

ANALYSIS OF NONEQUILIBRIUM DISSOCIATION KINETICS IN A BOUNDARY LAYER USING VARIOUS REACTION MODELS

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Values of the nonequilibrium macroscopic reaction rate for a nonisothermal boundary layer of a monatomic diluent gas are calculated using a number of models for thermal dissociation of diatomic molecules — anharmonic Morse oscillators. Analysis is performed for conditions where the diffusive transfer of excited molecules has a significant effect on the population of their upper vibrational levels, which does not only amount to change in vibrational temperature. Under the joint influence of diffusive transfer of molecules, vibrational exchanges, and reactions involving vibrationally excited particles, the local vibrational distribution functions are substantially nonequilibrium. The kinetic models considered take into account the possible contribution of the energy of molecular translational and rotational degrees of freedom to the energy required to overcome the reaction threshold. The effect of multiquantum vibrational–translational exchanges on the distribution of dissociating molecules in their upper vibrational levels is taken into account approximately.

Introduction. In the present paper, we consider the thermal dissociation of diatomic molecules under conditions where the dissociation energy Q is high compared to the thermal energy of the particles $O(kT)$ (k is the Boltzmann constant and T is the gas temperature). In this case, investigation of the dissociation kinetics is based on examination of properties of the high-energy tails of molecular distributions for the degrees of freedom of particles whose energy is assumed to be used to overcome the dissociation threshold Q . Until recently, this problem has been considered primarily for nonequilibrium reaction kinetics in a fixed gas (nonstationary formulation) or in a weakly nonuniform gas flow (quasistationary formulation). In the present paper, we study features of the nonequilibrium kinetics described by similar models of thermal dissociation, in substantially nonuniform nonisothermal flows with diffusive transfer of particles (for example, in a boundary layer).

At present, extensive use is made of the stepwise mechanism and the corresponding model of thermal dissociation, which assumes that the reaction occurs upon collisions of molecules at the upper vibrational levels with energy close to the dissociation threshold. In many papers, dissociation of molecules that are at intermediate vibrational levels is also considered possible. In this case, the deficiency in energy required to overcome the dissociation threshold is compensated for by the translational and rotational motion of particles (see, e.g., [1–9]).

Most of the available models of dissociation under nonequilibrium conditions are based on a two-temperature representation (i.e., it is assumed that the reaction rate constants depend on translational–rotational and vibrational temperatures) and are written with allowance for quasistationary distributions of molecules in the vibrational levels formed in the gas as a result of the reaction and vibrational exchanges. In some studies, the approximation of level vibrational kinetics is used [8]. In the present paper, we employ simple versions of these models to analyze the effect of presumed reaction mechanisms on nonequilibrium dissociation kinetics. In particular, for the stepwise dissociation mechanism, it was concluded in [10, 11] that it is necessary to invoke level vibrational kinetics to describe nonequilibrium dissociation in a nonisothermal boundary layer of a heated gas near a “cold” wall. We examine the question of whether this conclusion remains valid for the indicated models.

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Interest in the present problem is motivated by the fact that according to modern dissociation models, additional involvement of molecules at intermediate levels in the reaction can to be accompanied by collisions of molecules with particles, which are assumed to be in equilibrium distribution in velocities and rotational sublevels. In this case, the degree of nonequilibrium of the molecular vibrational distribution can decrease.

Models of Kinetic Processes. Below, we assume that dissociating molecules make up a small impurity in the monatomic inert gas. Therefore, recombination can be ignored and, among vibrational transitions, only VT exchanges are considered.

For the flows considered, the inequalities $\tau \leq \tau_R \ll \tau_d \sim \theta$ are valid. Here τ and τ_R are the characteristic times of translational and rotational relaxation, τ_d is the dissociation time, and θ is the characteristic time of flow. By virtue of this, we assume locally-equilibrium velocity distributions of the atoms and molecules and locally-equilibrium distributions of the molecules in rotational levels.

Let α be the number of vibrational level of a molecule with energy E_α^V ($\alpha \leq \beta$ and $E_\alpha^V \leq E_\beta^V \simeq Q$) whose dissociation occurs from level β . For this limiting version of the stepwise reaction mechanism (we call it the V mechanism), the microscopic rate of reaction from the α level W_α^V and the macroscopic rate of dissociation K_d^V are given by

$$W_\alpha^V = \delta_{\alpha\beta} Z_a P_\alpha^V Y_\alpha n, \quad \alpha \leq \beta; \quad (1)$$

$$K_d^V = \frac{Z_a}{n_a} P_\beta^V Y_\beta, \quad Z_a = n_a \sigma_a \sqrt{\frac{8kT}{\pi\mu}}. \quad (2)$$

Here Z_a is the gas-kinetic frequency of collision of the molecules with the inert atoms, σ_a is the gas-kinetic cross section of these collisions, μ is the normalized mass of the molecules and the atoms of the diluent gas, $Y_\alpha = n_\alpha/n$ (n_α is the number density of molecules with energy E_α^V), n and n_a are the number densities of the molecules and atoms, respectively (under the assumption that $n_a \gg n$), P_α^V is the ratio of the cross section of dissociation from the α level to the collision cross section for an unexcited molecule, which can be both smaller and larger than unity ($P_\alpha^V > 1$ when the actual frequency of collisions leading to disintegration of molecules at the α level exceeds the value of Z_a because of change in particle interaction laws due to severe vibrational excitation of a particle [12]). Values of Y_α are determined by solving the system of equations of vibrational level kinetics (see, e.g., [3, 4, 13, 14]).

We assume that dissociation can occur from any vibrational levels (i.e., for all $E_\alpha^V \leq Q$) if the deficiency in energy necessary for molecule dissociation is compensated for by the relative motion of colliding particles. A model of the reaction (we call it the TV model) can be formulated using the corresponding cross section:

$$\sigma_\alpha^{\text{TV}}(E) = 0, \quad E = \mu g^2/2 \leq Q - E_\alpha^V = E_\alpha^T, \quad \sigma_\alpha^{\text{TV}}(E) = \sigma_a P_\alpha^{\text{TV}} (1 - E_\alpha^T/E), \quad E > E_\alpha^T. \quad (3)$$

Here g is the relative velocity of a molecule and atom. Considering (3), for the microscopic rate of dissociation from the α level W_α^{TV} and the macroscopic reaction rate constant K_d^{TV} , we obtain the expressions

$$W_\alpha^{\text{TV}} = Z_a n P_\alpha^{\text{TV}} \exp\left(\frac{E_\alpha^V - Q}{kT}\right) Y_\alpha, \quad K_d^{\text{TV}} = \frac{Z_a}{n_a} \exp\left(-\frac{Q}{kT}\right) \sum_{\alpha=0}^{\beta} P_\alpha^{\text{TV}} \exp\left(\frac{E_\alpha^V}{kT}\right) Y_\alpha.$$

Similarly, the contribution of rotations to the reaction mechanism is allowed for using the TRV model. In particular, it is assumed that the molecules are stable if

$$E_{\alpha j}^{\text{VR}} \equiv E_\alpha^V + E_j^{\text{R}}(\alpha) < Q.$$

Here j is the rotational quantum number and $E_j^{\text{R}}(\alpha)$ is the energy of rotations of a molecule in the state αj . In addition, it is assumed that the deficiency in the energy $Q - E_{\alpha j}^{\text{VR}}$ necessary for molecule dissociation is compensated for by the energy of relative motion of colliding particles $\mu g^2/2$, and the dissociation cross section corresponds to model (3), in which the quantity $E_{\alpha j}^{\text{T}} \equiv Q - E_{\alpha j}^{\text{VR}}$ is used instead of E_α^{T} .

As a result, for the microscopic rate of dissociation from the state αj , we obtain the expression

$$W_{\alpha j}^{\text{TRV}} = Z_a n P_{\alpha j}^{\text{TRV}} \exp\left(\frac{E_{\alpha j}^{\text{VR}} - Q}{kT}\right) Y_{\alpha j}, \quad (4)$$

where $Y_{\alpha j} \equiv n_{\alpha j}/n = (n_\alpha/n)(n_{\alpha j}/n_\alpha) \equiv Y_\alpha Y_j(\alpha)$ ($n_{\alpha j}$ is the number density of molecules in the state αj).

Next, it is assumed that at specified energy $E_\alpha^V < Q$, molecules with rotational energy $E_j^{\text{R}}(\alpha) < Q - E_\alpha^V$ are stable. This means that in calculating W_α^{TRV} , one should sum up $W_{\alpha j}^{\text{TRV}}$ in (4) from j to $j(\alpha)_{\text{max}}$, and the rotational quantum number $j(\alpha)_{\text{max}}$ should correspond to the rotational energy $Q - E_\alpha^V$.

For the high-temperature flows considered, summation over j can be replaced by integration. In addition, one should take into account that in the case of homonuclear molecules, the quantum numbers j can be only even or only odd. These features do not influence the calculation result W_α^{TRV} by virtue of the high gas temperatures. Thus, for W_α^{TRV} , we obtain the formula

$$W_\alpha^{\text{TRV}} = Z_a n P_\alpha^{\text{TRV}} \frac{Q - E_\alpha^{\text{V}}}{kT} \exp\left(\frac{E_\alpha^{\text{V}} - Q}{kT}\right) Y_\alpha,$$

which leads to the following expression for the macroscopic dissociation rate constant:

$$K_d^{\text{TRV}} = \frac{Z_a}{n_a} \exp\left(-\frac{Q}{kT}\right) \sum_{\alpha=0}^{\beta} P_\alpha^{\text{TRV}} \frac{Q - E_\alpha^{\text{V}}}{kT} \exp\left(\frac{E_\alpha^{\text{V}}}{kT}\right) Y_\alpha.$$

The literature contains contradictory data on the probabilities of multiquantum exchanges. For example, Gonzales and Varhese [15] showed that for various collision models for the same conditions, the ratio of the probability of double-quantum exchanges to the probability of one-quantum exchanges is in the range of 10^{-7} to 1. Therefore, to determine the role of multiquantum exchanges in the nonequilibrium kinetics of thermal dissociation, we assume that in the gaseous medium considered there are only single and double-quantum (V–T) transitions, whose probabilities are related by the equality

$$P_{(\alpha+2)\rightarrow\alpha} = \eta_\alpha P_{(\alpha+1)\rightarrow\alpha}.$$

Here $\eta_\alpha = \eta \exp[A(\varepsilon_\alpha - q)]$, where $\varepsilon_\alpha \equiv E_\alpha^{\text{V}}/(kT)$, $q \equiv Q/(kT)$, and $\eta \leq 1$ and $A \leq 1$ are adjusting parameters. The adopted model is quite realistic. In particular, according to this model, the (V–T) transitions for most of the vibrational spectrum are adiabatic for gas temperatures typical of dissociation, and, hence, the probabilities of multiquantum exchanges should be rather low in this case [2, 3].

In all cases, we describe the probabilities of one-quantum VT exchanges by the well-known relation [2] $P_{(\alpha+1)\rightarrow\alpha} \equiv P_{\alpha+1}^\alpha = (\alpha+1)P_1^0 \exp(\delta^{\text{VT}}\alpha)$. It is valid subject to the condition that the transition is adiabatic, which is, strictly speaking, violated in the neighborhood of the upper vibrational level of the molecule. For example, for impurity N_2 in Ar, we have [3, 14]

$$\delta^{\text{VT}} = \frac{4}{3} \gamma_0 \frac{\Delta E}{E_1^{\text{V}}} \approx \frac{6.28}{\sqrt{T}}, \quad \gamma_0 = \frac{\pi E_1^{\text{V}}}{\hbar a_*} \sqrt{\frac{\mu}{2kT}} \approx \frac{628}{\sqrt{T}}.$$

Here γ_0 is the adiabaticity parameter of the $1 \rightarrow 0$ transition, ΔE is the anharmonicity of the vibrational spectrum, a_*^{-1} is the interaction radius of the colliding particles, T [K] is the gas temperature, and \hbar is the Planck constant.

Equations of Vibrational Level Kinetics. By virtue of the above assumptions, the equations solved below for Y_α can be written as

$$\frac{\partial n Y_\alpha}{\partial t} + \nabla(n Y_\alpha u + n Y_\alpha v_\alpha) = R_\alpha^{\text{VT}} - W_\alpha, \quad (5)$$

where

$$R_\alpha^{\text{VT}} = Z_a n P_1^0 (r_{\alpha+1}^\alpha + r_{\alpha-1}^\alpha + r_{\alpha+2}^\alpha + r_{\alpha-2}^\alpha),$$

$$r_{\alpha+1}^\alpha = (\alpha+1) \exp(\delta^{\text{VT}}\alpha) [Y_{\alpha+1} - \exp(-\varepsilon_{\alpha+1} + \varepsilon_\alpha) Y_\alpha],$$

$$r_{\alpha-1}^\alpha = \alpha \exp(\delta^{\text{VT}}(\alpha-1)) [\exp(-\varepsilon_\alpha + \varepsilon_{\alpha-1}) Y_{\alpha-1} - Y_\alpha],$$

$$r_{\alpha+2}^\alpha = \eta_\alpha (\alpha+1) \exp(\delta^{\text{VT}}\alpha) [Y_{\alpha+2} - \exp(-\varepsilon_{\alpha+2} + \varepsilon_\alpha) Y_\alpha],$$

$$r_{\alpha-2}^\alpha = \eta_{\alpha-2} (\alpha-1) \exp(\delta^{\text{VT}}(\alpha-2)) [\exp(-\varepsilon_\alpha + \varepsilon_{\alpha-2}) Y_{\alpha-2} - Y_\alpha]$$

(the expressions for W_α are given above). It should be noted that in Eq. (5), the terms r_{-2}^0 and r_{-1}^0 are absent for $\alpha = 0$, the terms r_{-1}^1 are absent for $\alpha = 1$, the terms $r_{\beta+1}^{\beta-1}$ are absent for $\alpha = \beta - 1$, and the terms $r_{\beta+1}^\beta$ and $r_{\beta+2}^\beta$ are absent for $\alpha = \beta$.

We assume that the vibrational relaxation time for molecules τ^{VT} , the characteristic time of flow θ , and the reaction time τ_d satisfy the conditions

$$\tau^{\text{VT}} \ll \theta \approx \tau_d. \quad (6)$$

In the present paper, we calculate the normalized function of distribution of dissociating molecules in vibrational levels $F_\alpha = Y_\alpha/Y_\alpha^0$ under the above assumptions of properties of the flow considered. Using conditions leading to implementation of the approximation of local strongly nonequilibrium solutions for the high-energy tails of the distributions Y_α , we transform the left side of Eq. (5) as is done in [10, 11, 14]. In particular, we assume that at the point of the flow considered, with satisfaction of conditions (6) and some restrictions from above on values of the nondimensional vibration energy $\varepsilon_\alpha \gg 1$, the solution of Eq. (5) has the same properties

$$|\nabla \ln F_\alpha| \ll |\nabla \ln Y_\alpha^0| \approx \varepsilon_\alpha |\nabla \ln T| \quad (7)$$

as for $\varepsilon_\alpha \approx 1$ on the “dome” of distributions of molecules in their vibrational levels (Y_α^0 is the locally-equilibrium Boltzmann distribution in E_α^V).

An important property of the distribution function F_α is that with satisfaction of conditions (6) and for $\varepsilon_\alpha \gg 1$, it can differ qualitatively from the functions Y_α and Y_α^0 , which vary much faster in this case. If inequalities (7) are satisfied, the function F_α can be calculated as a local function, i.e., a function that depends on local values of the macroparameters and their spatial derivatives [10, 11, 14]. Indeed, in the main approximation taking into account (7), in the kinetic equation, we can ignore terms with spatial derivatives of the unknown function F_α . This allows us to obtain an approximate nonequilibrium local solution for this function. Results of solving the kinetic equations for the tails of the molecular distributions show that with increase in the vibrational level number, the nonequilibrium local solution can become invalid. This can be due to a change of the sign of the distribution function calculated in the region of the tail or violation of conditions (6) or (7), for example, at the “cold” wall.

Using conditions (7) and neglecting obviously small terms as done in [10, 14], we bring the left side of Eq. (5) for the case of nonisothermal boundary-layer flow to the form

$$\frac{\partial n Y_\alpha}{\partial t} + \nabla(n Y_\alpha u + n Y_\alpha v_\alpha) = -D_\alpha Y_\alpha^0 F_\alpha \varepsilon_\alpha^2 (\nabla_y \ln T)^2 \quad (\varepsilon_\alpha \gg 1), \quad (8)$$

where D_α the diffusion constant for molecular diffusion in the diluent gas, which depends on E_α^V [12]. The y axis is directed along the normal to the streamlined surface. Thus, Eq. (5) reduces to a system of local linear algebraic equations for calculating the above distribution.

The solution obtained for F_α , which is asymptotic by virtue of (8) and conditions (7), must be joined to the solution obtained for $\varepsilon_\alpha \sim 1$, where $F_\alpha \approx 1$ because of fast VT relaxation. The joining is achieved by replacing, the equation with $\alpha = 0$ in (5) by the normalization condition $\sum_{\alpha=0}^{\beta} Y_\alpha^0 F_\alpha = 1$.

Numerical Results and Discussion. Numerical values of the rate constant for dissociation of nitrogen in argon were determined in the case of no motion in the gas ($\nabla \ln T = 0$), for various reaction models and VT-exchanges and for various values of the quantities included in these model. In particular, in the calculations, we assumed that over a wide range, the maximum and minimum values of the coefficients P_α^V , P_α^{TV} , and P_α^{TRV} are identical for all models considered and independent of the vibrational level number. Some calculations of the reaction rate constant were performed for conditions where values of P_α^V for all versions of the reaction mechanism were determined from the cross-sectional dimensions of the vibrationally excited molecules (Morse oscillators) that collided with atoms [12]. Let us consider these assumptions in greater detail.

From the physical viewpoint, P_α is the ratio of the cross section of atom–molecule collisions involving dissociation of the molecules from the α level to the gas-kinetic cross section of collisions of unexcited molecules and atoms. When the vibrational energy of a molecule becomes higher, the molecule cross section increases (first slightly and near the dissociation threshold, by an order of magnitude [12]). Therefore, for the chosen reaction models, the basic contribution to the reaction rate is made by molecules at the upper (uppermost in the case of the V model) vibrational levels. According to the estimates given in [12], for molecules simulated by Morse oscillators, the cross section of their collisions with atoms can be almost an order of magnitude higher than the gas-kinetic cross section if the vibration energy accumulated by the molecules is close to the dissociation energy. Therefore, for the coefficient P_α , the value of $P_\alpha \approx 10$, which does not depend on the vibrational level number, has the meaning of the upper bound of possible values for this quantity and the calculated macroscopic reaction rate. The value $P_\alpha \approx 1$ has the meaning of the lower bound for the same quantity. Thus, we can assume approximately that for the coefficients P_α , the admissible values that do not depend on the vibrational level number are in the range $1 \leq P_\alpha = P \leq 10$.

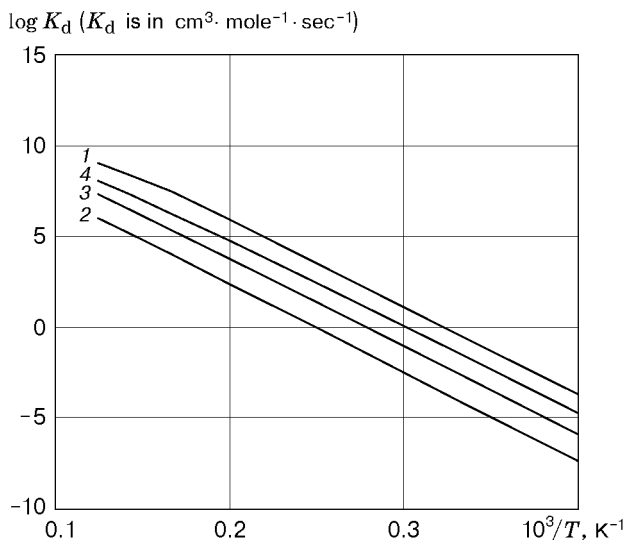


Fig. 1

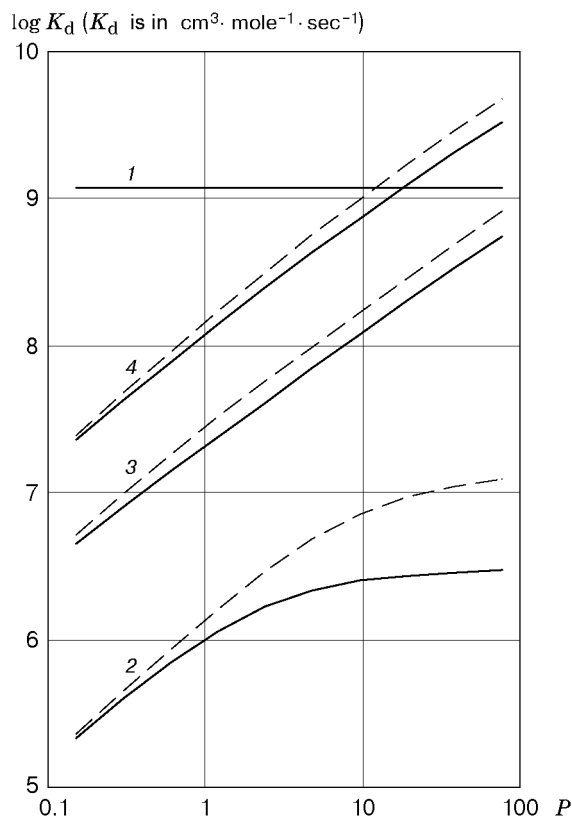


Fig. 2

TABLE 1

T, K	log $K_{d,\text{exp}}$ (K_d is in $\frac{\text{cm}^3}{\text{mole} \cdot \text{sec}}$)	$K_d/K_{d,\text{exp}}$								
		$P = 10$			Morse oscillator			$P = 1$		
		V, 10^{-4}	TV, 10^{-2}	TRV, 10^{-1}	V, 10^{-4}	TV, 10^{-2}	TRV, 10^{-1}	V, 10^{-4}	TV, 10^{-2}	TRV, 10^{-1}
4000	3.50	6.75	5.85	7.68	7.34	1.31	1.290	2.80	0.762	0.854
5000	5.89	7.59	5.73	6.15	8.27	1.29	1.060	3.11	0.788	0.724
6000	7.47	8.34	5.48	4.86	9.10	1.25	0.874	3.38	0.800	0.621
7000	8.40	13.80	7.87	5.77	15.10	1.85	1.110	5.58	1.230	0.819
8000	9.07	21.40	10.40	6.41	23.40	2.55	1.330	8.60	1.760	1.020

Figure 1 shows the temperature dependence of the dissociation rate constant for $P_\alpha = P = 1$ and $\eta_\alpha = 0$. Curve 1 corresponds to the experimental values of K_d recommended in [16], and curves 2–4 correspond to calculated values of K_d^V , K_d^{TV} , and K_d^{TRV} . Obviously, for $P_\alpha = P = 1$ and $\eta_\alpha = 0$, the values of K_d obtained using the V and TV models are considerably underestimated (by two or three orders of magnitude) compared to the experimental data. The temperature dependence of K_d is described more accurately (for given values of P_α and η_α) by the TRV reaction model, but in this case, too, the compared quantities differ by an order of magnitude.

Since the actual values of the adjusting parameters P_α and η_α are not known reliably, it is of interest to study the effect of these parameters on the quantity K_d .

Figure 2 gives calculated K_d for the models considered for various values of P and η_α in the gas at rest at the fixed temperature $T = 8000$ K ($\nabla \ln T = 0$). Solid curves correspond to the case $\eta_\alpha = 0$, and dashed curves correspond to $\eta_\alpha = 1$. The numbering of the curves in Fig. 2 corresponds to that adopted in Fig. 1.

Calculated dissociation rate constants for all above-mentioned models compared to experimental recommended values presented in Table 1 show that the choice of a realistic reaction model is important.

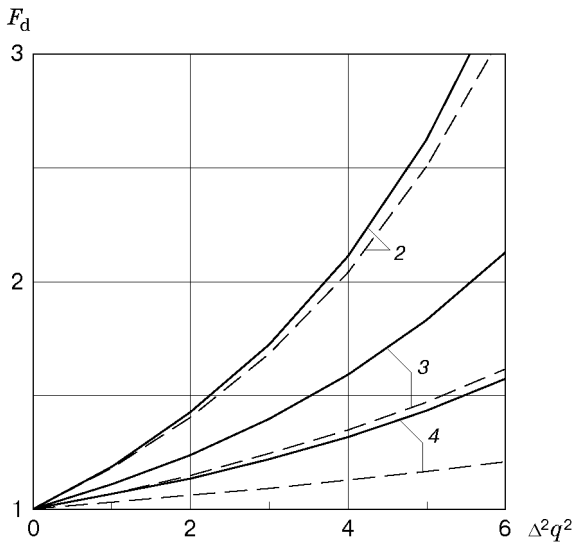


Fig. 3

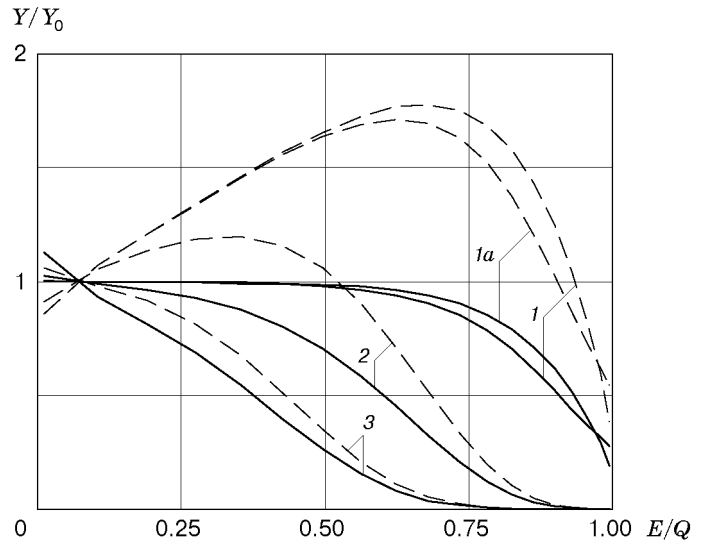


Fig. 4

The data presented in Figs. 1 and 2 and Table 1 show that among the thermal dissociation models used in the present paper, only the TV and TRV models (for large values of the parameter P) can give a fit to the experimental dissociation rate constant K_d . This is also true for calculations that take into account multiquantum vibrational transitions in the neighborhood of the upper β level.

Makashev and Provotorov [10] examined the effect of gas flow in a nonisothermal boundary layer on the dissociation rate of diatomic molecules — reduced harmonic oscillators. The reaction was described within the framework of the stagewise mechanism (V model). In this case, as in [14], it was not required to obtain a calculated value of K_d for the fixed gas that agreed with the experimental value. With allowance for properties of local nonequilibrium solutions for the vibrational distribution of molecules, it was assumed that the nonequilibrium rate constant for dissociation in a moving gas can be determined as the product of the exactly calculated nonequilibrium correction for motion and the experimentally determined constant K_d for the gas without motion. As is shown in [10, 14], this assumption results from the fact that for the V reaction model, the magnitude of the correction for motion is determined by solving the equations of level kinetics for vibration energies $E_\alpha^V < Q - O(kT)$, and the quantity K_d in a fixed or weakly nonhomogeneous gas is determined by solution in a much narrower range of energies near the dissociation threshold $Q - O(kT) < E_\alpha^V < Q$. We note that in the first case, the nonequilibrium distribution of molecules in levels is due to molecule transfer in a nonuniform temperature field, whereas in the second case, it is due mainly to “removal” of molecules from the upper levels as a result of to dissociation. In a nonisothermal boundary layer there is diffusion of excited particles toward lower gas temperatures. As a result, in this case, the nonequilibrium distribution is accompanied by a considerable overpopulation of the upper vibrational levels compared to their locally-equilibrium population.

Figure 3 gives corrections for motion $F_d \equiv K_d(\Delta^2 q^2)/K_d(0)$ calculated using various reaction models (solid and dashed curves correspond to $P = 1$ and 10, respectively). In the flow considered, the nonequilibrium distribution of molecules in vibrational levels is characterized, by virtue of (8), by the quantity $\Delta^2 q^2$ [10, 14], where $\Delta^2 \equiv D(\nabla_y \ln T)^2 (Z_\alpha P_1^0 \varepsilon_1)^{-1} \sim \tau^{VT}/\theta \ll 1$ (D is the diffusion constant of unexcited molecules); the numbering of the curves corresponds to Fig. 1. In the calculations, multiquantum vibrational transitions were ignored, and the gas temperature $T = 8000$ K.

From the data presented in Fig. 3 it follows that in calculations using the TV and TRV models, the magnitude of the correction for motion to the reaction rate constant is less significant than that for the V model. In addition, this correction decreases with increase in the parameter P . For example, for the TRV model at $P = 10$, the gas flow has little effect on the dissociation rate, unlike in calculations using the V model. These facts are explained as follows. Under the assumptions made above, the expression on the left side of the equations of level kinetics that defines the effect of diffusive transfer of excited molecules in a nonisothermal boundary layer on the population of vibrational levels Y_α is in inverse proportion to P_α [because of the diffusion constant of excited molecules D_α

[12], which decreases considerably (by an order of magnitude) with increase in the level number] and is directly proportional to the square of the product of ∇T and E_α^V . Nevertheless, for the upper vibrational levels, the value of this expression is maximal. However, for the TV and TRV models, the contribution to the reaction is made by molecules at lower vibrational levels. For such molecules, the relative contribution of diffusion processes to the balance of vibrational populations is smaller. Accordingly, for the TV model and especially for the TRV models, the total effect of the gas flow on the reaction rate is diminished.

The aforesaid is illustrated by the results of calculation of the given distributions $F = Y/Y_0$ presented in Fig. 4 at $T = 8000$ K and above $\Delta^2 = 0$ (solid curves) or $\Delta^2 q^2 = 4$ (dashed curves). The dissociation kinetics was described within the framework of the V reaction model (curves 1), the TV model (curves 2), and the TRV model (curves 3). In the calculations, we considered only single-quantum transitions, except for the V model, for which single- and double-quantum transitions (curves 1a) were also simultaneously taken into account for $\eta = 1$ and $A = 1$. The parameter P was set equal to 10. The curves obtained for the TV and TRV models with allowance for double-quantum transitions are not given in Fig. 4 because they practically coincide with the curves obtained for these models taking into account only single-quantum transitions.

For the three indicated models of dissociation, the decrease in the magnitude of the correction for motion to the reaction rate constant with increase in the parameter P (see Fig. 3) is due to the diminution of the effect of diffusion processes on the vibrational distribution function as a whole. For example, for the TRV model of dissociation, the intermediate and upper levels are considerably depleted compared to the populations of these levels for the V model (see Fig. 4), and, as a result, the effect of motion on the dissociation kinetics practically disappears.

Calculations taking into account double-level (V–T) transitions showed that for $\eta \approx 1$ and $A \approx 1$, the results change insignificantly: double-quantum transitions have an effect only on the populations of several upper levels and practically do not influence the dissociation rate constant calculated within the framework of the TV and TRV models. In the case of the V model, allowance for double-quantum transitions leads to a small increase in values of K_d .

For $\eta \approx 1$ and $A \ll 1$, the calculation results change significantly. In this case, the assumption that the (V–T) transitions are adiabatic breaks down. As a result, $P_{\alpha+2}^\alpha \ll P_{\alpha+1}^\alpha$ [2], and, hence, for $A \ll 1$, the quantity η can only be small.

Conclusions. The analysis of several models for thermal dissociation of diatomic molecules in a nonisothermal boundary layer allows the following conclusions to be drawn.

A calculated value for the dissociation rate constant close to the value measured experimentally and recommended for use can be obtained using the TV and TRV reaction models if the chosen values of the adjusting parameter P are sufficiently large.

Use of the model of double-quantum vibrational–translational transitions, which takes into account the adiabaticity of single-quantum transitions for most of the vibrational spectrum of molecules, does not lead to significant changes in calculated values of the dissociation rate constant and the correction for motion to it.

In calculations of the dissociation rate constant for a fixed or weakly nonhomogeneous gas, the effect of the gas flow is far less significant for the most realistic model than for the previously considered stagewise dissociation mechanism, which presumes only dissociation from the upper vibrational level.

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