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Abstract

Full Text

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On Deviations from the Boltzmann Distribution in the Dissociation of Diatomic Molecules

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The rate of dissociation of diatomic molecules in the reaction $AB \rightarrow A + B$ in binary collisions is determined by the probability of transition of the molecule AB from a bound vibrational state into the region of states with a continuous spectrum and by the distribution function with respect to vibrational energy. In the case when the transition probability in the discrete spectrum is less than the probability of dissociation from the upper levels into the continuum, one should expect deviations of the distribution from the Boltzmann distribution. In order to clarify the influence of the violation of the Boltzmann distribution on the rate of dissociation, let us make the following simplifying assumptions.

Suppose that diatomic molecules AB capable of dissociation are placed in a heat bath consisting of molecules C, and that the concentration of AB molecules is much smaller than the concentration of C molecules. Then collisions of AB with one another may be neglected. As a result of collisions between AB and C, the AB molecules will begin to dissociate, but, owing to the small concentration of AB, the equilibrium distribution of C will be maintained with high accuracy.

Suppose further that the probability of an inelastic collision of AB and C with transition of the molecule AB from quantum state n to state n' is proportional to the square of the matrix element of the vibrational coordinate of the AB molecule for the corresponding transition. This is valid in the case when the amplitude of vibrations of AB is smaller than the range of action of the intermolecular forces ([1]), and also when the amplitude of vibrations is small in comparison with $(\Delta k)^{-1}$, where Δk denotes the change in the wave vector $\mathbf{k}$ of the relative motion of AB and C in an inelastic collision ([2]).

As a model of a diatomic molecule, consider a quantum system having $n_0 + 1$ discrete, approximately equidistant levels of negative energy and a continuous spectrum of positive energy. The wave functions of the discrete spectrum of the corresponding potential well are, strictly speaking, different from the wave functions of the harmonic oscillator. However, the transition probabilities may, with sufficient accuracy, be taken to be the same as for the harmonic oscillator. This follows from the fact that even for a Morse oscillator with greater anharmonicity the matrix elements for transitions between neighboring levels differ little from the corresponding matrix elements of the harmonic oscillator, while the matrix elements for transitions between non-neighboring levels are considerably smaller than for transitions to a neighboring level ([3]). As for transitions

from the discrete to the continuous spectrum, for the Morse potential calculation shows that the matrix element of the coordinate decreases strongly with increasing transition energy; therefore one may assume that transition to the continuous spectrum occurs only from the upper level. Thus, the relaxation and dissociation of a system of oscillators placed in a heat reservoir is characterized by the probabilities

transition to the neighboring level $P_{n,n+1} = P_{01}(n+1)$ ([1]) at each collision and the probability of dissociation from the last level P_∞.

If $x_n(t)$ denotes the distribution function, i.e., the probability of finding an AB molecule on the n-th level, then the dependence of x_n on time is determined by the following system of equations, in which it is taken into account that the probabilities of activation and deactivation are related by the ratio $P_{n,n+1}/P_{n+1,n} = \exp(-\hbar\omega/kT) = \alpha$:

$$\begin{gathered} dx_n/dt = ZP_{10}\{\alpha n x_{n-1} - [n + (n+1)\alpha]x_n + (n+1)x_{n+1}\}, \\ n = 0, 1, 2, \ldots, n_0 - 1, \\ dx_{n_0}/dt = ZP_{10}\{\alpha n_0 x_{n_0-1} - n_0 x_{n_0}\} - ZP_\infty x_{n_0}. \end{gathered} \tag{1}$$

Here Z denotes the number of collisions of the molecules AB and C per second under the condition that $N_C = 1$ cm^{-3}. For $n_0 \to \infty$ this system becomes the system of equations for a harmonic oscillator that was considered in work ([4]).

We shall seek the solution of system (1) in the form of a superposition of terms $x_n = l_n(\mu)\exp(ZP_{10}\mu t)$. Then the coefficients μ are determined as the eigenvalues of the matrix of system (1). We denote these eigenvalues, in the order of increasing absolute value, by $\mu^{(0)}, \mu^{(1)}, \mu^{(2)}, \ldots$. They determine the rates of the relaxation process and of dissociation. The decomposition rate constant is determined by the equality

$$k = -\left(\frac{d}{dt}\sum_{n=0}^{n_0} x_n(t)\right) \Big/ \sum_{n=0}^{n_0} x_n(t) \tag{2}$$

and, generally speaking, depends on time, but for $t \gg |ZP_{10}\mu^{(1)}|^{-1} = t_0$ tends to the constant limiting value

$$k = -ZP_{10}\mu^{(0)}. \tag{3}$$

The eigenvalues and eigenvectors of the matrix $\hat{B}$ of the system of equations (1) can be found by using the theory of degenerate regular perturbations of I. M. Lifshitz ([5]). In doing so, small modifications are necessary, connected with the fact that the matrix of the zeroth approximation B^0 is not Hermitian. As B^0 we shall choose the matrix of the system of equations (1) for $n \to \infty$. Its eigenvalues and eigenvectors are given by the formulas ([4])

$$\begin{aligned} \mu_0^{(m)} &= (\alpha-1)m, \qquad m = 0, 1, 2, \ldots; \\ l_k^0(\mu_0^{(m)}) &= \alpha^{m/2}\sqrt{1-\alpha}\, F(-k, m+1, 1, 1-\alpha); \end{aligned} \tag{4}$$

$F(a, b, c, z)$ denotes the hypergeometric function. The vectors $l_k^0(\mu_0)$ are orthonormal with weight α^{-k}, i.e.,

$$\sum_{n=0}^{\infty} l_n^0(\mu_0)\alpha^{-n} l_n^0(\mu_0') = \delta_{\mu,\mu_0'}. \tag{5}$$

The perturbation matrix $\hat{\Lambda} = \hat{B} - \hat{B}^0$ must remove the transitions between the levels n_0 and $n_0 + 1$ and introduce the dissociation probability P_∞ from the level n_0. Its nonzero elements are as follows:

$$\Lambda_{n,n_0} = -P_\infty/P_{10} + \alpha(n_0+1), \qquad \Lambda_{n_0,n_0+1} = -(n_0+1),$$

$$\Lambda_{n_0+1,n_0} = -\alpha(n_0+1), \qquad \Lambda_{n_0+1,n_0+1} = (n_0+1).$$

To solve the system of equations

$$\sum_k (B_{ik} - \mu\delta_{ik})\, l_k(\mu) \equiv \sum_k (B_{ik}^0 - \mu\delta_{ik} + \Lambda_{ik})\, l_k(\mu) = 0 \tag{6}$$

the matrix $(\hat{B}^0 - \mu\hat{E})$ must be reduced to diagonal form; then the dimension of the determinant of system (6), from which the eigenvalues μ are found, will be lowered to the rank of the matrix $\hat{\Lambda}$. Following (5), we find

$$(\hat{B}^0 - \mu\hat{E})^{-1}_{ik} = \sum_{\mu_0} \frac{l_i^0(\mu_0) l_k^0(\mu_0)}{\mu_0 - \mu}\, \alpha^{-k} \equiv T_{ik}\alpha^{-k}. \tag{7}$$

The summation here is over all unperturbed eigenvalues μ_0. Multiplying (6) from the left by $(\hat{B} - \mu\hat{E})^{-1}$, we obtain the system of equations

$$\sum_k \left(\delta_{ik} + \sum_j T_{ij}\alpha^{-j}\Lambda_{jk} \right) l_k(\mu) = 0, \tag{8}$$

in which the elements T_{ij} depend on μ. Assuming that $\mu^{(0)} \ll \mu_0^{(1)}$, and using the expression for $F(-n, m+1, 1, 1-\alpha)$ in the form of the sum

$$\alpha^n \sum_{\nu=0}^{\infty} (1 - 1/\alpha)^\nu \binom{n}{\nu}\binom{m}{\nu},$$

one can calculate $T_{ij}(\mu^{(0)})$:

$$T_{ij}(\mu^{(0)}) = \alpha^i \left[\alpha^j \lambda^{(0)} - \frac{1}{(j+1)(1-\alpha)}\right], \quad j \le i; \qquad T_{ji}(\mu^{(0)}) = T_{ij}(\mu^{(0)}), \quad i \le j. \tag{9}$$

Here the substitution $\lambda^{(0)} = (\alpha - 1)/\mu^{(0)}$ has been made, and it is assumed that $i, j \gg 1$. The quantity $\mu^{(0)}$ is found from the condition that the determinant of the system of equations (8) be equal to zero; this determinant reduces to the form:

$$\begin{vmatrix} 1 + \dfrac{P_\infty}{P_{10}(1-\alpha)(n_0+1)} - \dfrac{P_\infty}{P_{10}}\alpha^{n_0}\lambda^{(0)} & 0 \\ \alpha\left[1 + \dfrac{P_\infty}{P_{10}(1-\alpha)(n_0+1)} - \dfrac{P_\infty}{P_{10}}\alpha^{n_0}\lambda^{(0)}\right] + \dfrac{\alpha}{1-\alpha}\Omega\left(\dfrac{1}{n_0^2}\right) & \dfrac{1}{1-\alpha}\Omega\left(\dfrac{1}{n_0^2}\right) \end{vmatrix} = 0.$$

Hence, taking (3) into account, we find

$$k = ZP_{10}(1-\alpha)\,\frac{P_\infty \alpha^{n_0}}{P_{10} + P_\infty/(1-\alpha)(n_0+1)}. \tag{10}$$

Solving now system (8), we find the distribution function $x_n(t)$ for $t \gg t_0$:

$$x_n(t) = A\alpha^n \left\{1 - \alpha^{n_0-n}\left(\frac{n_0+1}{n+1}\right)\frac{P_\infty}{P_\infty + P_{10}(1-\alpha)(n_0+1)}\right\}\exp(-kt). \tag{11}$$

The normalization coefficient A must be determined from the initial distribution. Physically it represents the fraction of the initial number N_0 of molecules that did not dissociate during the time $t \simeq t_0$. An estimate shows that if the AB molecules were initially at a lower temperature, then the number ΔN of molecules dissociated during $t \simeq t_0$ satisfies the inequality

$$\Delta N/N_0 \ll k/ZP_{10}(1-\alpha).$$

If, however, at the initial moment all molecules were at the level with energy E, then

$$\Delta N/N_0 \ll \exp[(E - n_0\hbar\omega)/kT].$$

It follows from (11) that, for small P_∞/P_{10}, the distribution function $x_n(t)$ differs little from the Boltzmann function $x_n = A\alpha^n$; for large P_∞/P_{10}, the equilibrium distribution is disturbed in such a way that the probability of finding the molecule AB at the upper level is close to zero. From the pre-exponential

factor in (11) one can find the energy region ε in which the Boltzmann distribution is substantially disturbed, i.e., the value of ε at which the second term in the brackets decreases by a factor of e. Assuming $P_\infty/P_{10} \gg (1-\alpha)(n_0+1)$, we find $\varepsilon = DkT/(D-kT)$ for $\varepsilon \ll D$, where ε is measured from the boundary of the continuous spectrum, and D denotes the dissociation energy, which, as follows from the model, satisfies the inequalities $n_0\hbar\omega \leq D \leq (n_0+1)\hbar\omega$.

The decomposition rate constant k in (10) can be rewritten in the form

$$k = k_0 \frac{p\exp(-D/kT)}{1 + p\frac{\hbar\omega}{D}\Big/\left[1-\exp\left(-\frac{\hbar\omega}{kT}\right)\right]}, \tag{12}$$

where $k_0 = ZP_{10}(1-\alpha)$ and $p = P_\infty/P_{10}$.

The assumptions made earlier, $n_0 \gg 1$, $t \gg t_0$, $\mu^{(0)} \ll \mu^{(1)}$, now take the form $D/\hbar\omega \gg 1$, $(1-\alpha)D/\hbar\omega\exp(-D/kT) \ll 1$. These inequalities are practically always fulfilled. The quantity $1/k_0$, according to (4), is the energy relaxation time of harmonic oscillators placed in a heat bath.

For a small disturbance of the equilibrium distribution, namely for $p \ll (1-\alpha)D/\hbar\omega$, (12) gives $k = ZP_\infty\exp(-D/kT)$. The decomposition rate constant is proportional to the probability of transition from the last discrete level into the continuous spectrum. Since $P_\infty \ll P_{10}(1-\alpha)D/\hbar\omega \lesssim 1$, the pre-exponential factor in this case is much smaller than the number of binary collisions.

The maximum value of k is reached under the condition $p = P_\infty/P_{10} \gg (1-\alpha)D/\hbar\omega$, which is usually fulfilled. In this case the rate constant is

$$k = k_0(1-\alpha)D/\hbar\omega\exp(-D/kT) \tag{13}$$

and is determined no longer by the probability of transition into the continuous spectrum, but by the probability P_{01}. The value k_0 depends on the temperature, the magnitude of the transmitted quantum $\hbar\omega$, and the radius of action of the intermolecular forces. For various molecules at ordinary temperatures, k_0 lies in the range $Z\cdot 10^{-2}$–$Z\cdot 10^{-10}$. Since usually $\alpha \ll 1$, $D/\hbar\omega \simeq 10 \div 10^2$, the maximum value of the pre-exponential factor in (13) is of the order of the number of binary collisions.

The principal shortcoming of the adopted model is the neglect of anharmonicity, i.e., the constancy of the quantum $\hbar\omega$. In reality, the magnitude of the vibrational quantum in diatomic molecules decreases with increasing number of the vibrational level. Since k_0 increases as $\hbar\omega$ decreases, this circumstance should lead to an increase of the pre-exponential factor in comparison with the pre-exponential factor for the adopted model. Experimental values of the pre-exponential factor for reactions $AB + C \to A + B + C$ often exceed the number

of collisions by two or three orders of magnitude. I express my sincere gratitude to Prof. N. D. Sokolov for discussion of the work.

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