7. S. Ormonde, "Vibrational relaxation theories and measurements," Rev. Mod. Phys., 47, No. 1 (1975).
8. V. P. Glushko (ed.), Thermodynamic Properties of Individual Substance (Handbook) [in Russian], Nauka, Moscow (1978).
9. V. M. Akulintsev and Yu. P. Neshchimenko, "Calculation of rate constants of vibrational–vibrational energy exchange," Inf. Byul. Khim Promyshlennosti, No. 5 (1979).
10. H. T. Powell, "Vibrational relaxation of carbon monoxide using a pulse discharge. II. T = 100, 300, 500°K," J. Chem. Phys., 63, No. 6 (1975).
11. G. L. Wolk, R. E. Weston, and G. W. Flynn, "Vibrational energy transfer between $^{12}C^{16}O$ and $^{13}C^{16}O$," Chem. Phys. Lett., 71, No. 3 (1980).
12. V. M. Akulintsev, N. M. Gorshunov, and Yu. P. Neshchimenko, "Calculation of isotope separation parameters in oxidation reactions of vibrationally excited nitrogen molecules in an airflow," Khim. Vys. Energ., 13, No. 6 (1979).

EQUILIBRIUM CONSTANT IN THE DIFFUSION THEORY OF CHEMICAL REACTIONS

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The correct determination of the domains in the phase plane that correspond to the initial and final stages is important to the construction of a diffusion model of a chemical reaction. In case [1] the system state passes a potential barrier with a maximum considerably exceeding the temperature of the medium, the reaction between the particles can be considered complete if the spacing between them is greater than the coordinate corresponding to the position of the maximum of the potential function. The reaction rate is determined here by the probability flux density through a "narrow place," the vertex of the potential barrier. In the problem of dissociation of a diatomic molecule, the situation is rather different. The potential function U(x) of atom interaction in the molecule (its main electronic term) takes on a constant value equal to the dissociation energy, starting with a certain spacing x_1. Although the atom interaction force vanishes for $x \geq x_1$ and the atoms can be considered free, it would be erroneous to assert that the dissociation reaction is completed upon removal of the atoms to a distance equal to x_1, and its rate is given by the flux at the point $x = x_1$. The Kramers model to compute the dissociation rates of diatomic molecules was first applied in [2] and it was shown that the values of the rate constants, which agreed correctly with experimental values, are not determined by the flux at the point $x = x_1$ but by the flux at the point $x = l$, where l is a certain parameter equal, in order of magnitude, to the particle mean free path in the medium. However, the parameter l was not defined rigorously in [2].

The purpose of this paper is to consider the problem of atom association in a diatomic molecule and to determine the equilibrium constants for direct and reverse reactions, from which the parameter l is found single-valuedly.

Since the build-up process for a Maxwell equilibrium velocity distribution for reacting particles is more rapid as compared with the process of Boltzmann coordinate distribution formation [2], we consider the Smoluchowski equation in the segment $[0, l]$:

$$\partial M_0/\partial t + \partial M_1/\partial x = 0, \quad M_1 = (\mu\gamma)^{-1}(KM_0 - T\partial M_0/\partial x), \tag{1}$$

where $M_0(x, t)$ is the probability density of detecting an atom at the distance x at the time t; $M_1(x, t)$, probability flux density; $K(x) = -\partial U/\partial x$, force of reacting atoms interaction; μ, their reduced mass; and γ and T, friction coefficient and the temperature of the surrounding medium.

Let us supplement (1) with the initial and boundary conditions

$$M_0(x, 0) = \delta(x - l); \tag{2}$$

$$M_1(0, t) = M_1(l, t) = 0, \tag{3}$$

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where $\delta(x)$ is the delta function.

Condition (2) means that the reacting atoms are at a distance l at the initial instant, and condition (3) corresponds to a "reflecting" boundary at the point $x = l$ while it would be "absorbing" in the dissociation problem [2].

We will assume the process of atom association into a molecule completed if the spacing between them becomes less than x_1. Here the recombination rate constant equals the probability flux density at this point $k = |M_1(x_1)|$.

Let us use the asymptotic solution, in the time, of (1), obtained in [2] with the boundary condition (3) taken into account at the point $x = 0$:

$$M_0 = f\exp\left(-\frac{U}{T}\right),\ f = f_0 + \beta_1(x)\frac{df_0}{dt} + \ldots,$$
$$\beta_1(x) = \frac{\mu\gamma}{T}\int_{x_0}^{x}\exp\left(\frac{U}{T}\right)g(x')\,dx',\ g(x) = \int_0^x \exp\left(-\frac{U}{T}\right)dx', \tag{4}$$

where x_0 is the spacing between the atoms in the molecule that corresponds to the minimum of the potential function $U(x)$, and f_0 is a certain time-dependent parameter.

At the point $x = l$ the boundary condition (3) is equivalent to conservation of normalization of the distribution function

$$\int_0^l M_0(x, t)\,dx = 1. \tag{5}$$

Substituting (4) into (5), we find a first-order differential equation in f_0, which yields when solved with the initial condition $f_0(0) = 0$

$$f_0 = g^{-1}(l)[1 - \exp(-t/\tau)], \tag{6}$$

where $\tau = g^{-1}(l)\int_0^l \exp\left(-\frac{U}{T}\right)\beta_1(x)\,dx$ is the characteristic time of atom association into a molecule. The formula for the probability flux density at the point $x = x_1$ hence has the form

$$M_1(x_1) = -\frac{g(x_1)}{\int_0^l \exp\left(-\frac{U}{T}\right)\beta_1(x)\,dx}\exp(-t/\tau). \tag{7}$$

For times $t \ll \tau$ the flux (7) is constant and yields the recombination rate constant

$$k = \frac{T}{\mu\gamma}\,\frac{g(x_1)}{\int_0^l \exp\left(-\frac{U}{T}\right)dx\int_{x_0}^{x}\exp\left(\frac{U}{T}\right)g(x')\,dx'}. \tag{8}$$

Let us first consider the case of relatively low temperatures of the medium governed by the inequality $\exp(-D/T)l \ll g(x_1)$, where D is the dissociation energy of the molecule.

The integral in the numerator of (8) equals [2]

$$g(x_1) = \omega^{-1}(2\pi T/\mu)^{1/2}, \tag{9}$$

where ω is the frequency of atom vibration in the molecule.

To compute the integral in the denominator of (8) we separate the domain of integration into three parts: $[0, x_0]$, $[x_0, x_1]$, $[x_1, l]$. The integral in the first domain is negative and is easily given an upper bound in absolute value:

$$\left|\int_0^{x_0}\right| < \int_0^{x_0} dx\exp\left(-\frac{U}{T}\right)\exp\left(\frac{U}{T}\right)\int_x^{x_0} x'\,dx' = \frac{x_0^3}{3}.$$

The following estimate

$$\int_{x_0}^{x_1} < \int_{x_0}^{x_1} dx \exp\left(-\frac{U}{T}\right) \exp\left(\frac{U}{T}\right) g(x)\, x < \frac{1}{2} x_1^2 g(x_1)$$

is valid for the integral in the second domain. The integral in the third domain yields the fundamental contribution in the denominator of (8) and equals

$$\int_{x_1}^{l} = \exp\left(-\frac{D}{T}\right) \int_{x_1}^{l} dx \left[\int_{x_0}^{x_1} \exp\left(\frac{U}{T}\right) g(x')\, dx' + \exp\left(\frac{D}{T}\right) g(x_1)(x - x_1) \right] = \exp\left(-\frac{D}{T}\right) l \int_{x_0}^{x_1} \exp\left(\frac{U}{T}\right) g(x)\, dx + g(x_1) \frac{l^2}{2} \simeq \frac{1}{2} l^2 g(x_1). \tag{10}$$

Substituting (9) and (10) into (8), we obtain

$$k = 2T/(\mu\gamma l^2) = 2T\sigma^2 N^2/(\mu\gamma),\ l = (\sigma N)^{-1}. \tag{11}$$

Dividing (11) by N^2, we find the association constant which is independent of the density of particles in the surrounding medium

$$k_A = 2T\sigma^2/(\mu\gamma). \tag{12}$$

In the high-temperature range governed by the inequality

$$\exp(-D/T) l \gg g(x_1),$$

the estimates for the numerator of (8) and the integrals of the denominator for the domains $[0, x_0]$ and $[x_0, x_1]$ are the same as for low temperatures. The integral in the denominator over the third segment $[x_1, l]$ is evaluated as follows:

$$\int_{x_1}^{l} = \exp\left(-\frac{D}{T}\right) \int_{x_1}^{l} dx \left\{ \int_{x_0}^{x_1} dx' \exp\left(\frac{U}{T}\right) g(x') + \exp\left(\frac{D}{T}\right) \int_{x_1}^{x} dx' \left[g(x_1) + \exp\left(-\frac{D}{T}\right)(x' - x_1) \right] \right\} = \tag{13}$$

$$= \exp\left(-\frac{D}{T}\right) l \int_{x_0}^{x_1} \exp\left(\frac{U}{T}\right) g(x)\, dx + g(x_1) \frac{l^2}{2} + \frac{l^3}{6} \exp\left(-\frac{D}{T}\right) \simeq \frac{l^3}{6} \exp\left(-\frac{D}{T}\right).$$

The integral (13) yields the main contribution to the denominator and the formula for the recombination rate takes the form

$$k_A = \frac{k}{N^2} = \frac{6NT\sigma^3}{\mu\gamma\omega} \left(\frac{2\pi T}{\mu}\right)^{1/2} \exp\left(\frac{D}{T}\right). \tag{14}$$

Comparing (12) and (14), we see that the atom recombination rate into a diatomic molecule changes its dependence on the molecule frequency and vibrations, the density N and the temperature T of the surrounding medium as the transition is made from comparatively low temperatures of the medium to high temperatures.

Now, let us divide the diatomic molecule dissociation rate found in [2] by the association rate, and let us find the equilibrium constant. Consequently, we obtain the identical expression for both low and high temperatures:

$$\frac{k_D}{k_A} = \frac{\omega}{2\sigma} \left(\frac{\mu}{2\pi T}\right)^{1/2} \exp\left(-\frac{D}{T}\right). \tag{15}$$

On the other hand, the equilibrium constant of the reaction

$$AB + M \underset{k_A}{\overset{k_D}{\rightleftarrows}} A + B + M$$

can also be obtained in the form of a ratio between the partial functions of the reacting particles:

$$k_D/k_A = Z_A Z_B / Z_{AB}. \tag{16}$$

Let us replace the partial functions in (16) by the classical statistical integrals

$$Z_A = \left(\frac{m_A T}{2\pi\hbar^2}\right)^{3/2},\ Z_B = \left(\frac{m_B T}{2\pi\hbar^2}\right)^{3/2},$$
$$Z_{AB} = Z_t Z_R Z_V \exp\left(\frac{D}{T}\right) = \left[\frac{(m_A + m_B) T}{2\pi\hbar^2}\right]^{3/2} \frac{(2)_{AB}\, \mu x_0^2 T}{\hbar^2} \frac{T}{\hbar\omega} \exp\left(\frac{D}{T}\right), \tag{17}$$

TABLE 1

Reaction formula (the third particle indicates the composition of the surrounding medium)	Values of the parameters utilized for the computation T, K; η, g·cm^{-1}; ν, cm^{-1} ($\nu = \omega/2\pi$); r = x_0, 1 nm	Theoretical value of the constant k_D, cm^3·mole^{-1}·sec^{-1}	Experimental value of the constant [5] k_D, cm^3·mole^{-1}·sec^{-1}
$O_2+Ar=O+O+Ar$	$T=1000$, $\eta=5{,}5\cdot10^{-4}$ $\nu=1580$, $r_0=0{,}06$ $x_0=0{,}12$	$k_D=1{,}4\cdot10^{15}\exp(-D/T)$	$k_D=(1-2{,}4)\cdot10^{15}\exp(-D/T)$
$H_2+Ar=H+H+Ar$	$T=1300$, $\eta=6{,}16\cdot10^{-4}$ $\nu=4400$, $r_H=0{,}03$ $x_0=0{,}074$	$k_D=0{,}8\cdot10^{15}\exp(-D/T)$	$k_D=2{,}3\cdot10^{15}\exp(-D/T)$
$H_2+H_2=H+H+H_2$	$T=1300$, $\eta=2{,}35\cdot10^{-4}$ $\nu=4400$, $r_H=0{,}03$ $x_0=0{,}074$	$k_D=2\cdot10^{15}\exp(-D/T)$	$k_D=8{,}2\cdot10^{15}\exp(-D/T)$
$Br_2+Ne=Br+Br+Ne$	$T=1300$, $\eta=7{,}8\cdot10^{-4}$ $\nu=323$, $r_{Br}=0{,}13$ $x_0=0{,}228$	$k_D=2\cdot10^{7}$	$k_D=3{,}6\cdot10^{7}$
$I_2+Ar=I+I+Ar$	$T=1000$, $\eta=5{,}5\cdot10^{-4}$ $\nu=214$, $r_I=0{,}133$ $x_0=0{,}267$	$k_D=1{,}2\cdot10^{15}\exp(-D/T)$	$k_D=1{,}5\cdot10^{15}\exp(-D/T)$
$HCl+Ar=H+Cl+Ar$	$T=3000$, $\eta^*=10^{-3}$ $\nu=2990$, $r_H=0{,}03$ $r_{Cl}=0{,}1$, $x_0=0{,}127$	$k_D=7{,}7\cdot10^{7}$	$k_D=5{,}3\cdot10^{7}$
$N_2+N_2=N+N+N_2$	$T=3000$, $\eta^*=8\cdot10^{-4}$ $\nu=2360$, $r_N=0{,}06$ $x_0=0{,}11$	$k_D=2\cdot10^{15}\exp(-D/T)$	$k_D=6{,}8\cdot10^{15}\exp(-D/T)$

$$(2)_{AB}=\begin{cases}1, & A=B,\\ 2, & A\neq B,\end{cases} \tag{17}$$

where $\hbar$ is the Planck constant and the sum of energies of sufficiently remote atoms is taken as zero.

After substituting (17) into (16), we have

$$\frac{k_D}{k_A}=\frac{\omega}{2(2)_{AB}\pi x_0^2}\left(\frac{\mu}{2\pi T}\right)^{1/2}\exp\left(-\frac{D}{T}\right). \tag{18}$$

Comparing (18) and (15), we find

$$\sigma=(2)_{AB}\pi x_0^2,\ l=(\sigma N)^{-1}, \tag{19}$$

where x_0 is the equilibrium spacing between atoms inthe molecule AB, hence σ agrees in order of magnitude with its geometric dimensions and the hypothesis in [2] about the approximate equality of the parameter l to the length of the mean free path in the medium is correct.

The rate constants were computed for a number of chemical reactions for the value (19) found for the parameter l, and the results are compared with experiment. The friction coefficient was estimated from the formula [2]: $\gamma = \mu(\gamma_A/m_A + \gamma_B/m_B)$, $\gamma_i = 6\pi r_i \eta/m_i$, $i = A, B$, where η is the viscosity coefficient of the medium whose value is presented in [3] as a function of the temperature T, and r_i and m_i are the radius and mass of the i-th reacting particle. The geometric dimensions of the particles and the parameters characterizing the potential of their interaction are taken from [4].

Results of the calculations are presented in Table 1. The asterisk on the symbol for the viscosity coefficient means that it is obtained by linear extrapolation of the experimental data [3] into the domain of temperatures being considered. If it is taken into account that in practice it is often necessary to know just the order of magnitude of the reaction constants, then the correspondence between the theoretical and experimental data [5] is comparatively good.

LITERATURE CITED

1. H. A. Kramers, "Brownian motion in a field of force and the diffusion model of chemical reactions," Physica (The Hague), 7, No. 4 (1940).
2. S. A. Reshetnyak and L. A. Shelepin, "On the diffusion theory of chemical reactions," Zh. Prikl. Mekh. Tekh. Fiz., No. 5 (1981).
3. I. K. Kikoin (ed.), Tables of Physical Quantities (Handbook) [in Russian], Atomizdat, Moscow (1976).
4. K. P. Mishchenko and A. A. Ravdel' (eds.), Brief Handbook of Physicochemical Quantities [in Russian], Khimiya, Leningrad (1972).
5. V. N. Kondrat'ev, Gas-Phase Reaction Rate Constants (Handbook) [in Russian], Nauka, Moscow (1970).