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Abstract

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E. E. NIKITIN

ON THE CALCULATION OF THE RATE OF DECOMPOSITION OF DIATOMIC MOLECULES

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In work (1) the rate constant of thermal decomposition of diatomic molecules and the distribution function over vibrational states under violation of the equilibrium thermal distribution were calculated. An essential point in this was the assumption that the vibrational quanta remain approximately constant right up to the dissociation boundary. In the present work the rate constant of the reaction AB + C → A + B + C is calculated without this restriction.

Let us suppose that upon collision in a diatomic molecule a transition occurs only between neighboring vibrational levels, and that dissociation of the molecule is possible only from the last discrete level (1). Let $P_{k,k-1}$ denote the probability of transition from level k to level $k-1$ in one collision, and P_∞ the probability of transition from the last, n-th, discrete level to a state with a continuous energy spectrum. Let us further suppose that the Maxwellian distribution of the colliding molecules is preserved. This assumption is also justified quite accurately when the dissociation energy is greater than $\bar{k}T$ (the percentage correction to the reaction rate when the violation of the Maxwellian distribution is taken into account is of order $\bar{k}T/25D$ (2)). In this case the probability of vibrational excitation of a molecule in a collision with a transition from level $k-1$ to level k is related to $P_{k,k-1}$ by the relation

$$P_{k-1,k} = P_{k,k-1} \exp\left(-\frac{E_{k,k-1}}{\bar{k}T}\right) \equiv \alpha_k P_{k,k-1}, \tag{1}$$

which follows from the principle of detailed balance. In this expression $E_{k,k-1}$ denotes the energy difference between levels k and $k-1$.

If $x_k(t)$ denotes the distribution function, i.e., the probability of finding the molecule at the k-th level, then its change with time is described by the following system of equations:

$$\left\{ \frac{dx_k}{dt} = Z\{\alpha_k P_{k,k-1} x_{k-1} - (P_{k,k-1} + \alpha_{k+1} P_{k+1,k}) x_k + P_{k+1,k} x_{k+1}\}; \right. \tag{2}$$

$$k = 0, 1, \dots, n,$$

with boundary conditions $x_{-1} = x_{n+1} = 0$, meaning that the vibrational spectrum of the molecule contains $n + 1$ levels. In the system of equations (2), Z denotes the number of collisions of AB and C in 1 sec., and the notation $P_\infty = P_{n,n+1}\alpha_{n+1}$ has been introduced.

The general solution of the system has the form

$$x_k(t) = \sum_{m=0}^{n} A_k(\mu_m) \exp(-\mu_m t), \tag{3}$$

where μ_m are the eigenvalues of the matrix $\hat{B}$ of the right-hand side of the system (m numbers these eigenvalues in order of increasing μ).

If $P_{n,n+1} = 0$, then for the corresponding matrix $\hat{B}^{(0)}$ the eigenvalues form a sequence $\mu_n^{(0)}$. The first eigenvalue $\mu_0^{(0)} = 0$ then corresponds to the thermal equilibrium distribution.

If $P_{n,n+1} \neq 0$, then, in accordance with the general theory of local perturbations ([3]), all μ_m are shifted relative to $\mu_m^{(0)}$ in one direction, namely $\mu_m > \mu_m^{(0)}$ for $P_{n,n+1} > 0$. If $\mu_0 \ll \mu_1$, then for $t \gg 1/\mu_1$ it follows from (3) that the distribution function decays exponentially, which corresponds to decomposition. An estimate shows that the condition $\mu_0 \ll \mu_1$ is satisfied for most reactions (for example, at $T = 1000^\circ$, $D = 100$ kcal/mole, $\mu_0 \sim \mu_1 \cdot 10^{-8}$). Under this same condition the lowest eigenvalue of the matrix can be found by expanding its determinant $D(\hat{B} - \mu\hat{I})$ at zero in powers of μ and retaining only the linear term.

The calculation gives

$$\mu_0 = Z \Bigg/ \left[\sum_{j=0}^{n} \exp\left(-\frac{E_j}{kT}\right) \sum_{s=j}^{n+1} \exp\left(\frac{E_s}{kT}\right) \Big/ P_{s,s-1} \right], \tag{4}$$

where the summation is over all discrete levels. In expression (4) the second sum in brackets depends only weakly on the lower limit of summation, since the terms increase strongly with increasing number s. Therefore it may be taken outside the summation sign over j, and the lower summation limit may be replaced by unity. The sum over j is then simply equal to the vibrational sum of states Q. Taking into account that the equilibrium distribution function is determined by the formula

$$x_k^{(0)} = \exp\left(-\frac{E_k}{kT}\right) \Big/ Q,$$

expression (4) can be rewritten in the more transparent form:

$$\mu_0 = Z \Big/ \left[\frac{1}{x_n^{(0)} P_\infty} + \sum_{k=1}^{n} \frac{1}{x_k^{(0)} P_{k,k-1}} \right]. \tag{5}$$

To calculate μ_0, note that usually the relation $x_n^{(0)} P_\infty \gg x_k^{(0)} P_{k,k-1}$ is fulfilled. In this case only the second term remains in (5)—the sum over transitions in the discrete spectrum. If one takes into account that near the dissociation threshold $E_{k,k-1} < kT$, and $P_{k,k-1}$ depends only weakly on E_k for small quanta, then the summation may be replaced by integration, and $P_{k,k-1}$ may be taken out from under the integral sign at the point $E = D$:

$$\sum_{k=1}^{n} \frac{1}{x_k^{(0)} P_{k,k-1}} \simeq \frac{1}{\mathcal{E}} \int_0^D \frac{dE}{x(E)P(E)} \simeq \frac{kT}{\mathcal{E} P(D)} \exp\left(\frac{D}{kT}\right) Q. \tag{6}$$

Here $\mathcal{E}$ denotes a certain mean quantum near the dissociation threshold.

After these transformations formula (5) takes the form:

$$\mu_0 = Z \left(\frac{\mathcal{E}}{D}\right) \left(\frac{D}{kT}\right) P(D) \exp\left(-\frac{D}{kT}\right) \Big/ Q. \tag{7}$$

Transitions between non-neighboring levels can be approximately taken into account if the quantity μ_0, determined by formula (7), is summed over all "parallel paths" of decomposition. In this case $\mathcal{E} P(D)$ in (7) should be replaced by $\sum_n \mathcal{E}_n P_n(D)$, where the index n corresponds to transitions to a neighboring level through 1, 2, etc. levels. The probability $P_n(D)$ depends only weakly on the transferred energy $\mathcal{E}_n$ when the collision time τ is small compared with the characteristic transition time $\hbar/\mathcal{E}_n$. If, however, τ is large compared with $\hbar/\mathcal{E}_n$, then $P_n(D)$ decreases rapidly (exponentially) with increasing $\mathcal{E}_n$ (adiabatic collisions ([4])). The minimal value $\mathcal{E}_N$ for which $P_n(D)$

begins to decrease sharply, can be found from the condition

$$\mathcal{E}_N \tau / \hbar \sim 1. \tag{8}$$

The collision time τ is determined by the expression $\tau = \rho/v$, where ρ is the radius of action of the short-range (exchange) forces, and v is the mean relative velocity of the colliding molecules. As follows from experiments on ultrasonic dispersion, the quantity ρ is approximately the same for all molecules and is equal to 0.2–0.3 Å.

Taking into account the normalization condition $\sum_n P_n = 1$ and the fact that $P_n(D)$ depends only weakly on $\mathcal{E}_n$ for $\mathcal{E}_n < \mathcal{E}_N$, we obtain

$$\sum_n \mathcal{E}_n P_n(D) \approx \frac{\mathcal{E}_N}{2} \sim \frac{\hbar}{\rho}\sqrt{\frac{2\bar{k}T}{\pi m}}.$$

Here m is the reduced mass of the colliding molecules.

Thus, taking nonadiabatic transitions into account, formula (7) takes the form

$$\mu_0 \sim Z\,\frac{\hbar}{\rho}\sqrt{\frac{4}{\pi m D}}\left(\frac{D}{\bar{k}T}\right)^{1/2}\exp\left(-\frac{D}{\bar{k}T}\right)/Q. \tag{9}$$

The dissociation rate constant k is equal in magnitude to μ_0, averaged over the rotational states of the molecule AB:

$$k = \int \mu_0(D_{\text{eff}})\exp\left(-\frac{E_{\text{rot}}}{\bar{k}T}\right)\frac{dE_{\text{rot}}}{\bar{k}T}. \tag{10}$$

Here $D_{\text{eff}} = D - \lambda E_{\text{rot}}$, and the factor λ depends in a complicated way on E_{rot} and lies in the interval $0 < \lambda < 1$. The decrease in the effective dissociation energy arises due to centrifugal forces and can be calculated for each particular case.

Since, in deriving formula (7), the internal degrees of freedom of molecule C were not taken into account, it is applicable to the case of collisions of diatomic molecules AB with an atom. An example of such a reaction is the dissociation of bromine: $Br_2 + Ar \to Br + Br + Ar$,* studied over a broad temperature interval (300–2000°K) ([5]). The experimental dissociation rate constant is

$$k = 6\cdot 10^{-2} Z_0\left(\frac{D}{\bar{k}T}\right)^{1.97}\exp\left(-\frac{D}{\bar{k}T}\right), \tag{11}$$

where Z_0 is the gas-kinetic number of collisions. This formula is valid when k changes by a factor of 10^{27}; therefore the temperature dependence of the preexponential factor may be regarded as established.

A numerical calculation of D_{eff} for Br_2 shows that for $E_{\text{rot}} < D$ the factor λ depends only weakly on E_{rot} and is approximately 0.9. Integration of (10) then gives $k \approx 10\mu_0(D)$. To estimate μ_0 in accordance with (9), we note that in the temperature interval 300–2000°K one may put $Q \approx \bar{k}T/\hbar\omega$. Taking into account that the number of collisions Z for a vibrationally excited molecule may exceed the gas-kinetic number of collisions by a factor of 3–4, and that there are two electronic states ($^1\Sigma_g^+$ and $^3\Pi_{1u}$) that converge–

* The calculation of the dissociation rate of Br_2 was carried out by Rice ([6]). The author did not take into account the disturbance of the equilibrium distribution and rotation, and associated the increased preexponential factor with a larger

statistical weight of the energy region of order kT near the dissociation limit. When the disturbance of the equilibrium distribution is taken into account, as is evident, for example, from (5), the greater density of levels near the dissociation threshold cannot increase the dissociation rate constant. An analogous problem was solved by Carey ([7]), who, however, without justification assumed a transition from the lower vibrational levels into the region of the continuous energy spectrum.

pertaining to one and the same dissociation energy D, the estimate of the decay rate constant in accordance with (9) leads to the expression:

$$k \sim 5 \cdot 10^{-2} Z_0 \left(\frac{D}{kT}\right)^{1.5} \exp\left(-\frac{D}{kT}\right). \quad (12)$$

Thus, the calculated and experimental values of the decay rate constants agree in order of magnitude (the quantity $(D/kT)^{1/2}$ varies within the limits 3–7 in the temperature interval studied).

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Institute of Chemical Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.