DISTURBANCE OF EQUILIBRIUM VELOCITY AND ROTATIONAL
DISTRIBUTIONS OF DISSOCIATING DIATOMIC MOLECULES

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1. Thermal dissociation of diatomic molecules often takes place under conditions when the energy threshold of the reaction — the dissociation energy Q — considerably exceeds the average thermal energy of the particles, of order kT, where k is the Boltzmann constant and T is the gas temperature. In investigations of reaction kinetics one usually uses the "ladder" model, according to which molecules dissociate form upper vibrational levels whose energy E_α (α is the level number) is close in value to Q. According to this model, in flows or nonsteady processes when the condition $\tau_{VT} << \vartheta$ is satisfied (τ_{VT} is the vibrational relaxation time and ϑ is the characteristic time of flow or of the process), a quasisteady distribution of the molecules with respect to E_α, which for $E_\alpha \approx Q$ can differ considerably from an equilibrium Boltzmann distribution, is formed in a gas under the action of the flow of molecules along the vibrational levels caused by the reaction. This, in turn, causes a departure of the reaction rate from the equilibrium value [1].

Motion of the gas, while influencing the populations of vibrational levels (the more so, the higher the energy of the level), is also capable of altering the dissociation rate. As follows from [2, 3], however, for sufficiently low values of the ratio τ_{VT}/ϑ the influence of motion on the reaction kinetics can be neglected. This is just the case considered in the paper. Moreover, it is assumed that the dissociating diatomic molecules comprise a small admixture in a monatomic inert gas.

Kinetic investigations of the above-described dissociation model are usually based on the assumption that the distributions of the molecules by velocities $\xi_{\alpha j}$ and rotational energies E_j (j is the rotational level number) are in equilibrium. The smallness of the times of translational and rotational relaxation, τ_e and τ_{RT}, in comparison with the characteristic reaction time $\tau_C \approx \tau_e \exp (Q/kT)$ serves as an argument [4-6]. For $E_\alpha \approx Q$, however, the probability of dissociation of a molecule in a collision with an atom may be finite, while the dependence of this probability and the probabilities of other inelastic collisions on the velocities and internal energies of the particles may lead to the fact that the development of a flow of molecules along the vibrational levels is accompanied by an increase in the "loss" of molecules from ndividual rotational levels or a decrease in the number of molecules in a certain interval of velocities $\xi_{\alpha j}$. Therefore, smallness of τ_e and τ_{RT} in comparison with τ_C actually is not a criterion of equilibrium of the distributions over $\xi_{\alpha j}$ and E_j of molecules with $E_\alpha \approx Q >> kT$.

The foregoing is confirmed in [7], where the velocity distribution of molecules dissociating from an upper vibrational level is calculated by the Monte Carlo method and its considerable difference from a Maxwellian distribution is determined, as well as the departure of the reaction rate from equilibrium, connected with this difference. The solution was obtained under several assumptions: a Boltzmann distribution was E_α, rotations are not taken into account, and the influence of the reaction products is neglected.

In connection with the above, in the paper we investigate the quasisteady distributions of dissociating molecules over $\xi_{\alpha j}$ and E_j, as well as the influence of a disturbance in the equilibrium character of such distributions on the kinetics of dissociation.

2. Let us obtain the equation of the main approximation for $f_{\alpha j}$ — the distribution function of the dissociating molecules over $\xi_{\alpha j}$, E_j, and E_α. In the spatially uniform case the Boltzmann equation has the form

$$\frac{\partial f_{\alpha j}}{\partial t} = J_{\alpha j} \equiv \frac{1}{\tau_e} \left(J_{\alpha j}^e + R J_{\alpha j}^R + P_\alpha J_{\alpha j}^V + K_\alpha J_{\alpha j}^C \right). \tag{2.1}$$

Here the integrals, normalized to the corresponding frequencies, of elastic and rotationally and vibrationally inelastic collisions of molecules with inert atoms, as well as of collisions leading to reactions, are designated as $J^e_{\alpha j}$, $J^R_{\alpha j}$, $J^V_{\alpha j}$, and $J^C_{\alpha j}$. The values of the probabilities of inelastic collisions characteristic for the ranges of $\xi_{\alpha j}$ and E_j under consideration,

$$|\xi_{\alpha j}| \sim (kT/m)^{1/2}, \quad E_j \sim kT \tag{2.2}$$

are designated as R, P_α, and K_α. In (2.2) and later m is the mass of a molecule.

Integrating (2.1) over $\xi_{\alpha j}$ and summing the result first over j and then over α, we obtain the equations

$$\frac{\partial N_{\alpha j}}{\partial t} = \frac{1}{\tau_e}(R I^R_{\alpha j} + P_\alpha I^V_{\alpha j} + K_\alpha I^C_{\alpha j}), \quad I_{\alpha j} = \int J_{\alpha j} d\xi_{\alpha j}; \tag{2.3}$$

$$\frac{\partial N_\alpha}{\partial t} = \frac{1}{\tau_e}(P_\alpha I^V_\alpha + K_\alpha I^C_\alpha), \quad N_\alpha = \sum_j N_{\alpha j}, \quad I_\alpha = \sum_j I_{\alpha j}; \tag{2.4}$$

$$\frac{\partial N}{\partial t} = \frac{1}{\tau_e}\sum_\alpha K_\alpha I^C_\alpha \equiv NW, \quad W \approx \tau_C^{-1} \tag{2.5}$$

for $N_{\alpha j}$, N_α, and N [$N_{\alpha j}$ is the number density of molecules in the state (αj), N_α is the same for the vibrational level with the energy E_α, and N is the total number density of molecules].

By virtue of the exponential smallness of the populations of upper vibrational levels with energies $E_\alpha \approx Q$, for which $K_\alpha = O(1)$, the characteristic reaction time τ_C for $Q \gg kT$ is exponentially long compared with τ_e. Therefore, the situation when

$$\tau_C \gg \max\left(\tau_e, \tau_e R^{-1}, \tau_e P_\alpha^{-1}\right) \tag{2.6}$$

is realistic.

We note that the time scale τ_C is not present explicitly in Eq. (2.1), it is not determined until the solution, and it enters into the problem through (2.5), i.e., through the moments $f_{\alpha j}$ [8]. Such a situation is possible only for $Q \gg kT$.

Omitting the solution over time intervals of the order of τ_e, $\tau_e R^{-1}$, and $\tau_e P^{-1}$, when the distributions over $\xi_{\alpha j}$, E_j, and E_α are formed, we consider Eq. (2.1) at times $t \approx \tau_C$. We assume that here $f_{\alpha j}$ does not depend explicitly on t but through those moments $f_{\alpha j}$ and distribution functions of other components of the mixture which vary over this time scale. The solution confirms this assumption (also see [1, 2, 9]). In the spatially uniform case N and N_a, the number density of dissociated atoms, are such moments, in accordance with (2.5). As a result, we find

$$\frac{\partial f_{\alpha j}}{\partial t} = \frac{\partial f_{\alpha j}}{\partial N}\frac{\partial N}{\partial t} + \frac{\partial f_{\alpha j}}{\partial N_a}\frac{\partial N_a}{\partial t} \approx \frac{f_{\alpha j}}{\tau_C} \ll J_{\alpha j} \approx \frac{f_{\alpha j}}{\tau_e}, \tag{2.7}$$

$$\frac{\partial N_{\alpha j}}{\partial t} \approx \frac{N_{\alpha j}}{\tau_C}, \quad \frac{\partial N_\alpha}{\partial t} \approx \frac{N_\alpha}{\tau_C}.$$

We note that the equation for $J_{\alpha j}$ = obtained from (2.1) with allowance for (2.7) is solvable only for W = 0, which is at variance with the assumption that the composition of the mixture is not in equilibrium at times $t \approx \tau_C$. The contradiction is connected with the fact that, by virtue of $Q \gg kT$, different sections of the vibrational spectrum make the main contribution to the reaction rate NW and the derivative $\partial N/\partial t$ which, in reality, are comparable with each other in magnitude, despite (2.7).

To remove the contradiction, we transform the system of equations (2.1) as follows. Let $F_{\alpha j}$, B_j, and B_α be equilibrium distributions of the molecules over $\xi_{\alpha j}$, E_j, and E_α, respectively, normalized to unity. Neglecting the interaction of rotations and vibrations, we shall take the internal energy of a molecule in the state (αj) as equal to the sum of E_α and E_j. In this case $B_{\alpha j} = B_\alpha B_j$ can be considered as the equilibrium distribution of the molecules over E_α and E_j.

We multiply both sides of (2.3) by $F_{\alpha j}$ and subtract from (2.1). With the help of B_j and (2.4) we do the same with respect to (2.3), while with the help of B_α and (2.5) we do the same with respect to (2.4). The combination of the resulting equations and (2.5) is equivalent to

(2.1): Each of these equations is a projection of (2.1) onto one of the mutually orthogonal subspaces of the functions $\xi_{\alpha j}$, E_j, and E_α, expanded "about" $F_{\alpha j}B_{\alpha j}$ with respect to orthogonal polynomials of these arguments. Applying the estimates (2.7) to the resulting equations and using (2.6), we write the equations of the main approximation in the form

$$J_{\alpha j}^e + R\left(J_{\alpha j}^R - F_{\alpha j}I_{\alpha j}^R\right) + P_\alpha\left(J_{\alpha j}^V - F_{\alpha j}I_{\alpha j}^V\right) + K_\alpha\left(J_{\alpha j}^C - F_{\alpha j}I_{\alpha j}^C\right) = 0; \tag{2.8}$$

$$RI_{\alpha j}^R + P_\alpha\left(I_{\alpha j}^V - B_j I_\alpha^V\right) + K_\alpha\left(I_{\alpha j}^C - B_j I_\alpha^C\right) = 0; \tag{2.9}$$

$$P_\alpha I_\alpha^V + K_\alpha I_\alpha^C - B_\alpha \sum_\gamma K_\gamma I_\gamma^C = 0; \tag{2.10}$$

$$\frac{\partial N}{\partial t} = \frac{1}{\tau_e}\sum_\gamma K_\gamma I_\gamma^C \equiv NW. \tag{2.11}$$

Equations (2.8)-(2.10) are also valid in the case of spatially nonuniform flows, where the scales of variation of $f_{\alpha j}$ and the macroscopic parameters with time and over the coordinates are tied to the form of the boundary or initial conditions if the scale of variation of the flow is $L \approx \tau_C u$ (u is the velocity of the gas, comparable with the speed of sound). Here the left side of (2.11) has the form $\partial N/\partial t + \nabla N\mathbf{u}$.

One can show that at times $t \approx \tau_C$ or scales $L \approx \tau_C u$ the atomic components of the mixture have a Maxwellian velocity distribution to within $\sim\tau_e/\tau_C$. At the same time, solutions of the system of equations (2.8)-(2.11) for upper vibrational levels can differ strongly from equilibrium distributions owing to the presence of a "sink" or "source" of molecules, finite in intensity, in the reaction. One can ascertain this by substituting equilibrium distributions over $\xi_{\alpha j}$, E_j, and E_α and nonequilibrium values of the concentrations into the system: The system is not satisfied.

3. At first, for simplicity, we neglect the disturbance in the Maxwellian distribution of the dissociating molecules. In this case Eqs. (2.9)-(2.11) can be solved. Assuming that the molecules undergo vibrational transitions only between neighboring levels, we write the first of them in the form

$$Z\left[\sum_q \left(R_{\alpha q}^{\alpha j}Y_{\alpha q} - R_{\alpha j}^{\alpha q}Y_{\alpha j}\right) + \sum_q \left(P_{\alpha-1q}^{\alpha j}Y_{\alpha-1q} + P_{\alpha+1q}^{\alpha j}Y_{\alpha+1q} - P_{\alpha j}^{\alpha-1q}Y_{\alpha j} - P_{\alpha j}^{\alpha+1q}Y_{\alpha j}\right)\right] = B_{\alpha j}W - W_{\alpha j}, \tag{3.1}$$

where $W_{\alpha j}$ is the partial reaction rate, normalized to N, for molecules in the state (αj):

$$W_{\alpha j} = \frac{K_\alpha I_{\alpha j}^C}{\tau_e N} = ZK_{\alpha j}\left(B_{\alpha j}H - Y_{\alpha j}\right), \quad H = \frac{N_a^2}{N}\left(\frac{N}{N_a^2}\right)_{eq}; \tag{3.2}$$

Z is the collision frequency; $Y_{\alpha j} = N_{\alpha j}N^{-1}$; $R_{\alpha j}^{\alpha q}$ is the probability of an R–T transition $(\alpha j \to \alpha q)$; $P_{\alpha j}^{\alpha\pm1q}$ are the probabilities of V–R and V–T transitions $(\alpha j \to (\alpha \pm 1)q)$; $K_{\alpha j}$ is the probability of dissociation of a molecule from the state (αj); the equilibrium value of the ratio N/N_a^2 is designated by the index eq.

Equation (2.10) follows from (3.1) and (3.2) after summation over j:

$$Z\sum_{qj}\left(P_{\alpha-1q}^{\alpha j}Y_{\alpha-1q} + P_{\alpha+1q}^{\alpha j}Y_{\alpha+1q} - P_{\alpha j}^{\alpha-1q}Y_{\alpha j} - P_{\alpha j}^{\alpha+1q}Y_{\alpha j}\right) = -w_\alpha, \quad w_\alpha = W_\alpha - B_\alpha W, \quad W_\alpha = \sum_j W_{\alpha j}. \tag{3.3}$$

The probabilities $R_{\alpha j}^{\alpha q}$ and $P_{\alpha j}^{\alpha\pm1q}$ satisfy the relations

$$R_{\alpha j}^{\alpha q}B_j = R_{\alpha q}^{\alpha j}B_q, \quad P_{\alpha j}^{\alpha\pm1q}B_{\alpha j} = P_{\alpha\pm1q}^{\alpha j}B_{\alpha\pm1q}, \tag{3.4}$$

valid for Maxwellian distribution functions of the colliding partners. On the strength of the linearity of Eqs. (3.1) and (3.3) with respect to $Y_{\alpha j}$, we seek their solution in the form

$$Y_{\alpha j} = B_{\alpha j}(1 + \chi_\alpha + y_{\alpha j}), \quad \sum_j B_j y_{\alpha j} = 0, \quad \sum_\alpha B_\alpha\chi_\alpha = 0; \tag{3.5}$$

with the functions $\varphi_{\alpha j} = y_{\alpha j}(1 + \chi_\alpha)^{-1}$ and χ_α, determining the departures of the distributions over E_j and E_α from equilibrium distributions, not assumed to be small in comparison with unity. Substituting (3.5) into (3.3), using proof by induction we obtain for χ_α the expression

$$\chi_\alpha = \chi_0 + \sum_{\delta=1}^\alpha \frac{1}{ZP_\delta^{\delta-1}B_\delta}\sum_{\gamma=\delta}^\beta w_\gamma + \sum_{\delta=1}^\alpha\sum_{qh}\pi_{\delta h}^{\delta-1q}B_h\left(y_{\delta-1q} - y_{\delta h}\right), \tag{3.6}$$

771

on the basis of which, and with allowance for (3.4) and (3.5), we write Eq. (3.1) as

$$ZB_{\alpha j}\left[\sum_q R_{\alpha j}^{\alpha q}(y_{\alpha q}-y_{\alpha j})+\sum_q P_{\alpha j}^{\alpha-1q}(y_{\alpha-1q}-y_{\alpha j})+\right.$$
$$\left.+\sum_q P_{\alpha j}^{\alpha+1q}(y_{\alpha+1q}-y_{\alpha j})-P_{\alpha j}^{\alpha-1}S_\alpha+P_{\alpha j}^{\alpha+1}S_{\alpha+1}\right]=(\pi_{\alpha j}^{\alpha-1}B_jW_\alpha-W_{\alpha j})+$$
$$+B_j(\pi_{\alpha j}^{\alpha-1}-\pi_{\alpha j}^{\alpha+1})\sum_{\gamma=\alpha+1}^{\beta}W_\gamma+W\left[B_{\alpha j}(1-\pi_{\alpha j}^{\alpha-1})-B_j(\pi_{\alpha j}^{\alpha-1}-\pi_{\alpha j}^{\alpha+1})\sum_{\gamma=\alpha+1}^{\beta}B_\gamma\right]. \tag{3.7}$$

In (3.6) and (3.7) we use the notation

$$P_{\alpha j}^{\alpha\pm1}=\sum_q P_{\alpha j}^{\alpha\pm1q}, \quad P_\alpha^{\alpha\pm1}=\sum_j B_j P_{\alpha j}^{\alpha\pm1}, \quad \pi_{\alpha j}^{\alpha\pm1q}=P_{\alpha j}^{\alpha\pm1q}(P_\alpha^{\alpha\pm1})^{-1}, \tag{3.8}$$
$$\pi_{\alpha j}^{\alpha\pm1}=\sum_q \pi_{\alpha j}^{\alpha\pm1q}, \quad S_\alpha=\sum_{qh}\pi_{\alpha h}^{\alpha-1q}B_h(y_{\alpha-1q}-y_{\alpha h}),$$

β being the number of the variational level with the maximum energy.

By virtue of (3.4), the probabilities $P_{\alpha\bar{j}}^{\alpha\pm1}$ satisfy the equalities $P_{\alpha j}^{\alpha\pm1}B_{\alpha j}=P_{\alpha\pm1}^{\alpha j}B_{\alpha\pm1}$, where $P_{\alpha\pm1}^{\alpha j}=\sum_q P_{\alpha\pm1q}^{\alpha j}B_q$. From this it is seen that $P_{\alpha j}^{\alpha\pm1}=P_\alpha^{\alpha\pm1}$ and $\pi_{\alpha j}^{\alpha\pm1}=1$, if $P_{\underline{\alpha+1}}^{\alpha j}$ depend on E_j in the same way as on B_j. The reverse statement is also valid.

Now let us assume that $K_{\alpha j}=K_\alpha^0\equiv\sum_h B_h K_{\alpha h}$ and $P_{\alpha j}^{\alpha\pm1}=P_\alpha^{\alpha\pm1}$. Then the right side of (3.7) is equal to $B_jW_\alpha-W_{\alpha j}=ZK_\alpha^0 B_{\alpha j}y_{\alpha j}$ for all α, i.e., we obtain a homogeneous system of equations for $y_{\alpha j}$, the form of which does not depend on the degree of nonequilibrium of the flow. Since $y_{\alpha j}\equiv0$ in equilibrium, it follows that this system has only trivial solutions. Thus, we can conclude that the dependence $K_{\alpha j}$ and $P_{\alpha\bar{j}}^{\alpha\pm1}$ on E_j (see Sec. 1) is the direct cause of the disturbance of the equilibrium rotational distribution of the dissociating molecules.

The further advance in the analysis of the properties of the distribution that develops over E_j enables us to assume that the dissociation takes place only from the upper β-th vibrational level. Here $K_{\alpha j}=0$ for $\alpha<\beta$ and $W=W_\beta$. In this case we can obtain the following expressions for $Y_\beta=\sum_j Y_{\beta j}$, $W_{\beta j}$, and W using (3.2), (3.6), and (3.8):

$$MY_\beta=B_\beta[1+B_\beta K_\beta^0 L_p(H-C)+S_*],$$
$$MW_{\beta j}=ZK_{\beta j}B_{\beta j}[(H-1)+B_\beta K_\beta^0 L_p(C-y_{\beta j})-S_*-y_{\beta j}], \tag{3.9}$$
$$MW=ZK_\beta^0 B_\beta[(H-1)-S_*-C],$$

where

$$L_p=L_\beta-l, \quad L_\alpha=\sum_{\delta=1}^{\alpha}(P_\delta^{\delta-1}B_\delta)^{-1}\left(1-\sum_{\gamma=\delta}^{\beta}B_\gamma\right)_, \quad l=\sum_{\varkappa=1}^{\beta}B_\varkappa L_\varkappa,$$
$$M=1+B_\beta K_\beta^0 L_p, \quad C=\sum_j\varkappa_{\beta j}B_jy_{\beta j}, \quad \varkappa_{\beta j}=K_{\beta j}(K_\beta^0)^{-1},$$
$$S_*=S-b, \quad S=\sum_{\delta=1}^{\beta}S_\delta, \quad b=\sum_{\varkappa=1}^{\beta}B_\varkappa\sum_{\delta=1}^{\varkappa}S_\delta.$$

Substituting (3.9) into (3.7), we write the equations for $y_{\alpha j}$ in the form

$$ZB_{\beta j}\left\{M\left[\sum_q R_{\beta j}^{\beta q}(y_{\beta q}-y_{\beta j})+\sum_q P_{\beta j}^{\beta-1q}(y_{\beta-1q}-y_{\beta j})-P_{\beta j}^{\beta-1}S_\beta-K_{\beta j}y_{\beta j}\right]+\right. \tag{3.10}$$
$$\left.+\left[\pi_{\beta j}^{\beta-1}-\varkappa_{\beta j}+B_\beta(1-\pi_{\beta j}^{\beta-1})\right]K_\beta^0 S_*+\left[\pi_{\beta j}^{\beta-1}+K_{\beta j}B_\beta L_p+B_\beta(1-\pi_{\beta j}^{\beta-1})\right]K_\beta^0 C\right\}=$$
$$=ZB_{\beta j}K_\beta^0(H-1)\left[\pi_{\beta j}^{\beta-1}-\varkappa_{\beta j}+B_\beta(1-\pi_{\beta j}^{\beta-1})\right];$$

$$ZB_{\alpha j}M\left[\sum_q R_{\alpha j}^{\alpha q}(y_{\alpha q}-y_{\alpha j})+\sum_q P_{\alpha j}^{\alpha-1q}(y_{\alpha-1q}-y_{\alpha j})+\sum_q P_{\alpha j}^{\alpha+1q}(y_{\alpha+1q}-y_{\alpha j})-P_{\alpha j}^{\alpha-1}S_\alpha+P_{\alpha j}^{\alpha+1}S_{\alpha+1}\right]+ \quad \text{(3.11)}$$

$$+ ZK_\beta^0 B_{\beta j} \left[\left(\pi_{\alpha j}^{\alpha-1} - \pi_{\alpha j}^{\alpha+1} \right) \left(1 - \sum_{\gamma=\alpha+1}^{\beta} B_\gamma \right) + B_\alpha \left(1 - \pi_{\alpha j}^{\alpha-1} \right) \right] (C + S_*) =$$

$$= ZK_\beta^0 B_{\beta j} (H-1) \left[\left(\pi_{\alpha j}^{\alpha-1} - \pi_{\alpha j}^{\alpha+1} \right) \left(1 - \sum_{\gamma=\alpha+1}^{\beta} B_\gamma \right) + B_\alpha \left(1 - \pi_{\alpha j}^{\alpha-1} \right) \right];$$

the parameter α in (3.11) is $\alpha = \beta - 1, \beta - 2, \ldots, 0$. From this it is seen that for $\pi_{\alpha j}^{\alpha \pm 1} = \varkappa_{\beta j} = 1$ we obtain a homogeneous sytem of equations for $y_{\alpha j}$ possessing only a trivial solution. By virtue of $Q \gg kT$, terms proportional to $B_\beta \left(1 - \pi_{\beta j}^{\beta-1} \right)$, $B_\alpha \left(1 - \pi_{\alpha j}^{\alpha-1} \right)$ and $\sum_{\gamma=\alpha+1}^{\beta} B_\gamma$ can be neglected in Eqs. (3.10) and (3.11) for the upper vibrational levels.

As is seen from the structure of the equations, the functions $y_{\alpha j}$ are proportional to $(H - 1)$. Noting this and turning to (3.9) and the definitions of S_* and C, we find that a disturbance of the equilibrium distribution over E_j, just as for that over E_α (see [1]), does not affect the value of the equilibrium constant of the dissociation reaction. Moreover, the ratio between the rates of the forward and reverse chemical processes also remains in equilibrium in a calculation of the partial reaction rate $W_{\beta j}$. However, by virtue of (3.6) and (3.9), a departure of the distribution over E_j from equilibrium leads to a change in the population of the upper vibrational level and, as a consequence, to a change in the dissociation rate constant. To estimate the size of these effects, we consider the properties of the solution for $y_{\alpha j}$.

We can assume that the departure of the distribution over E_j from equilibrium grows with an increase in E_α. First, it is well known that for $E_\alpha \approx kT$ this departure has an exponentially small value $\sim \tau_{RT} \tau_C^{-1} \sim \tau_e (R\tau_C)^{-1}$. At upper levels, however, where $E_\alpha \approx Q \gg kT$, the departure may be finite by virtue of the finite value of the "discrepancy" in Eqs. (3.10) and (3.11) when equilibrium distributions over E_j are substituted into them. Second, the flow of molecules along the vibrational levels caused by the reaction leads to a greater difference from an equilibrium over E_α, the higher the number of the vibrational level under consideration [see (3.6)], since the amount of the flow determined by the reaction is provided by an ever smaller number of molecules. The strong degree of noncompensation of the "appearance" and "disappearance" of molecules with a given energy E_j that develops in this case also, evidently, grows with an increase in E_α. The departure of the distribution over E_j from equilibrium should increase as a result. On the strength of this, we write the estimates

$$\sum_q P_{\alpha j}^{\alpha-1 q} (y_{\alpha-1 q} - y_{\alpha j}) = O (P_\alpha y_\alpha),$$

$$\sum_q P_{\alpha j}^{\alpha+1 q} (y_{\alpha+1 q} - y_{\alpha j}) = O \left(P_\alpha \frac{B_{\alpha+1}}{B_\alpha} y_{\alpha+1} \right),$$

and using them, we represent the solution for $y_{\alpha j}$ in the form

$$y_{\beta j} = (H-1) y_{\beta j}^*, \quad y_{\alpha j} = (H-1) \frac{B_\beta}{B_\alpha} y_{\alpha j}^*, \quad \alpha = \beta - 1, \beta - 2, \ldots, \tag{3.12}$$

where the functions $y_{\beta j}^*$ and $y_{\alpha j}^*$ are close to each other in order of magnitude,

$$y_{\beta j}^* \approx \frac{P_\beta K_\beta}{(P_\beta + K_\beta)(R + P_\beta + K_\beta)}, \quad y_{\alpha j}^* \approx \frac{P_\beta K_\beta}{(P_\beta + K_\beta)(R + P_\alpha)}, \tag{3.13}$$

and depend relatively weakly (in comparison with B_α) on E_α, since $P_\alpha \lesssim R \approx 1$. The expressions (3.12) and (3.13) support the reasoning about the form of disturbance of the distribution over E_j and show that the disturbance can be finite for levels with $E_\alpha \approx Q$ for $R \approx R_\beta \approx K_\beta$. In this case finite corrections go into the population of an upper vibrational level, into the probabilities of V–T transitions and dissociation, and into the macroscopic reaction rate.

If $P_\beta \ll K_\beta$, the values of $y_{\beta j}$ decreases, in accordance with (3.13), since the reaction rate decreases in this case, as well as the flow of molecules over the vibrational levels, connected with it and disturbing the equilibrium distribution over E_α and E_j. Let us consider this case in more detail. Here we can use (3.9), (3.12), and (3.13) to obtain the estimates

$$W \approx ZB_\beta P_\beta (H-1) \left\{ 1 + \left[\frac{P_\beta}{K_\beta}\right]^V + \left[\frac{P_\beta}{R+K_\beta}\right]^R \right\}, \tag{3.14}$$

$$W_{\beta j} \approx ZB_{\beta j} P_\beta (H-1) \left\{ 1 + \left[\frac{K_\beta}{R+K_\beta}\right]^{V,R} + \left[\frac{P_\beta}{K_\beta}\right]^V + \left[\frac{P_\beta}{R+K_\beta}\right]^R \right\},$$

$$1 + \chi_\beta \approx H + (H-1) \left\{ \left[\frac{P_\beta}{K_\beta}\right]^V + \left[\frac{P_\beta}{R+K_\beta}\right]^R \right\},$$

$$\varphi_{\beta j} = \frac{y_{\beta j}}{1+\chi_\beta} \approx \frac{(H-1)}{1+\chi_\beta} \left[\frac{P_\beta}{R+K_\beta}\right]^R.$$

In (3.14) the symbols $[\ldots]^V$ and $[\ldots]^R$ mean that the contribution of the corresponding order is due to the disturbance of the equilibrium distribution over E_α or over E_j. From (3.14) it is seen that in the spatially uniform case with $P_\beta \ll K_\beta$ a finite disturbance of the equilibrium distribution over E_j, $\varphi_{\beta j} \approx K_\beta (R + K_\beta)^{-1}$, is possible only in the initial stage of the reaction, when $H \approx P_\beta / K_\beta$. This disturbance also makes a finite contribution to the population of an upper vibrational level. For $P_\beta / K_\beta \ll H < 1$, when the departure of Y_β from B_β is still large, the functions $\varphi_{\beta j}$ decrease considerably: $\varphi_{\beta j} \approx (H-1) P_\beta [H(R + K_\beta)]^{-1}$. Their contribution to the population of the vibrational level with an energy E_β is also small. We note that the chnages in $W_{\beta j}$ can be finite here, although the changes in

$W = \sum_j W_{\beta j}$ connected with the disturbance of the B_j distribution are small: The finite

corrections vanish in the summation over j.

The approximate calculation of $y_{\alpha j}$ should be based on the properties of these functions defined by (3.12) and (3.13). If the disturbance of B_j takes place with $E_j \approx kT$, then it is appropriate to approximate the dependence of $y_{\alpha j}$ on E_α and E_j using the expansion

$$y_{\alpha j} = (H-1) \frac{B_\beta}{B_\alpha} \sum_{k=0}^{\infty} \sum_{r=1}^{\infty} d^{(k,r)} p_\alpha^{(k)} \Pi_j^{(r)},$$

where $\Pi_j^{(r)}$ are Waldman–Trubenbacher polynomials of E_j; $p_\alpha^{(k)}$ are polynomials introduced through the expressions

$$p_\alpha^{(0)} = 1, \quad p_\alpha^{(1)} = \frac{E_\alpha - \varepsilon_V}{Q}, \quad \sum_{\alpha=0}^{\beta} b_\alpha p_\alpha^{(k)} p_\alpha^{(h)} = 0, \quad k \neq h,$$

$$b_\alpha = \exp\left(\frac{E_\alpha}{kT}\right) \left[\sum_{\gamma=0}^{\beta} \exp\left(\frac{E_\gamma}{kT}\right)\right]^{-1}, \quad \varepsilon_V = \sum_{\alpha=0}^{\beta} E_\alpha b_\alpha \approx Q$$

and possess good convergence for $E_\alpha \approx Q$. In the case when $R \gg P_\beta \approx K_\beta$, the system (3.10), (3.11) in the main approximation breaks up into a series of independent equations,

$$M \sum_q R_{\beta j}^{\beta q} (y_{\beta q} - y_{\beta j}) = (H-1) K_\beta^0 (\pi_{\beta j}^{\beta-1} - \varkappa_{\beta j}), \tag{3.15}$$

$$M \sum_q R_{\alpha j}^{\alpha q} (y_{\alpha q} - y_{\alpha j}) = (H-1) \frac{B_\beta}{B_\alpha} K_\beta^0 (\pi_{\alpha j}^{\alpha-1} - \pi_{\alpha j}^{\alpha+1}),$$

the last of which is written under the assumption that $E_\alpha \gg kT$. In accordance with (3.15), in a first approximation with respect to the polynomials $\Pi_j^{(r)}$ we find

$$y_{\alpha j} \approx (H-1) A_\alpha^{(1)} \Pi_j^{(1)} \frac{B_\beta}{B_\alpha}, \quad \Pi_j^{(1)} = \frac{E_j - E_R}{kT}, \quad E_R = \sum_h B_h E_h, \tag{3.16}$$

$$A_\beta^{(1)} = \frac{K_\beta^0 \sum_j B_j E_j \left(\pi_{\beta j}^{\beta-1} - \varkappa_{\beta j}\right)}{M \sum_{qj} R_{\beta j}^{\beta q} B_j (E_q - E_j)},$$

$$A_\alpha^{(1)} = \frac{K_\beta^0 \sum_j B_j E_j \left(\pi_{\alpha j}^{\alpha-1} - \pi_{\alpha j}^{\alpha+1}\right)}{M \sum_{qj} R_{\alpha j}^{\alpha q} B_j (E_q - E_j)}.$$

4. The solution to the problem of the velocity distribution of the dissociating molecules, or at least an analysis of its general properties like that made in Sec. 3, require cumbersome transformations and calculations in the general case. As an illustration, therefore, we consider a reaction model when the molecules dissociate frm an upper vibrational level, while the cross sections of elastic and inelastic collisions between molecules and inert atoms satisfy the conditions

$$\sigma^e \gg \sigma^R \gg \sigma^C \approx \sigma^V. \tag{4.1}$$

We shall assume that $t \approx \tau_C$ or $L \approx \tau_C u$. By virtue of the smallness of the concentration of molecules, the distribution functions of the atomic components differ from Maxwellian distributions by the exponentially small terms $\sim \tau_e/\tau_C$. We represent the solution for $f_{\alpha j}$ in the form

$$f_{\alpha j} = f_{\alpha j}^{(0)} + \varepsilon f_{\alpha j}^{(1)} + \dots, \; f_{\alpha j}^{(0)} \approx f_{\alpha j}^{(1)}, \; \varepsilon = \tau_e/\tau_C \ll 1,$$
$$f_{\alpha j}^{(0)} = f_{\alpha j}^{eq}(1 + \chi_\alpha + y_{\alpha j} + \Phi_{\alpha j}) = f_{\alpha j 0}\left(1 + \Phi_{\alpha j}^*\right), \; f_{\alpha j 0} = N_{\alpha j} F_{\alpha j},$$
$$\Phi_{\alpha j} = (1 + \chi_\alpha + y_{\alpha j})\Phi_{\alpha j}^*, \; \int f_{\alpha j}^{eq} \Phi_{\alpha j} d\xi_{\alpha j} = 0, \tag{4.2}$$

where $f_{\alpha j}^{(0)}$ is the solution of Eq. (2.8) of the main approximation; $f_{\alpha j}^{eq} = N F_{\alpha j} B_{\alpha j}$; $f_{\alpha j 0}$ is the Maxwellian distribution of molecules in the state (αj); the functions $\Phi_{\alpha j}^*$ characterize the disturbance of $f_{\alpha j 0}$. In connection with its definition, $\Phi_{\alpha j}^*$ are considerably exceed $\Phi_{\alpha j}$ in magnitude, which is connected with the depletion of the population of the upper vibrational levels due to the "sink" of molecules into the reaction. We obtain the solution for $\Phi_{\alpha j}$ for levels with energies $E_\alpha \ll kT$, where the disturbance of $f_{\alpha j 0}$ is greatest.

One can show that for the adopted conditions $y_{\alpha j}$ in the main approximation satisfy Eqs. (3.15), the approximate solution of which is given by Eqs. (3.16). The functions $\Phi_{\alpha j}$ are found from the equations

$$MB_{\alpha j}F_{\alpha j}\int F_0\left(\Phi_{\alpha j}' - \Phi_{\alpha j}\right)d\Gamma_{\alpha j}^e d\xi = B_{\beta j}F_{\alpha j}K_\beta^0(H-1)\Lambda_{\alpha j} - MB_{\alpha j}F_{\alpha j}\sum_q r_{\alpha j}^{\alpha q}(y_{\alpha q} - y_{\alpha j}), \; \alpha = \beta, \; \beta-1, \; \beta-2, \; \dots, \tag{4.3}$$

which, under the condition (4.1), follow from (2.8)-(2.10) after the substitution of the solution in the form (4.2) and the determination, using proof by induction, of the expression for χ_α through W, $y_{\alpha j}$, and $\Phi_{\alpha j}$ (see below), neglecting definitely small terms in the equation. In (4.3) F_0 is the Maxwellian distribution of inert atoms, normalized to unity; $d\Gamma = g d\sigma$; g is the relative velocity; σ is the cross section of the corresponding process in a collision; ξ is the velocity of the inert atoms;

$$\Lambda_{\beta j} = \Pi_{\beta j}^{\beta-1} - X_{\beta j}; \; \Lambda_{\alpha j} = \Pi_{\alpha j}^{\alpha-1} - \Pi_{\alpha j}^{\alpha+1}, \; \alpha < \beta;$$

$$P_\alpha^{\varkappa\pm1}\Pi_{\alpha j}^{\alpha\pm1} = \sum_q \int F_0 d\Gamma_{\alpha j}^{\alpha\pm1q} d\xi; \; r_{\alpha j}^{\alpha q} = \int F_0 d\Gamma_{\alpha j}^{\alpha q} d\xi;$$

$$K_\beta^0 X_{\beta j} = \int F_0 d\Gamma_{\beta j}^C d\xi.$$

The conditions of solvability of (4.3) — orthogonality of the right side of the equation to unity in integration over $\xi_{\alpha j}$ — are satisfied by virtue of (3.15). The uniqueness of the solution is assured by the normalization of $\Phi_{\alpha j}$ [see (4.2)]. The functions $\Phi_{\alpha j}$ equal zero only when the conditions $\Lambda_{\alpha j} = 0$ and $y_{\alpha j} = 0$ are satisfied simultaneously. For $H \neq 1$ the second of them is satisfied if $P_{\alpha j}^{\pm1}$ and $K_{\beta j}$ do not depend on E_j. By its definition, $\Lambda_{\alpha j} = 0$

when $X_{\beta j}$ and $\Pi_{\alpha j}^{\alpha+1}$ do not depend on $\xi_{\alpha j}$ and E_j and hence are identically equal to Z/n. Here and later n is the density of inert atoms. Consequently, in the general case $\Phi_{\alpha j} \neq 0$ and their values are given by the estimates

$$\Phi_{\beta j} \approx (H - 1) K_\beta P_\beta (K_\beta + P_\beta)^{-1}, \quad \Phi_{\alpha j} \approx \Phi_{\beta j} B_\beta B_\alpha^{-1}, \quad \alpha < \beta. \tag{4.4}$$

In a first approximation in Sonine polynomials, for $\Phi_{\alpha j}$ we find

$$\Phi_{\alpha j} = - a_{\alpha j}^{(1)} S_{1/2}^{(1)}(w^2), \quad \mathbf{w} = (\xi_{\alpha j} - \mathbf{u})(m/2kT)^{1/2},$$

$$a_{\alpha j}^{(1)} = (H - 1) B_\beta \left[\dot{A}_\alpha^{(1)} M \sum_q b_{\alpha j}^{\alpha q} (\varepsilon_q - \varepsilon_j) - K_\beta^0 \lambda_{\alpha j} \right] (16 \mu_m M B_\alpha \Omega_{12}^{(11)})^{-1}.$$

Here the integrals $\Omega\binom{11}{12}$ are determined in [10]; $\varepsilon_j = E_j/kT$; $\mu_m = m(m + m_i)^{-1}$; m_i is the mass of an inert atom; the coefficients $A\binom{1}{\alpha}$ are given by the expressions (3.16);

$$\lambda_{\beta j} = \frac{b_{\beta j}^{\beta-1}}{P_\beta^{\beta-1}} - \frac{b_{\beta j}^C}{K_\beta^0}; \quad \lambda_{\alpha j} = \frac{b_{\alpha j}^{\alpha-1}}{P_\alpha^{\alpha-1}} - \frac{b_{\alpha j}^{\alpha+1}}{P_\alpha^{\alpha+1}}, \quad \alpha < \beta;$$

with $b_{\alpha j}^{\alpha \pm 1} = \sum_q b_{\alpha j}^{\alpha \pm 1 q}$. The quantities b are defined as

$$b = \left(\frac{\mu}{2\pi kT} \right)^{3/2} \int \exp \left(-\frac{\mu g^2}{2kT} \right) \frac{\mu g^2}{2kT} d\Gamma dg, \quad \mu = \mu_m m_i.$$

With allowance for $\Phi_{\alpha j} \neq 0$, the expressions (3.6) and (3.9), the first of which must be simplified for the model of a reaction from the level $\alpha = \beta$, are altered as follows: The additional term

$$D_\alpha = \sum_{\delta=1}^{\alpha} n \left(Z P_\delta^{\delta-1} \right)^{-1} \sum_{qh} B_h \int F_{\delta h} F_0 \left(\Phi_{\delta-1 q}' - \Phi_{\delta h} \right) d\Gamma_{\delta h}^{\delta-1 q} d\xi d\xi_{\delta h} \tag{4.5}$$

appears on the right in (3.6), the sum $D_\beta^* = D_\beta - \sum_{\varkappa=1}^{\beta} B_\varkappa D_\varkappa$ and

$$\Delta_\beta = n \left(Z K_\beta^0 \right)^{-1} \sum_h B_h \int F_{\beta h} F_0 \Phi_{\beta h} d\Gamma_{\beta h}^C d\xi d\xi_{\beta h} \tag{4.6}$$

with a minus sign must be added to the expression for W from (3.9) inside the brackets on the right, and

$$1 + K_\beta^0 B_\beta L_p (H - C - \Delta_\beta) + S_* + D_\beta^* \tag{4.7}$$

must appear in the expression for Y_β from (3.9) inside the brackets on the right.

These changes have a general character and are valid, e.g., in the case when all the collisional cross sections are comparable with each other. When the conditions (4.1) are satisfied, the contribution of $y_{\alpha j}$ and $\Phi_{\alpha j}$ to W, Y_β, and χ_α can be neglected. For $K_\beta \approx P_\beta \approx R \approx 1$, when the above solution is invalid and suitable only for estimates, one can show, using (4.4) and the expressions for the W, Y_β, and X_α altered with allowance for (4.5)-(4.7), that the disturbance of $f_{\beta j0}$ is finite here and introduces finite corrections to the reaction rate and the populations of energy levels. Since $\Phi_{\alpha j}$ are proportional to $(H - 1)$, the disturbance does not change the equilibrium dissociation constant. In accordance with (4.4), the value of $\Phi_{\alpha j}$ decreases in proportion to $B_\beta B_\alpha^{-1}$ with a decrease in E_α.

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OPTIMIZATION OF ELECTRODYNAMIC ACCELERATION REGIMES

FOR CYLINDRICAL CONDUCTORS

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At the present time electromagnetic accelerators which use the action of an impulsive electromagnetic field on a current-carrying conductor appear to be promising devices for the study of high-speed collisions. In the regime using separate sources for the accelerating magnetic field and the current in the conductor being accelerated it is possible to bring cylindrical conductors up to velocities exceeding 12 km/sec [1]. Acceleration regimes have been calculated previously [2] assuming independence of the current density in the conductor from the accelerating magnetic field. However, as analysis of transient electromagnetic processes occurring in the interaction of an impulsive electromagnetic field with a cylindrical conductor shows [3], the maximum current density, limited by heating conditions, depends significantly on the induction of the accelerating magnetic field. In the present study we will analyze regimes for electrodynamic acceleration of cylindrical conductors with consideration of diffusion of both the intrinsic and the external impulsive magnetic field within the conductor.

We will use an idealized two-dimensional calculation model in which an infinitely long conductor with axial current i is located in a homogeneous transverse accelerating magnetic field with induction B. We will assume that the current and magnetic field induction vary with time as follows:

$$B = B_0[1 - \exp(-t/T)], \quad i = i_0[1 - \exp(-t/T)]\eta(t - t_0),$$

where $\eta(t - t_0)$ is a unit function [4].

Such current forms can be realized with power supply from high-Q inductive supplies with time constants much greater than the acceleration time [5]. Similar forms can be obtained from capacitive supplies with active load switching [6]. Introduction of a delay time t_0 permits more complete use of the magnetic field induction, which, as will be shown below, allows attaining additional velocity in some cases.