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Abstract

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THE VIBRATIONAL DISTRIBUTION FUNCTION OF POLYATOMIC MOLECULES IN UNIMOLECULAR DECOMPOSITION

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It is known that the thermal decomposition of polyatomic molecules proceeds according to a unimolecular law at high pressures and according to a bimolecular law at low pressures, the transition from the unimolecular law to the bimolecular one being associated with a violation of the Boltzmann distribution over the vibrational states of the decomposing molecule near the dissociation boundary (see, for example, (^{1})). The disturbance of the equilibrium distribution in bimolecular decomposition has been studied in a number of works (^{2}-^{6}) on the basis of a stochastic model. In unimolecular decomposition, the disturbance of the equilibrium distribution near the dissociation limit is small and does not affect the rate of decomposition. However, in this case the disturbance of equilibrium in the region of energies exceeding the dissociation energy E_0 may be important for possible secondary reactions. In particular, this is possible when the molecule AB decomposes by two different pathways

$$\mathrm{AB + M \rightarrow A + B + M;} \tag{1}$$

$$\mathrm{AB + M \rightarrow A' + B' + M,} \tag{2}$$

where decomposition (2), proceeding with the larger dissociation energy, leads to the formation of active particles whose secondary reactions determine the rate of some process (for example, chain development). In this case reaction (1), leading to a decrease in the population of vibrational levels at $E > E_0$, reduces the rate of reaction (2). In qualitative form this circumstance was noted by A. E. Shilov (^{7}) in studying the thermal decomposition of ethyl bromide. The primary reactions are the reactions of unimolecular decomposition

$$\mathrm{C_2H_5Br \rightarrow HBr + C_2H_4}, \qquad E_0 \approx 53\ \text{kcal/mol}; \tag{1a}$$

$$\mathrm{C_2H_5Br \rightarrow Br + C_2H_5}, \qquad E_0 \approx 65\ \text{kcal/mol}, \tag{2a}$$

of which the second can lead to chain decomposition according to the scheme

$$\mathrm{Br} + \mathrm{C_2H_5Br} \to \mathrm{C_2H_4Br} + \mathrm{HBr};$$

$$\mathrm{C_2H_4Br} \to \mathrm{C_2H_4} + \mathrm{Br}.$$

It turned out that in the case where, in accordance with the general theory of chain reactions, process (2a) should have led to an increase in the decomposition rate, this does not occur. However, the additional introduction of bromine atoms into the volume increases the decomposition rate, which confirms the mechanism given above. In this work the disturbance of the equilibrium distribution in the region $E > E_0$ in the unimolecular decomposition of polyatomic molecules is investigated.

The nonequilibrium distribution function must be determined from the solution of the kinetic equation describing vibrational relaxation and decomposition, the decomposition rate being determined by the lowest eigenvalue μ_0 of the stochastic matrix ([2]-[6]). Since in the case of polyatomic-

molecules undergo substantially multiquantum vibrational excitation, the kinetic equation can be written in the form of the integral equation

$$\frac{\partial x(\varepsilon)}{\partial t} = \int K(\varepsilon, \varepsilon')\, d\varepsilon' - Z^* x(\varepsilon) - k(\varepsilon) x(\varepsilon), \tag{3}$$

in which $x(\varepsilon)$ denotes the distribution function, depending on the dimensionless energy $\varepsilon = E/kT$; Z^* is the number of AB and M collisions effective in vibrational relaxation; $k(\varepsilon)$ is the differential rate of decomposition; the kernel $K(\varepsilon, \varepsilon')$ describes vibrational relaxation, with $\int K(\varepsilon, \varepsilon') d\varepsilon' = Z^*$ ([5]). Equation (3) can usually ([8]) be reduced to the diffusion equation

$$\frac{\partial x}{\partial t} = D \frac{\partial}{\partial \varepsilon} \left[\frac{\partial x}{\partial \varepsilon} + f'(\varepsilon) x \right] - k(\varepsilon) x, \tag{4}$$

which, for $k = 0$, is satisfied by the equilibrium distribution function $x_0(\varepsilon) = \exp[-f(\varepsilon)]$. In this equation D has the meaning of the mean square energy transferred to the decomposing molecules per unit time, $D = Z\overline{\xi^2}$ (Z is the gas-kinetic number of AB and M collisions). In what follows we shall regard D as a constant quantity, although in fact it is only necessary that D depend on ε more weakly than k. The lowest eigenvalue μ_0 of the operator on the right-hand side of equation (4) can be found by the variational method

$$\mu_0 = \min \left\{ \frac{\int \exp(-f) \left[D(\partial\psi/\partial\varepsilon)^2 + k\psi^2(\varepsilon) \right] \, d\varepsilon}{\int \exp(-f) \psi^2(\varepsilon) \, d\varepsilon} \right\}, \tag{5}$$

where ψ is the varied function for which the normalization integral in the denominator exists.

As a model of the decomposing molecule we take the Kassel model (^{1})—a system of $s+1$ harmonic oscillators, for which $f(\varepsilon) = \varepsilon - s\ln\varepsilon$; in this case $k(\varepsilon) = \nu(1-\varepsilon_0/\varepsilon)^s$, where $\varepsilon_0 = E_0/kT$ and $\nu \approx 10^{13}$ sec^{-1} is a quantity of the order of the frequency of molecular vibrations. In what follows we shall measure Z in units of ν, so that we set $\nu = 1$. With the aid of simple variational functions, one of which is identically equal to a constant and the second has the form of a step, it is not difficult to obtain from (5)

$$\mu_0 = \min \begin{cases} D\,\dfrac{\varepsilon_0^s}{s!}\exp(-\varepsilon_0), \\ \exp(-\varepsilon_0). \end{cases} \tag{6a}$$

(6b)

i.e., expressions for the rates of bimolecular (6a) and monomolecular (6b) decomposition, with the transition region between them determined by the condition $D\varepsilon_0^s/s! \simeq 1$. The nonequilibrium distribution function satisfies the equation

$$-\mu_0 x = D\left(x' + f'x\right)' - kx. \tag{7}$$

The solution of this equation is not difficult to obtain in the case $\varepsilon_0 \gg s$, which is of greatest interest from the experimental point of view (large activation energy and a molecule that is not too complex). This condition coincides with the condition of applicability of the Kassel formula for the decomposition rate.

Let us first consider the case of high pressures, i.e. $D \sim 1$. Substituting in (7) $x = y\exp(-f/2)$, we obtain

$$y'' - U(\varepsilon)y = 0, \qquad U(\varepsilon) = \left[\frac{(f')^2}{4} + \frac{k-\mu_0}{D}\right], \tag{8}$$

where in $U(\varepsilon)$ we have neglected f'' in comparison with $(f')^2$, using the inequality $\varepsilon_0/s \gg 1$. The approximate solution of (8), taking into account the small correction

at f'' has the form

$$y = \frac{\text{const}}{U^{1/4}}\exp\left(-\int\sqrt{U}\,d\varepsilon\right) \tag{9}$$

provided the inequality $U'/U^{3/2} \equiv \chi \ll 1$ is satisfied. It is not difficult to verify that the condition $D \sim 1$ satisfies this inequality. Moreover, it is easy to show that, in integrating in (9), μ_0 may be neglected.

Thus, for the distribution function one obtains the expression

$$x(\varepsilon) = \begin{cases} \exp[-f], & \varepsilon \ll \varepsilon_0; \\ \sqrt[4]{\dfrac{(f_0')^2}{(f')^2 + 4k/D}} \exp\left[-\dfrac{f}{2} - \displaystyle\int_0^{\varepsilon} \sqrt{\dfrac{(f')^2}{4} + \dfrac{k}{D}}\, d\varepsilon\right], & \varepsilon \gg \varepsilon_0, \end{cases} \tag{10}$$

which, for sufficiently large D, has the form

$$x(\varepsilon) = \exp(-f) \exp\left[-\frac{1}{D}\int_{\varepsilon_0}^{\varepsilon} \frac{k}{f'}\, d\varepsilon\right], \quad \varepsilon \gg \varepsilon_0. \tag{11}$$

Here and below the notation $f(\varepsilon_0) = f_0,\ f'(\varepsilon_0) = f_0'$ is introduced.

It follows from (10) and (11) that, as a result of monomolecular decay at pressures far from the pressures of the transition region, the vibrational population at $E > E_0$ decreases in comparison with the equilibrium one. This relative decrease ρ of the equilibrium population is determined by the second factor in (11), which for $E - E_0 = \Delta E \ll E_0$ can be rewritten in the usual variables in the form

$$\rho = \exp\left[-\frac{\nu}{Z}\left(\frac{\Delta E}{E_0}\right)^s \frac{\Delta E \cdot kT}{(s+1)\,\mathcal{E}^2}\right]. \tag{12}$$

In the case of low pressures the approximation (9) is invalid, since the condition $\chi \ll 1$ is not satisfied for energies close to the threshold. Therefore it is necessary to match the exact solution of equation (4) in the region of small $\Delta\varepsilon = \varepsilon - \varepsilon_0$,

$$y'' - \left[\frac{(f_0')^2}{4} + \frac{1}{D}\left(\frac{\Delta\varepsilon}{\varepsilon_0}\right)^s\right] y = 0 \tag{13}$$

with the asymptotic solution (9). Equation (13) can be solved exactly by the Laplace transform method; however, investigation of the general case is rather complicated. Taking into account the low-pressure condition $D \ll 1$, one may replace (13) by a simpler equation, whose solution satisfying the necessary boundary conditions at infinity is expressed in terms of the Bessel function:

$$y'' - \frac{1}{D}\left(\frac{\Delta\varepsilon}{\varepsilon_0}\right)^s y = 0, \quad y(\Delta\varepsilon) = C\sqrt{\Delta\varepsilon}\, K_{\frac{1}{s+2}}\left(\frac{2\Delta\varepsilon^{(s+2)/2}}{(s+2)\sqrt{D}\,\varepsilon_0^{s/2}}\right). \tag{14}$$

The solution (14) approximately satisfies equation (13) in the region $(f_0')^2/4 \ll (\Delta\varepsilon/\varepsilon_0)^s/D$. The region $\delta\varepsilon$, in which the exact and approximate solutions differ substantially, is determined by the condition

$$\delta\varepsilon \sim \varepsilon_0 (D/4)^{1/s}, \tag{15}$$

so that integration of equation (13) over the region $0 < \Delta\varepsilon < \delta\varepsilon$ with the initial condition $y(0) = \exp(-f_0/2)$ leads to a factor of order

$$\exp\left[-\frac{\varepsilon_0}{2}(D/4)^{1/s}\right].$$

Then extrapolation of the solution (14) to $\Delta\varepsilon = 0$ and matching with the equilibrium distribution function, taking the transition region $\delta\varepsilon$ into account, leads to the expression

$$x(\varepsilon) = \exp[-f/2] \cdot \sqrt{\frac{2}{\pi}} \sin\frac{\pi}{s+2} \left[(s+2)\sqrt{D}\,\varepsilon_0^{s/2}\right]^{1/(s+2)} \times$$

$$\times \exp\left[-\frac{\varepsilon_0}{2}(D/4)^{1/s}\right] K_{\frac{1}{s+2}}\left(\frac{2\Delta\varepsilon^{(s+2)/2}}{(s+2)\sqrt{D}\,\varepsilon_0^{s/2}}\right). \tag{16}$$

Calculation, on the basis of this formula, of the relative decrease in population in the transition region $D\varepsilon_0^s/s! \approx 1$ gives, after applying the asymptotic expansion of the Bessel function,

$$\rho \approx \frac{\sqrt{2\pi}\,e}{s^2} \exp\left[-\frac{s}{e}\right] \exp\left\{-\frac{2}{(s+2)\sqrt{s!}}\left(\frac{\Delta E}{kT}\right)^{s/2+1} + \frac{\Delta E}{2kT}\right\}. \tag{17}$$

Expression (17) coincides, up to a constant factor, with formula (10), in which the integration should be carried out under the assumption $(f')^2/4 \ll k/D$ for small ε. This corresponds to the condition of smooth matching of the solutions in the two regions. The appearance in (17) of an additional pre-exponential factor less than unity is quite natural, since the transition from high pressures ($D \approx 1$) to low pressures ($D\varepsilon_0^s/s! \approx 1$) increases the disturbance of the equilibrium distribution. It should be noted, however, that in many cases the factor $\frac{\sqrt{2\pi}\,e}{s^2}\exp[-s/e]$ is not essential for a qualitative estimate, so that in practice the asymptotic solution (10) may be used despite the failure of the inequality $\chi \ll 1$.

At pressures below the transition region, a qualitative estimate in accordance with (10), taking into account $\mu_0 = D\varepsilon_0^s/s! \exp(-\varepsilon_0)$, shows that the distribution function begins to decrease sharply in the immediate vicinity of the threshold ε_0, which also determines the bimolecular kinetics of the decomposition.

Thus, the decomposition rate constant (2) may be estimated on the basis of formulas (6a) or (6b), into which the factor ρ, accounting for the disturbance of the equilibrium distribution, should be introduced. In this case the decomposition rate (2) turns out to depend exponentially on the number of collisions, which cannot be conveyed within the framework of the formal kinetics of a two-stage process (1) and (2). In the calculation given above, the insufficiently well-defined parameter is the transferred mean-square energy $\overline{\mathcal{E}}^2$. From the foregoing it is clear that the quantity $\overline{\mathcal{E}}^2$ must be referred to vibrationally excited AB molecules with energy E near the threshold E_0. Since, in collisions of AB and M, multiquantum transitions occur predominantly (which fundamentally distinguishes the dissociation process of polyatomic and diatomic molecules), one may approximately put $\overline{\mathcal{E}}^2 \approx (kT)^2$.

It should be noted that a nonequilibrium distribution function of the type considered here may be important for calculating the spectrum of stabilized fluorescence [9]. The vibrational distribution function in the excited electronic state must be described by an inhomogeneous equation analogous to (8). The function $k(\varepsilon)$ in this case has the meaning of the probability of a radiationless transition; the fact that a substantial dependence of the fluorescence intensity on the stabilizing additive is observed experimentally indicates a strong dependence of k on ε near some threshold, i.e., just as in the case of the dependence of the decomposition cross section on energy. The nonequilibrium distribution function should in principle influence the shape of the high-frequency wing of the stabilized-fluorescence band.

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