of molecular dissociation inside the shock wave. In this formulation with verified values of chemical-reaction rates, this model can be used in exact numerical calculations of hypersonic flow, taking into account approximately the translational nonequilibrium in the shock-wave front region.

1. Formulation of the Problem. In considering dissociation inside the shock wave, which is caused by the first high-energy collisions of "beam" molecules with molecules randomly distributed in the shock wave,

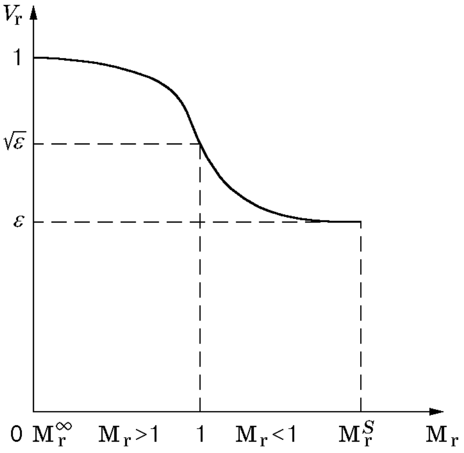

Fig. 2. Characteristic zones of flow deceleration in the shock wave.

one can naturally assume that dissociation occurs simultaneously with the processes of viscous and thermal dissipations. Therefore, it is reasonable to consider these processes in characteristic (supersonic, transonic, and supersonic) regions of flow deceleration in the shock wave. These regions are shown schematically in Fig. 2 ($V_r = u_r/u_{b,\infty}$ is the relative velocity, $M_r = u_r/\sqrt{\gamma R T_r/\mu_{A_2}}$ is the Mach number, γ is the ratio of specific heats, R is the universal gas constant, T is the temperature, μ_{A_2} is the molecular mass, and $\varepsilon = (\gamma-1)/(\gamma+1)$); the subscripts "r" and "b" refer to the parameters of the flux of random and "beam" molecules, respectively.

The following assumptions may be made for an approximate analytical calculation of dissociation inside the shock-wave front, which is caused by translational nonequilibrium.

1) Dissociation is caused only by collisions with high-energy molecules of the "beam" [temperature ("Arrhenius") dissociation is ignored];

2) There is no dissociation in the supersonic part of the shock wave (see Fig. 2);

3) Dissociation proceeds effectively in the transonic and subsonic regions of the shock wave.

The above assumptions are based on the following data.

1. "Arrhenius" dissociation in all previous studies was insignificant inside a thin shock front. Gorinov and Magomedov argue [10] that the assumption about the "frozen" (in terms of dissociation) wave front is valid for hypersonic air flows up to free stream velocities $V_\infty \leqslant 7$ km/sec.

2. In the front (supersonic) part of the shock wave, the relative velocity of the "beam" molecules $u_b - u_r$ is small up to the transonic region, where $u_r \neq u_b$. The value of u_r here is of the order of the velocity of sound: $u_r \simeq \sqrt{\varepsilon}\, u_b$ [11, 12]. For this reason, the shock mechanism of collisions between the "beam" molecules and random molecules does not work in the supersonic part of the shock wave; the process of dissociation proceeds in the "Arrhenius" form, and its role is negligibly small.

3. In the transonic and subsonic parts of the shock wave, the velocity of "random" molecules is small and varies from transonic ($u_r \approx \sqrt{\varepsilon}\, u_b$) to subsonic ($u_r \approx \varepsilon u_b$) at the rear front [12]. The relative velocity of "beam" and "random" molecules is maximum: $u_b - u_r \approx u_b$; hence, the nonequilibrium dissociation caused by decomposition of "random" molecules due to their collisions with "beam" molecules is also maximum in this region. However, it should be borne in mind that the concentration of "beam" molecules decreases here due to elastic collisions in the front region of the shock wave.

Thus, in the approximate analytical investigation, the problem is divided into two parts. In the first part of the shock wave, where the velocity of "random" molecules is high ($u_r \approx u_b$) and their velocity relative to the "beam" is low ($u_r - u_b \ll u_b$), we consider the flow of a perfect gas and calculate the concentrations of "beam" molecules. In the second part of the shock wave, because of the low mass mean velocity of randomly moving molecules ($\varepsilon \leqslant V_r \leqslant \sqrt{\varepsilon}$), the change in the relative velocity is ignored ($u_b - u_r \approx u_b$). In this region, the effective concentration of atoms due to the nonequilibrium dissociation of "random" molecules is calculated.

2. System of Equations Describing the Motion of a Translationally Nonequilibrium Medium Inside the Shock-Wave Front (Binary Mixture of Atoms A and Molecules $\mathbf{A_2}$). The system of equations of continuity, motion, energy, state, and variation of the molecular-beam density and mass concentration of atoms has the following form:

$$\hat{\rho} + \rho V_{\rm r} = 1; \tag{2.1}$$

$$\rho V_{\rm r}^2 + \hat{\rho} + p - \frac{4}{3}\, H_{\rm r}^{\omega}\, \frac{dV_{\rm r}}{d\xi} = 1; \tag{2.2}$$

$$\rho V_{\rm r}(H_{\rm r} + \alpha_{\rm A} H_{\rm A}^0) + \frac{1}{2}\,\rho + \frac{1}{2}\,\rho V_{\rm r}^3 - \frac{H_{\rm r}^{\omega}}{\rm Pr}\,\frac{dH}{d\xi} - \frac{4}{3}\,H_{\rm r}^{\omega}\,\frac{dV_{\rm r}^2/2}{d\xi} + ({\rm Le} - 1)(H_{\rm r} + \alpha_{\rm A} H_{\rm A}^0)\,\frac{d\alpha_{\rm A}}{d\xi} = \frac{1}{2}; \tag{2.3}$$

$$p = \rho\,\frac{1 + \alpha_{\rm A}}{2}\,\theta_{\rm r}; \tag{2.4}$$

$$\frac{d\hat{\rho}}{d\xi} = -\frac{5}{8\sqrt{2}}\,\frac{\gamma - 1}{\gamma}\,H_{\rm r}^{1-\omega}(F_{\rm el} + F_{in})\hat{\rho}\,\frac{1 - \hat{\rho}}{V_{\rm r}}; \tag{2.5}$$

$$\frac{d}{d\xi}\Big(\frac{H_{\rm r}^{\omega}}{{\rm Sc}_{\rm A}}\Big)\frac{d\alpha_{\rm A}}{d\xi} + \frac{d(\rho\alpha_{\rm A}V_{\rm r})}{d\xi} = \frac{5}{8\sqrt{2}}\,\frac{\gamma - 1}{\gamma}\,H_{\rm r}^{1-\omega_{\rm inel}}\,\frac{\hat{\rho}(1 - \hat{\rho})}{V_{\rm r}}. \tag{2.6}$$

Here $\hat{\rho} = \rho_{\rm b}/\rho_{{\rm b},\infty}$ is the relative density of "beam" molecules, $\rho = \rho_{\rm r}/\rho_{{\rm b},\infty}$ is the relative concentration, $V_{\rm r} = u_{\rm r}/u_{{\rm b},\infty}$ and $V_{\rm b} = u_{\rm b}/u_{{\rm b},\infty} \equiv 1$ are, respectively, the relative velocities of "random" and "beam" molecules, $\rho_{{\rm b},\infty}$ is the mass-mean density (according to the "beam"–continuous medium model, the mass-mean velocity of the "beam" molecules in the incoming flow is $u_{{\rm b},\infty} = u_{\rm b} = {\rm const}$ [6–8]), $p = p_{\rm r}/(\rho_{{\rm b},\infty} u_{\rm b}^2)$ is the relative pressure in the continuous medium with randomly moving molecules, $\theta_{\rm r} = 2RT_{\rm r}/\mu_{{\rm A}_2}$ is the dimensionless temperature of the randomly moving medium, $\alpha_{\rm A} = \rho_{\rm A}/(\rho_{\rm A} + \rho_{{\rm A}_2})$ is the mass concentration of atoms, $h_{\rm r}$ is the specific static enthalpy, $\xi = x/l$ ($l = k_{\rm r} u_{\rm b}^{2\omega - 1}/\rho_{\rm b}$, where $k_{\rm r}$ is a constant in the power dependence of viscosity on the temperature $T_{\rm r}$), $H_{\rm r} = h_{\rm r}/u_{\rm b}^2$, $H_{\rm A}^0 = h_{\rm A}^0/u_{\rm b}^2$ is the dimensionless enthalpy of formation of atoms (or dissociation energy), and Pr and Le are the Prandtl and Lewis numbers, respectively, and ${\rm Sc}_{\rm A}$ is the Schmidt number for the atomic component. The parameters $F_{\rm el}$ and $F_{\rm inel}$ are proportional to elastic and inelastic collisions of "beam" molecules with "random" molecules, which lead to dissociation. According to [6], we have

$$F_{\rm el}(z) = \frac{1}{2}\Big[\exp(-z^2) + \Big(2z + \frac{1}{z}\Big)\frac{\sqrt{\pi}}{2}\,{\rm erf}\,(z)\Big], \tag{2.7}$$

where $z = (u_{\rm b} - u_{\rm r})/\sqrt{2RT_{\rm r}/\mu_{{\rm A}_2}}$ and ${\rm erf}\,(z) = \dfrac{2}{\sqrt{\pi}}\displaystyle\int\limits_0^z \exp(-y^2)\,dy$ is the Gauss error integral.

After the simplest transformations, the expression for $F_{\rm inel}$ obtained in [2] may be transformed to a relation similar to (2.7):

$$F_{\rm inel} = \frac{\theta_+}{2z}\,F_{\rm el}(\theta_-) + \frac{\theta_-}{2z}\,F_{\rm el}(\theta_+) + \frac{\sqrt{\pi}}{4}\,\frac{\sqrt{\theta_{\rm d.r.}}}{z}\Big[\frac{{\rm erf}\,(\theta_+)}{\theta_+} - \frac{{\rm erf}\,(\theta_-)}{\theta_-}\Big]. \tag{2.8}$$

Here $\theta_+ = \sqrt{\theta_{\rm d.r.}} + z$ and $\theta_- = \sqrt{\theta_{\rm d.r.}} - z$, where $\theta_{\rm d.r.} = T_{\rm d}/T_{\rm r}$ ($T_{\rm d} = E_{\rm d}/k$ is the characteristic temperature corresponding to the threshold energy of dissociation, $E_{\rm d}$ is the energy of dissociation of molecules, and k is the Boltzmann constant).

Velikodnyi [2] used two Maxwellian distributions with different mean macroscopic velocities and temperatures. The "beam"–continuous medium model is a special case of this approximation, since the delta-shaped velocity-distribution function for "beam" molecules is obtained by the limiting transition from the corresponding Maxwellian distribution of particles in the free stream as $T_{\rm b} \to 0$.

Taking into account the continuity equation (2.1), the total-energy equation (2.3) admits an exact solution for ${\rm Pr} = {\rm Sc}_{\rm A} = 3/4$ and ${\rm Le} = 1$, which has the following form:

$$H_{\rm r} + \alpha_{\rm A} H_{\rm A}^0 + \frac{V_{\rm r}^2}{2} = \frac{1}{2}. \tag{2.9}$$

Relation (2.9) extends a similar energy integral obtained in [7] to the "beam–random" medium model in a perfect gas without chemical transformations to the case of dissociation.

Taking into account (2.9), for a constant mean heat capacity c_p and molecular weight $\bar{\mu}$, the expression for the reduced temperature θ_r of the random medium is

$$\theta_\mathrm{r} = \frac{\gamma - 1}{\gamma}(1 - V_\mathrm{r}^2 - \alpha_\mathrm{A}\theta_\mathrm{d}) \qquad \Big(\theta_\mathrm{d} = \frac{2R}{\bar{\mu}}\,\frac{T_\mathrm{d}}{u_\mathrm{b}^2}, \qquad \bar{\mu} = \frac{\alpha_\mathrm{A}}{\mu_\mathrm{A}} + \frac{\alpha_{\mathrm{A}_2}}{\mu_{\mathrm{A}_2}}\Big).$$

3. Boundary Conditions for a System of Equations Describing the Motion of a Translationally Nonequilibrium Medium Inside the Front of a "Viscous" Shock Wave. The boundary conditions for system (2.1)–(2.9) are the free-stream conditions in the hypersonic "beam" of molecules incoming onto the wave ($\xi \to -\infty$) $V_\mathrm{r} = \hat{\rho}_{\mathrm{A}_2} = 1$ and $T_\mathrm{r} = p_\mathrm{r} = \alpha_\mathrm{A} = \rho_{\mathrm{A}_2} = 0$ and the following conditions at the rear front of the shock wave, which extend the corresponding known Rankine–Hugoniot conditions [13] to the case of a translationally nonequilibrium dissociating mixture ($\xi \to \infty$):

$$V_\mathrm{r} = \varepsilon_s, \quad \rho_\mathrm{r} = \frac{1}{\varepsilon_s}, \quad \hat{\rho}_s = 0, \quad p_\mathrm{r} = \frac{1 + \alpha_s}{2\varepsilon_s}\,\theta_\mathrm{r}, \quad \theta_\mathrm{r} = \frac{\gamma - 1}{\gamma}\,(1 - \varepsilon_s^2 - \alpha_s\theta_\mathrm{d}),$$

$$\alpha_s = \frac{5}{8\sqrt{2}}\,\frac{\gamma - 1}{\gamma}\int\limits_{-\infty}^{\infty} H_\mathrm{r}^{1-\omega}F_\mathrm{inel}\,\frac{\hat{\rho}(1 - \hat{\rho})}{V_\mathrm{r}}\,d\xi, \quad \varepsilon_\mathrm{r} = \frac{\gamma - 1}{\gamma + 1}\Big[1 + \frac{\alpha_s}{2}\,(1 + \alpha_s)\theta_\mathrm{d} - 1\Big] + O\Big(\frac{\gamma - 1}{\gamma + 1}\Big)^2.$$

The quantities marked by the subscript s correspond to the parameters of the "beam–random" medium for $\xi \to \infty$.

To be used in practical applications, formula (2.8) may be approximately represented in the following form:

$$\frac{F_\mathrm{inel}}{F_\mathrm{el,max}} = \Big[2p_\mathrm{el}\,\frac{(\sqrt{\theta_\mathrm{d}} - 1)^{2s}}{\theta_\mathrm{r}^{s+1/2}} + 1\Big]\sqrt{\frac{\theta_\mathrm{r}}{\pi}}\,\exp\Big(-\frac{(\sqrt{\theta_\mathrm{d}} - 1)^2}{\theta_\mathrm{r}}\Big)$$

$$\simeq \frac{2p_\mathrm{el}D_\gamma^{2s} + \sqrt{\varepsilon_\gamma}}{\sqrt{\pi}}\,\exp\Big(-\frac{D_\gamma^2}{1 - \alpha\theta_\mathrm{d}}\Big) \quad \text{for} \quad \theta_\mathrm{d} \geqslant 1; \tag{3.1}$$

$$\frac{F_\mathrm{inel}}{F_\mathrm{el,max}} = 1 - \theta_\mathrm{d} + \frac{1 + \sqrt{\theta_\mathrm{d}}}{2}\,\frac{\sqrt{\theta_\mathrm{r}}}{\pi}\,\exp\Big(-\frac{(1 - \sqrt{\theta_\mathrm{d}})^2}{\theta_\mathrm{r}}\Big)$$

$$= 1 - \theta_\mathrm{d} + \frac{1 + \sqrt{\theta_\mathrm{d}}}{2}\sqrt{\frac{\varepsilon_\gamma}{\pi}}\,\exp\Big(-\frac{D_\Gamma^2}{1 - \alpha\theta_\mathrm{d}}\Big) \quad \text{for} \quad \theta_\mathrm{d} \leqslant 1. \tag{3.2}$$

Here $F_\mathrm{el,max} = \pi d_\mathrm{A}^2 u_\mathrm{b}(1 - V_\mathrm{r})$, $D_\gamma = (\sqrt{\theta_\mathrm{d}} - 1)/\varepsilon_\gamma$, and $D_\Gamma = (1 - \sqrt{\theta_\mathrm{d}})/\varepsilon_\gamma$.

4. Formulas for the Degree of Translationally Nonequilibrium Dissociation in the Shock-Wave Front. To determine the degree of nonequilibrium dissociation α_A, it is reasonable to consider first the solution of Eq. (2.6) in the so-called inviscid approximation, i.e., with the diffusion process ignored. In this approximation, Eq. (2.5) acquires the form

$$\frac{d(\rho V_\mathrm{r}\alpha_\mathrm{A})}{d\xi} = \frac{5}{8\sqrt{2}}\,\frac{\gamma - 1}{\gamma}\,H_\mathrm{r}^{1-\omega}F_\mathrm{inel}\,\frac{\hat{\rho}(1 - \hat{\rho})}{V_\mathrm{r}}. \tag{4.1}$$

In Eq. (4.1), we pass from the variable ξ to the variable $\hat{\rho}$ using Eqs. (2.1) and (2.6):

$$(1 - \hat{\rho})\,\frac{d\alpha_\mathrm{A}}{d\hat{\rho}} = \alpha_\mathrm{A} - F_\mathrm{el}^\mathrm{inel}. \tag{4.2}$$

Here $F_\mathrm{el}^\mathrm{inel} \equiv (F_\mathrm{inel}/F_\mathrm{el})/(1 + F_\mathrm{inel}/F_\mathrm{el})$. Equation (4.2) is an equation with separating variables and has the following solution:

$$\int\limits_0^{\alpha_\mathrm{A}}\frac{d\alpha}{F_\mathrm{el}^\mathrm{inel} - \alpha} = \ln\frac{1 - \hat{\rho}}{1 - \hat{\rho}_0}. \tag{4.3}$$

Here $\hat{\rho}_0$ is the relative density of the hypersonic "beam" of molecules in the beginning of the zone of developed dissociation, where $\alpha_{\rm A} \simeq 0$, and $V_{\rm r} \simeq \sqrt{\varepsilon}$ has the order of the relative velocity of sound.

The equality that turns to zero the denominator in the integrand of Eq. (4.3),

$$F_{\rm el}^{\rm inel} \equiv \frac{F_{\rm inel}/F_{\rm el}}{1 + F_{\rm inel}/F_{\rm el}} = \alpha_{\rm A}, \tag{4.4}$$

yields the maximum possible degree of nonequilibrium dissociation in the problem considered. From the physical point of view, it corresponds to a state, where the increase in the concentration of "random" molecules due to their elastic collisions with "beam" molecules is compensated by the decrease in concentration due to inelastic collisions, which lead to nonequilibrium dissociation of "random" molecules.

To calculate the primitive function in the left side of Eq. (4.3), we represent the quantity $F_{\rm el}^{\rm inel}$ as an explicit function of the atomic concentration $\alpha_{\rm A}$. Taking into account that $\alpha_{\rm A}\theta_{\rm d} < 1$, we expand the exponent in (3.1) into a series and transform it to a form convenient for integration:

$$F_{\rm el}^{\rm inel} \equiv \frac{F_{\rm inel}}{F_{\rm el,max}} \simeq C_m \exp{(-\omega_m \beta)}. \tag{4.5}$$

Here $C_m = (2p_{\rm el} D_\gamma^{2s} + 1)\sqrt{\varepsilon_\gamma/\pi}\exp{(-D_\gamma^2)}$, $\varepsilon_\gamma = (\gamma - 1)/\gamma$, $\omega_m = D_\gamma^2 \theta_{\rm d} \alpha_m$, $\alpha_m = C_m/(1 + C_m)$, and $\beta = \alpha/\alpha_m$. From here, we obtain

$$\frac{F_{\rm el}^{\rm inel}}{1 + F_{\rm el}^{\rm inel}} \simeq \frac{C_m \exp{(-\omega_m\beta)}}{1 + C_m \exp{(-\omega_m\beta)}} \simeq \alpha_m\Big(1 - \frac{1 - \exp{(-\omega_m\beta)}}{1 + C_m}\Big) \equiv \alpha_m(1 - \delta_m\beta), \tag{4.6}$$

where $\delta_m = \omega_m/(1 + C_m)$.

In deriving Eq. (4.6), we took into account that $\omega_m < 1$. The quantity $1 - \exp{(-\omega_m\beta)}$ is replaced by the first two terms of expansion into a Taylor series: $1 - \exp{(-\omega_m\beta)} \simeq 1 + \omega_m\beta$.

With allowance for Eqs. (4.5) and (4.6), formula (4.3) takes the form

$$\int\limits_0^\beta \frac{dz}{1 - (1 + \delta_m)z} = \ln\frac{1 - \hat{\rho}}{1 - \hat{\rho}_0}. \tag{4.7}$$

From here, we obtain

$$\frac{\alpha_{\rm A}}{\alpha_m} = (1 + \delta_m)^{-1}\left[1 - \Big(\frac{1 - \hat{\rho}_0}{1 - \hat{\rho}}\Big)^{1+\delta_m}\right]. \tag{4.8}$$

For small values of the parameter δ_m corresponding to two limiting transitions $D_\gamma^2 \to \infty$ and $D_\gamma^2 \to 0$, since $\delta_m \sim \omega_m \sim D_\gamma^2 \exp{(-D_\gamma^2)}$, formula (4.8) reduces to a simpler form

$$\frac{\alpha_{\rm A}}{\alpha_m} \to \frac{\hat{\rho}_0 - \hat{\rho}}{1 - \hat{\rho}}. \tag{4.9}$$

On the right side of the shock wave, where $\hat{\rho}(\xi) \to 0$ as $\xi \to \infty$, the concentration of atoms is $\alpha_{\rm A} = \alpha_s$, and

$$\alpha_s = \alpha_m[1 - (1 - \hat{\rho})^{1+\delta_m}](1 + \delta_m)^{-1}, \tag{4.10}$$

$$\alpha_s \to \alpha_m\hat{\rho}_0 \quad \text{for} \quad \delta_m \to 0. \tag{4.11}$$

Formulas (4.5)–(4.11) are applicable in the "under-threshold" regime of dissociation, where $\theta_{\rm d} \geqslant 1$ or $T_{\rm d} \geqslant T_{\rm kin}$ $[T_{\rm kin} = \mu_{{\rm A}_2} u_{{\rm b},\infty}^2 (1 - V_{\rm r})^2/(2R)]$.

Using a similar procedure of expansion of the exponent in (3.2) for $\theta_{\rm d} \leqslant 1$ or $T_{\rm d} \leqslant T_{\rm kin}$, we obtain

$$\frac{\alpha_{\rm A}}{\alpha_M} = (1 + \Delta_M)^{-1}\left[1 - \Big(\frac{1 - \hat{\rho}_0}{1 - \hat{\rho}}\Big)^{1+\Delta_M}\right]. \tag{4.12}$$

Here $\alpha_M = (1 - \theta_{\rm d} + C_M)/(2 - \theta_{\rm d} + C_M)$, $C_M = ((1 + \sqrt{\theta_{\rm d}})/2)\sqrt{\varepsilon_\gamma/\pi}\exp{(-D_\Gamma^2)}$, $D_\Gamma^2 = (1 - \sqrt{\theta_{\rm d}})^2/2$, and $\Delta_M = C_M\theta_{\rm d}D_\Gamma^2/(2 - \theta_{\rm d} + C_M)^2$.

Formulas (4.5)–(4.12) correspond to the case, where both the "beam" molecules and the "random" molecules dissociate in inelastic collisions. If we take into account only the dissociation of "random" molecules, then the relative dissociation rate $F_{\mathrm{el}}^{\mathrm{inel}}/(1+F_{\mathrm{el}}^{\mathrm{inel}})$ should be replaced by $F_{\mathrm{el}}^{\mathrm{inel}}(1-\alpha_{\mathrm{A}})/(1+F_{\mathrm{el}}^{\mathrm{inel}}(1-\alpha_{\mathrm{A}}))$, and the parameters δ_m, Δ_M, and α_s in Eqs. (4.8) and (4.12) by $\delta'_m = \delta_m + \alpha_m(1-\alpha_m)$, $\Delta'_M = \Delta_M + \alpha_M(1-\alpha_M)$, and $\alpha'_s \approx \alpha_s$, respectively.

It follows from Eqs. (4.5)–(4.12) for nonequilibrium dissociation that the degree of dissociation α_{A} depends on the generalized coordinate of the reaction: the concentration of molecules of the hypersonic "beam" $\hat{\rho}$ and the parameters of the problem θ_{d}, D_γ^2, D_Γ^2, p_{el}, γ, and s. It also follows from (4.5)–(4.12) that the maximum degrees of nonequilibrium dissociation (4.4) are not reached, since $\hat{\rho}_0$ is always smaller than unity because of the decrease in density of "beam" molecules during elastic collisions.

Due to temperature dissociation, the equation for the change in the atomic concentration α_{A} may be written as

$$\frac{d[(1-\hat{\rho})\alpha_{\mathrm{A}}]}{d\xi} = \frac{5}{8\sqrt{2}}\,\frac{\gamma-1}{\gamma}\,H_{\mathrm{r}}^{1-\omega}F_{\mathrm{el}}^{\mathrm{inel}}\frac{1-\hat{\rho}}{V_{\mathrm{r}}}\Big[(1-\alpha_{\mathrm{A}})^2 + (1+\alpha_{\mathrm{A}})\hat{\rho} + (1-\alpha_{\mathrm{A}})\alpha_{\mathrm{A}}\frac{1-\hat{\rho}}{V_{\mathrm{r}}}\Big]. \qquad (4.13)$$

Here $F_{\mathrm{el}}^{\mathrm{inel}}$ is the velocity of the equilibrium temperature ("Arrhenius") dissociation, and the terms in square brackets correspond to the following types of collisions: $A_2^{\mathrm{r}} + A_2^{\mathrm{r}}$, $A_2^{\mathrm{r}} + A_2^{\mathrm{b}}$, $A^{\mathrm{r}} + A_2^{\mathrm{b}}$, and $A_2^{\mathrm{r}} + A^{\mathrm{r}}$.

Passing to the variable $\hat{\rho}$, Eq. (4.14) may be written as

$$(1-\hat{\rho})\,\frac{d\alpha_{\mathrm{A}}}{d\hat{\rho}} = -\alpha_T\,\exp\left(\omega_E(1-\alpha_{\mathrm{A}})\right)\frac{(1-\alpha_{\mathrm{A}})(1-\hat{\rho})}{\hat{\rho}} + \alpha_{\mathrm{A}}. \qquad (4.14)$$

Here $\alpha_T = ((2p_{\mathrm{el}}D_E^{2s+1}+1)/V_{\mathrm{r}})\sqrt{\varepsilon_\gamma/\pi}\,\exp\left(-D_E^2(1+\theta_{\mathrm{d}})\right)$, $\omega_E = D_E^2\theta_{\mathrm{d}}$, $D_E^2 = \theta_{\mathrm{d}}/\varepsilon_\gamma$, and $V_{\mathrm{r}} \simeq \varepsilon = (\gamma-1)/(\gamma+1)$.

Ignoring the last term in Eq. (4.14) in our estimates (since we have $\hat{\rho} < 1$ in the zone of developed dissociation and $\hat{\rho} > 1$ on the right side of the shock wave), we obtain the following relation for α_{A}:

$$-\mathrm{Ei}\left[-\omega_E(1-\alpha_{\mathrm{A}})\right] = -\mathrm{Ei}\left(-\omega_E\right) + \alpha_T\,\ln\frac{\hat{\rho}}{\hat{\rho}_0}. \qquad (4.15)$$

Here $-\mathrm{Ei}\,(-x) = \int\limits_x^\infty \frac{\exp(-y)}{y}\,dy$ is the integral exponential function.

The second term in the right side of Eq. (4.15) tends to infinity as $\hat{\rho} \to 0$. It follows from here that the temperature ("Arrhenius") dissociation of molecules is completed by their full dissociation as $\hat{\rho} \to 0$, i.e., $\alpha_{\mathrm{A}} = 1$. It is known that this state is observed at distances of the order of many mean free paths behind the dissociation zone adjacent to the "viscous" shock wave [13] under the condition that the rate of three-particle recombination is small.

Since in the problem considered it is of interest to determine first of all the concentration of atoms formed only within the thickness of the "viscous" shock, we confine ourselves to a small finite value of the ratio $\hat{\rho}/\hat{\rho}_0$, assuming that

$$\hat{\rho}/\hat{\rho}_0 \simeq \hat{\rho}_k/\hat{\rho}_0 = 0.1. \qquad (4.16)$$

The concentration of atoms formed due to temperature dissociation α_s^T was determined from Eqs. (4.15) and (4.16).

To compare the concentrations of atoms α_s and α_s^T with the equilibrium values α_{eq}, we use the Lighthill–Freeman dissociation model [13]. In accordance with this model, the condition of equal rates of molecular dissociation and three-particle recombination of atoms is

$$(1-\alpha_{\mathrm{eq}})\,\exp\Big(-\frac{T_{\mathrm{d}}}{T}\Big) = \frac{\rho}{\rho_{\mathrm{d}}}\,\alpha_{\mathrm{eq}}^2. \qquad (4.17)$$

Here ρ_{d} is a parameter depending on the properties of the molecular gas. Taking into account the notation introduced above, Eq. (4.17) can be conveniently written in the following form:

$$\ln\frac{\alpha_{\mathrm{eq}}^2}{1-\alpha_{\mathrm{eq}}} = \ln\frac{\rho_{\mathrm{d}}}{\rho_0} + \ln\frac{\varepsilon_s}{2} + \frac{z}{7} + \ln\left[1+(1+\alpha_{\mathrm{eq}})(1-\alpha_{\mathrm{eq}}\theta_{\mathrm{d}})\right] - \frac{D_E^2}{1-\alpha_{\mathrm{eq}}\theta_{\mathrm{d}}}. \qquad (4.18)$$

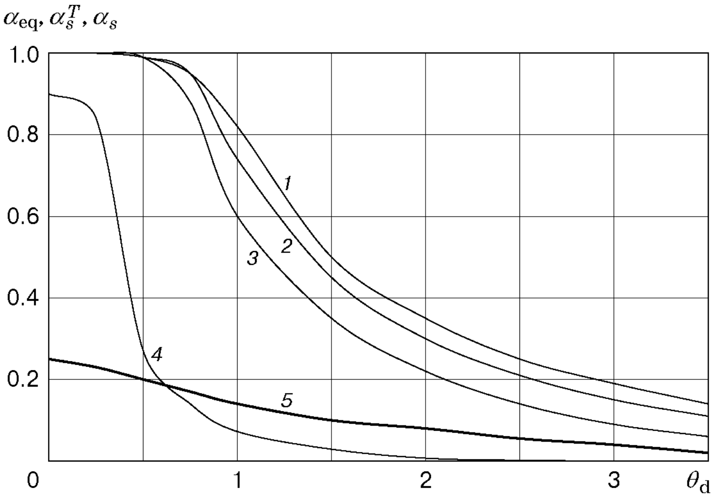

Fig. 3. Degrees of equilibrium dissociation $\alpha_{\rm eq}$, temperature dissociation α_s^T, and nonequilibrium dissociation α_s as functions of the dimensionless energy of dissociation $\theta_{\rm d}$ for $p_{\rm el} = 0.1$, $s = 1$, $\gamma = 1.4$, $\hat{\rho}_0 = 0.5$, and $\rho_0 = 1.25$ kg/m^3: curves 1–3 refer to $\alpha_{\rm eq}$ for $z = 0$, 40, and 80 km, respectively; curves 4 and 5 refer to α_s^T and α_s, respectively.

Here $\varepsilon_s = (\gamma - 1)/(\gamma + 1)$, $\rho_0 = 1.25$ kg/m^3, $\rho_{\rm d} = 1.5 \cdot 10^5$ kg/m^3, and z [km] is the altitude in the Earth's atmosphere.

For

$$D_E^2 < \frac{z}{7} + \ln \frac{\varepsilon_s \rho_{\rm d}}{2\rho_0}, \tag{4.19}$$

it is convenient to solve Eq. (4.18) by the following iterative scheme:

$$\alpha_{{\rm eq},k+1} = 1 - D_E^2/\{z/7 + \ln(\varepsilon_s\rho_{\rm d}/(2\rho_0)) - \ln(\alpha^2_{{\rm eq},k}/(1-\alpha_{{\rm eq},k})) + \ln[1 + (1+\alpha_{{\rm eq},k})(1 - \alpha_{{\rm eq},k}\theta_{\rm d})]\}. \tag{4.20}$$

If condition (4.19) cannot be fulfilled, the transcendental equation (4.20) can be solved by Newton's method choosing, for example, the quantity $\theta_{\rm d}^{-1}$ as the zero approximation $\alpha_{{\rm eq},0}$. For small values of the relative energy of dissociation $\theta_{\rm d} \leqslant 1$, when the value of $\alpha_{\rm eq}$ is close to unity and condition (4.19) is not satisfied, it is convenient to use the following iterative scheme:

$$\frac{\alpha^2_{{\rm eq},k+1}}{1 - \alpha_{{\rm eq},k+1}} = q_k = 10^4 \exp\Big(\frac{z}{7}\Big)\Big\{1 + (1 - \alpha_{{\rm eq},k})(1 - \alpha_{{\rm eq},k}\theta_{\rm d}) \exp\Big[-\frac{D_E^2}{1 - \alpha_{{\rm eq},k}\theta_{\rm d}}\Big]\Big\},$$

$$\alpha_{{\rm eq},k+1} = \frac{q_k}{2}\Big(\sqrt{1 + \frac{4}{q_k}} - 1\Big).$$

Figure 3 shows the degree of nonequilibrium dissociation α_s as a function of the dimensionless energy of dissociation $\theta_{\rm d}$. The values of α_s are compared with the corresponding values of the degree of temperature dissociation α_s^T and equilibrium values $\alpha_{\rm eq}$ for different flight altitudes z in the Earth's atmosphere (the density of the incoming hypersonic "beam" was $\rho_{\rm b} \simeq \rho_0 \exp(-z/7)$, where $\rho_0 = 1.25$ kg/m^3 [13]).

It follows from Fig. 3 that, for high values of the relative energy of dissociation ($\theta_{\rm d} > 1.5$), the concentrations α_s^T are negligibly small as compared to α_s. However, the values of α_s and α_s^T become comparable for $\theta_{\rm d} \approx 1$, the temperature dissociation is completed by full decomposition of molecules for $\theta_{\rm d} > 0.5$ ($\alpha_s^T = 1$ in the absence of three-particle recombination), and the degree of nonequilibrium dissociation due to the reduction of the energy barrier (due to the great difference in the "beam" and "random medium" velocities) is majorated by Eq. (4.4).

A comparison of equilibrium values $\alpha_{\rm eq}$ with α_s, $\alpha'_{\rm eq}$, and α_s^T shows that $\alpha_{\rm eq}$ is greater than these parameters almost within the entire range of $\theta_{\rm d}$. However, it should be noted that the equilibrium concentration of atoms $\alpha_{\rm eq}$ is actually reached far downstream of the "viscous" shock wave.

Thus, the degree of dissociation of a binary mixture of gases (A and A_2) in the model "beam"–continuous medium in the front of a hypersonic shock wave in a wide range of θ_d is rather high in contrast to the "Arrhenius" model of temperature dissociation.

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