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Thermodynamic Approach to the Calculation of the Rate Constants of Monomolecular Reactions in the Strong-Collision Limit

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Abstract—A thermodynamic approach to the calculation of the dissociation (recombination) rate constants of polyatomic molecules in the strong-collision limit is suggested. The approach is based on the density of states obtained by the inverse Laplace transform of the integral expression for the statistical sum of the internal degrees of freedom of the molecule. Although the mathematical apparatus of this model is rather simple, it enables one to take into account the real energy distribution of molecular states. The potential of this method is demonstrated for O_3, H_2O, H_2O_2, CH_4, and C_2H_6. The results obtained are compared with data calculated using other methods. The temperature dependence of the collision efficiency correction β_c is analyzed for water and ethane.

Monomolecular thermal processes (dissociation and recombination) are important in combustion and atmosphere chemistry [1]. Under conditions that are of practical interest, most monomolecular reactions occur at low or medium pressures [1]. The dissociation rate constant in the low-pressure limit is calculated from the equation [2]

$$k_{d,0} = \beta_c k_{d,sc}, \tag{1}$$

where $k_{d,sc}$ is the rate constant in the strong-collision limit and β_c is the collision efficiency correction (its value does not exceed unity). To calculate the reaction rate constant in a medium-pressure region, one should know β_c and the related average amounts of energy given up or received by a molecule per collision [3]. Although there are a number of theoretical methods for calculating β_c [4], the determination and systematization of β_c data using Eq. (1), experimentally measured $k_{d,0}$ data, and calculated $k_{d,sc}$ data are still playing an important role in the theory and applications of monomolecular reactions. This approach seems attractive, because the rate constant in the strong-collision limit can be rather easily calculated using the following formula [5]:

$$k_{sc} = Z_{L-J} \int\limits_{\Omega(E > E_0)} f_{int}(E) \mathrm{d}E, \tag{2}$$

where Z_{L-J} is the frequency factor of binary collisions and $f_{int}(E)$ is the Boltzmann distribution for the internal degrees of freedom. Here, integration is performed over an energy region higher than the reaction barrier. Vibrations, internal rotations, and the external rotation that corresponds to the lowest principal moment of inertia (absent for linear molecules) are classified as internal degrees of freedom [5]. The two other external rotations are only partially active, since only part of their energy is involved in surmounting the reaction barrier because of the constraints imposed by the angular momentum conservation law [4–6]. In the strong-collision limit, which takes into account the contribution of these partially active rotations, the dissociation rate constant has the following form (in our own notation) [6]:

$$k_{d,\,sc} = Z_{L-J}[Q_{int}(T)]^{-1} \int\limits_0^\infty \left\{ \int\limits_{E_J}^\infty \rho_{int}(E) e^{-E/RT} \mathrm{d}E \right\} \times (RT)^{-1} \mathrm{e}^{E_r/RT} \mathrm{d}E_r, \tag{3}$$

where $Q_{int}(T)$ is the statistical sum for the internal degrees of freedom, $E_r = E_r(J)$ is the energy of the two external rotations corresponding to the two highest principal moments of inertia for the equilibrium length of the dissociating bond and the rotational quantum number J, $E_J(E_r)$ is the dissociation barrier for the rotating molecule, and $\rho_{int}(E)$ is the energy level density distribution for the internal degrees of freedom. If the tensile energy of the cleaving bond is described by the Lenard-Jones potential (potential 6-12), then the expression for $E_J(E_r)$ will take the form [6]

$$E_J = 4D_e\left(\frac{E_r}{6D_e}\right)^{1.5} - E_r + E_0, \tag{4}$$

where $D_e = (E_0 + 0.5h\nu_{cr})$, E_0 is the energy for the rotational quantum number $J = 0$, h is the Planck constant, and ν_{cr} is the vibration frequency of the cleaving bond.

By performing integration by parts [6] and passing from integration with respect to $\mathrm{d}E_J$ to integration with respect to dE_r in the second of the integrals obtained, we arrive at

$$k_{d,\,sc} = Z_{L-J}[Q_{int}(T)]^{-1}\left\{\int_{E_0}^{\infty}\rho_{int}(E)e^{-E/RT}dE\right. \tag{5}$$

$$\left.+\int_{0}^{E_{r,\,max}}\left[1-\left(\frac{E_r}{6D_e}\right)^{0.5}\right]\rho_{int}(E_J(E_r))e^{-(E_J(E_r)+E_r)/RT}dE_r\right\},$$

where $E_{r,\,max}$ is found from the constraint $E_J(E_{r,\,max}) = 0$.

Thus, only the function $\rho_{int}(E)$ should be determined to calculate the rate constant in the strong-collision limit.

If the molecule is viewed as a system of harmonic oscillators, one can use the empirical formula for $\rho_{int}(E)$ [7]. However, the contributions from the external and internal rotations and the anharmonicity of vibrations should be taken into account for real molecules. This can be done, in principle, using the convolution method [6]. However, in this case, we have to introduce several simplifications, whose consequences are unpredictable. Furthermore, the resulting expressions will contain sums of series and will be rather cumbersome [2].

The alternative approach to density-of-states calculations proposed in [8] and developed in [9, 10] is based on the inverse Laplace transform of the integral expression for the statistical sum of internal degrees of freedom [9],

$$Q_{int}(\beta) = \int_{0}^{\infty}\rho_{int}(E)e^{-\beta E}dE, \tag{6}$$

where $Q_{int}(\beta)$ is the statistical sum for internal degrees of freedom, $\beta = 1/RT$, R is the universal gas constant, and T is temperature, in combination with the steepest descent method. The following expression was thus obtained (in our own notation) [9]:

$$\rho_{int}(E) = Q_{int}(\beta^*)e^{\beta^* E}[2\pi(\partial^2\ln Q_{int}/\partial\beta^2)_{\beta=\beta^*}]^{-0.5}, \tag{7}$$

where β^* is the β value in the saddle point of the integrand in the inverse Laplace transform. The β^* value can be found by solving the transcendental equation [9]

$$(\partial\ln Q_{int}/\partial\beta)_{\beta=\beta^*} = -E, \tag{8}$$

where E is the internal energy of the molecule. Thus, $\rho_{int}(E)$ for a given E is calculated in two steps: the transcendental equation (8) is solved to determine β^*, and the latter and E are substituted into Eq. (7). Clearly, it is necessary to know the $Q_{int}(\beta)$ function for these calculations. Furthermore, this approach is rather laborious, requiring the solution of the transcendental equation (8) in each integration step in Eq. (5).

In this work, we propose a new approach to the calculation of DOS from Eq. (7) and of the tabulated thermodynamic functions $\Phi^0(T)$, $H^0(T) - H^0(0)$, and $C_p^0(T)$ [11]. Indeed, using $T = 1/R\beta$ as a variable, one can write the following expression for ideal gases [11]:

$$Q_{int}(T)Q_{ext}(T) = \exp(\Phi^0(T)/R), \tag{9}$$

where $Q_{ext}(T)$ is the statistical sum for the external degrees of freedom (the two external rotations corresponding to the two highest principal moments of inertia and the three translational degrees of freedom) under a pressure of 1 atm, which is given by

$$Q_{ext}(T) = (T/273)V_0/N_A(2\pi kmT/N_A h^2)^{1.5} \tag{10}$$

$$\times[8\pi^2 k/h^2(I_1I_2)^{0.5}T/\sigma] = 6.4\times10^{36}m^{1.5}(I_1I_2)^{0.5}T^{3.5},$$

where $V_0 = 22\,400$ cm^3 is the molar volume of ideal gas at 273 K, k is the Boltzmann constant, m is the molecular weight, N_A is Avogadro's number, h is the Planck constant, I_1I_2 is the ratio of the two highest moments of inertia of the molecule, and σ is the symmetry number.

The energy of the internal degrees of freedom is

$$E = H^0(T) - H^0(0) - 3.5RT. \tag{11}$$

Here, as is required for passing from the enthalpy to the energy of ideal gas, the energy of the external degrees of freedom ($2.5RT$), which is the sum of $RT/2$ per degree of freedom and RT, is subtracted from the total enthalpy.

It has been demonstrated [8] that

$$\begin{aligned} d^2Q_{int}(\beta)/d\beta^2 &= C_{int}(\beta)/(R\beta^2) \\ &= (RT)^2C_{int}(T)/R, \end{aligned} \tag{12}$$

where $C_{int}(T) = C_p(T) - 3.5R$ is the heat capacity of the internal degrees of freedom of a molecule.

Thus, the density of states for the internal degrees of freedom with an energy E at a temperature T can be represented as

$$\begin{aligned} &\rho_{int}(E(T)) \\ &= (RTQ_{ext}(T))^{-1}[2\pi(C_p(T)/R - 3.5)]^{-0.5} \\ &\times\exp[\Phi^0(T)/R + (H^0(T) - H^0(0))/RT - 3.5]. \end{aligned} \tag{13}$$

Substituting tabulated T values and the corresponding values of thermodynamic functions [11], as well as $Q_{ext}(T)$ calculated from molecular constants [11] using formula (10), into Eqs. (11) and (13), we obtained a discrete function $\rho_{int}(E)$. This function was then interpolated using a polynomial of degree 7: $\ln\rho_{int}(E) = b_0 + b_1g + b_2g^2 + b_3g^3 + b_4g^4 + b_5g^5 + b_6g^6 + b_7g^7$, where $g = \ln(E)$ [12] (Table 1). The $\rho_{int}(E)$ plot for ethane is shown in Fig. 1. For all of the molecules examined (O_3, H_2O,

Table 1. Polynomial coefficients for calculating the energy level density for the internal degrees of freedom of the molecules ($\rho_{int}(E)$)

Coefficient	O_3	H_2O	H_2O_2	CH_4	C_2H_6
b_0	1.6114	0.6900	2.0181	1.4603	1.9640
b_1	–0.3290	–0.5555	–0.2138	–0.7647	–0.2267
b_2	0.0100	–0.0566	0.1373	0.1150	0.1662
b_3	–0.0935	0.0647	0.0192	0.2343	0.1137
b_4	0.2326	0.0152	0.0149	–0.1139	–0.0329
b_5	–0.1010	-9.1263×10^{-3}	-4.5472×10^{-3}	0.0300	9.5911×10^{-3}
b_6	0.0173	1.5863×10^{-3}	6.6174×10^{-4}	-3.5519×10^{-3}	-9.1319×10^{-4}
b_7	-1.0327×10^{-3}	-9.4520×10^{-5}	-4.0118×10^{-5}	1.5804×10^{-4}	2.1350×10^{-5}

Note: $\ln\rho_{int}(E) = b_0 + b_1g + b_2g^2 + b_3g^3 + b_4g^4 + b_5g^5 + b_6g^6 + b_7g^7$, where $g = \ln(E)$.

H_2O_2, CH_4, and C_2H_6), the correlation coefficient in this polynomial interpolation was at least 0.9999. The calculations were performed using the SigmaPlot 8.0 graphical editor. Similar results were obtained with polynomials of other degrees, for example, 5 and 9.

To check the accuracy of this method for calculating $\rho_{int}(E)$, we substituted $\rho_{int}(E)$ into Eq. (6), integrated the resulting expression, and compared the value obtained (Q_{calc}) with the initial $Q_{int}(T)$ value (Q_{th}) (Table 2). Clearly, noticeable deviations are observed at low temperatures. This is most likely to be due to the essentially discrete character of the level distribution at low energies (correspondingly, at low temperatures). Above 1000 K, where the main contribution to the statistical sum is from high-energy levels, $Q_{calc}(T)$ and $Q_{th}(T)$ are in good agreement, which becomes still better as the temperature is increased. This means that the calculated function $\rho_{int}(E)$ exactly reproduces the distribution of energy levels for the internal degrees of freedom of the molecule at temperatures near the dissociation barrier.

Substituting the calculated density-of-state function $\rho_{int}(E)$ into Eq. (5) and integrating the resulting expression, we obtained the dissociation rate constant in the strong-collision limit for the molecules examined (Table 2). For a convenient comparison in a wide temperature range, the rate constants were normalized to $\exp(-E_0/RT)$ (E_0 is the energy barrier of the reaction): $A_{d,0} = k_{d,0}/\exp(-E_0/RT)$. The binary-collision frequency factors Z_{L-J} were taken from the literature [2], and the dissociation energies were calculated from the enthalpies of formation of the reactants and products at 0 K.

As a whole, the results obtained here agree well with calculations carried out by the convolution method [2]. However, significant discrepancies (up to 120%) are observed in some cases, especially for molecules with internal rotation (H_2O_2 and C_2H_6). This can be due to the fact that internal rotations were only roughly taken into account in [2]. In the calculation of the thermodynamic functions underlying our approach, the contribution of the internal rotations was taken into account more precisely by direct summation over the states of the hindered rotor [11]. Furthermore, we took into account the anharmonicity (except for C_2H_6), including the cross terms and the interactions between the rotational and vibrational degrees of freedom.

Thus, the method suggested is based on a rather precise mathematical procedure and takes into account the real structure of molecular levels. At the same time, it is computationally simple.

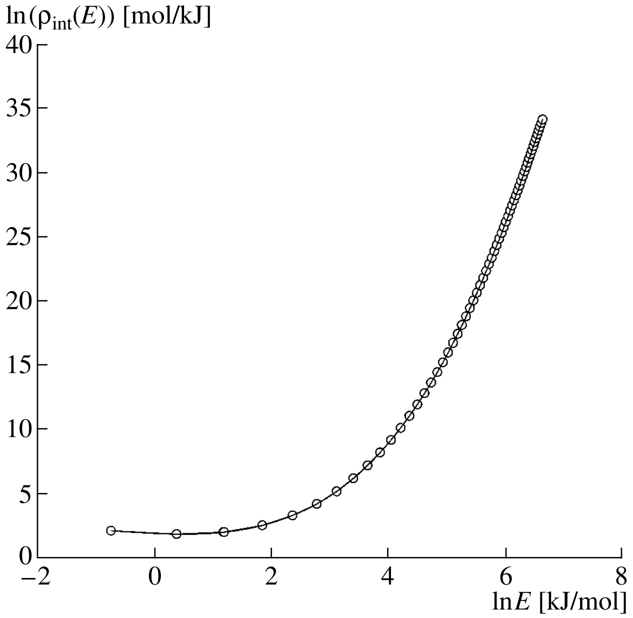

Fig. 1. $\rho_{int}(E)$ plot for the internal degrees of freedom of ethane.

Table 2. Calculated preexponential factors ($A_{d,0}$) and dissociation rate constants for the molecules examined and the statistical sums for internal degrees of freedom derived from thermodynamic data (Q_{th}) and calculated from the density-of-states distribution (Q_{calc})

T, K	$Z_{L-J} \times 10^{14}$	Q_{th}	Q_{calc}	$A_{d,0} \times 10^{17}$
O_3				
200	1.46	11.15	4.04	0.82 (0.68)
300	1.61	14.22	7.63	0.89 (0.72)
400	1.73	17.81	12.02	0.89 (0.90)
800	2.11	43.02	41.02	0.67 (0.52)
1000	2.26	64.81	64.96	0.56 (0.42)
1200	2.39	94.90	97.61	0.46 (0.34)
1400	2.51	135.15	141.5	0.39 (0.26)
H_2O				
200	1.69	4.08	1.69	4.5 (3.7)
300	1.80	4.97	2.72	5.0 (4.1)
1000	2.39	10.21	9.20	6.5 (5.1)
2000	2.92	22.29	23.30	5.3 (4.2)
3000	3.31	45.31	48.7	3.7 (2.9)
6000	4.16	254.6	271.4	1.2 (1.1)
10000	5.10	1348.0	1400.0	0.43 (–)
H_2O_2				
200	1.83	14.35	7.00	66.0 (120.0)
300	2.00	20.68	13.86	62.6 (110.0)
400	2.14	28.41	22.58	57.0 (110.0)
800	2.58	86.13	86.10	32.7 (60.0)
1000	2.76	141.7	144.4	24.1 (44.0)
1200	2.91	234.3	234.0	17.7 (27.0)
1400	3.05	350.0	364.0	13.1 (19.0)
CH_4				
300	2.07	11.35	5.36	5.3×10^4 (3.4×10^4)
1000	2.91	45.96	45.76	3.3×10^4 (2.1×10^4)
2000	3.63	536.9	543.9	5.2×10^3 (3.6×10^3)
3000	4.16	5.21×10^3	5.08×10^3	8.5×10^2 (6.7×10^2)
4000	4.6	3.62×10^4	3.62×10^4	1.8×10^2 (1.6×10^2)
5000	4.97	2.21×10^5	2.04×10^5	4.8×10 (4.7×10)
C_2H_6				
200	1.93	14.81	7.43	2.1×10^8 (4.9×10^8)
300	2.12	22.55	16.57	1.8×10^8 (3.6×10^8)
400	2.28	35.74	31.44	1.4×10^8 (2.6×10^8)
1000	2.95	915.8	950.0	1.1×10^7 (1.5×10^7)
1500	3.34	1.42×10^4	1.50×10^4	1.1×10^6 (1.2×10^6)
2000	3.67	1.90×10^5	1.93×10^5	1.1×10^5 (1.2×10^5)
2500	3.94	1.93×10^6	1.95×10^6	1.7×10^4 (1.7×10^4)

Note: Z_{L-J} and $A_{d,0}$ are expressed in cm^3 mol^{-1} s^{-1}. The $A_{d,0}$ values in parentheses were calculated in [2].

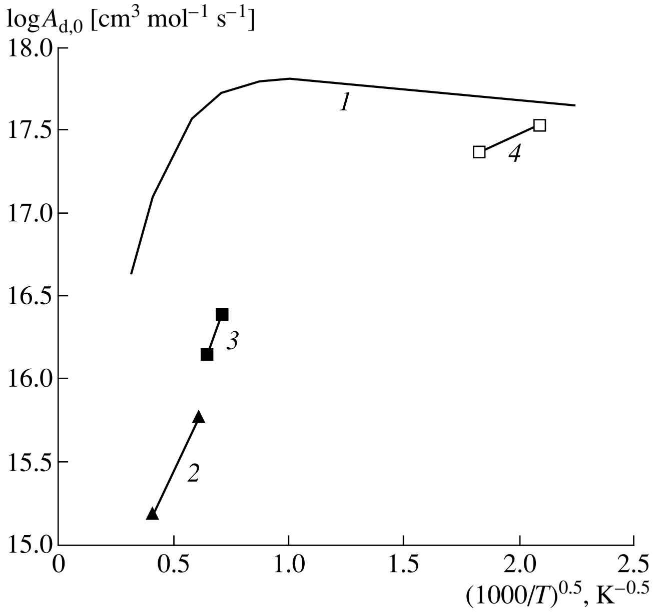

Fig. 2. (*1*) Dissociation rate constants of H_2O calculated in the strong-collision limit, the same constants measured in (*2*) [13] and (*3*) [14], and (*4*) the same constants derived from the experimental rate constant of the $H + OH^{\cdot} = H_2O$ recombination [15]. The abscissa is taken to be $(1000/T)^{0.5}$ to obtain a more uniform scale.

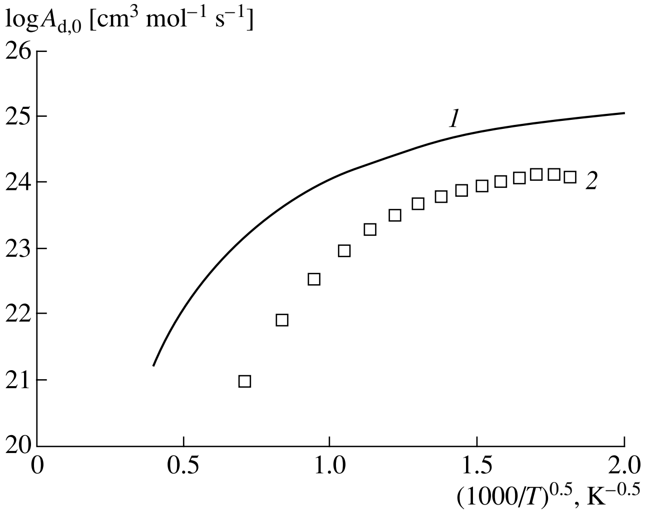

Fig. 3. (*1*) Dissociation rate constant of C_2H_6 calculated in the strong-collision limit as compared to (*2*) the same constant derived from the recommended $CH_3^{\cdot} + CH_3^{\cdot} = C_2H_6$ recombination rate constant [1] based on experimental data. The abscissa is taken to be $(1000/T)^{0.5}$ to obtain a more uniform scale.

Comparing the rate constant calculated in the strong-collision limit with experimental data, one can estimate the temperature dependence of the collision efficiency correction β_c. An example of such a comparison is shown in Figs. 2 and 3 for water and ethane. Clearly, β_c decreases with increasing temperature. Similar behavior of these and some other molecules was observed in an earlier study [2].

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