DIFFUSION THEORY OF CHEMICAL REACTIONS

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1. Introduction. The theory of Brownian motion of a particle in a medium [1] is often used in kinetics. In particular, it is employed in the theory of electron-ion recombination [2], chemical reactions [3], moderation of neutrons [4], and phase transformations [5]. All of these problems are described by similar kinetic equations.

In this paper, based on a unified approach [6, 7] to the solution of linear kinetic equations, we examine the diffusion theory of chemical reactions. Its basic assumptions were formulated in [4]. The starting points in the theory are the equations of motion of reacting particles in the presence of a random force, originating from the action of the surrounding medium on the reagents. The state of the system in this model is determined by the values of the velocity v and coordinate x and is represented by a point in the phase plane. The chemical reaction is viewed as the wandering of the image point in the phase plane out of the region corresponding to the initial substances into the region corresponding to the final substances.

The random process corresponding to the motion of the image point in the phase plane is described by the kinetic equations of the Fokker–Planck type for the probability density. Even for the simplest bimolecular reaction, the procedure of integrating this equation is very complicated. The problem of overcoming the potential barrier is examined in [8]. It was solved assuming that the gas temperature is small compared to the height of the potential barrier. In this case, the flux of the probability density over the top of the potential barrier can be viewed as a constant and it is possible to reduce the problem to one of solving the stationary kinetic equation. Later, Kramers' theory was updated [9-12].

A more rigorous approach to calculating the rate constants of chemical reactions depends on the nonstationary solution of the kinetic equation. Thus, in [13], for an interaction potential of reacting particles with a special form, the solution was sought in the form of a series in terms of the characteristic functions and characteristic values of the problem. However, in view of the difficulties related to obtaining the characteristic values and the characteristic functions for an interaction potential of arbitrary form, the results of the work have not been generalized.

In order to find the nonstationary solutions, the method of quasistationary distribution functions (QDF) can be used [7]. According to this method, the distribution function is sought in the form of a series in powers of a specified evolution operator $\hat{E}$. The most interesting stage in establishing equilibrium is described by a distribution function that takes into account only the terms of zero and first order in the operator $\hat{E}$. In what follows, we will obtain the rate constant of a bimolecular chemical reaction for an arbitrary interaction potential and arbitrary relation between the gas temperature and height of the potential barrier.

Following Kramers, we will make the transition from the equations of motion of particles in a bimolecular reaction to the kinetic equation for the probability density distribution function

$$\frac{\partial\rho}{\partial t} = -\frac{K(x)}{\mu}\frac{\partial\rho}{\partial v} - v\frac{\partial\rho}{\partial x} + \gamma\frac{\partial}{\partial v}\left(v\rho + \frac{T}{\mu}\frac{\partial\rho}{\partial v}\right), \tag{1.1}$$

where $\rho(x, v, t)dxdv$ is the probability for finding the system at time t in a state with coordinates in the vicinity of the point (x, v) in the phase plane; $K(x) = -dU/dx$ [U(x) is the interaction potential for the reacting particles]; μ is the reduced mass of the reacting particles; γ is the effective coefficient of friction of the surrounding medium; T is the temperature of the medium in energy units.

Reducing the problem of the interaction of two reacting particles in the usual way to the problem of the motion of a single particle with reduced mass in the field U(x) in the presence of a random force, it is possible to express the effective coefficient of friction in terms of the coefficients of friction of the reagents

$$\gamma = \left(\frac{\mu}{m_1}\right)\gamma_1 + \left(\frac{\mu}{m_2}\right)\gamma_2,$$

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where m_1 and m_2 are the masses of the reacting particles; γ_1 and γ_2 are their coefficients of friction.

The stationary solution of Eq. (1.1) is the Maxwell–Boltzmann distribution function

$$\rho_e \sim \exp(-\mu v^2/2T - U/T).$$

We introduce into the analysis the moments of the distribution

$$M_n = \int \rho v^n dv.$$

Multiplying the left and right sides of (1.1) by v^n and integrating with respect to v, taking into account the boundary conditions $v^n\rho, \quad v^n \frac{\partial\rho}{\partial v}\Big|_{v\to\infty} = 0$, we obtain the moment equations

$$\frac{\partial M_n}{\partial t} = n\frac{K(x)}{\mu} M_{n-1} - \frac{\partial M_{n+1}}{\partial x} - n\gamma M_n + n(n-1)\frac{\gamma T}{\mu} M_{n-2},$$

where n = 0, 1, 2, ... ($M_{-1} = M_{-2} = 0$).

Let us examine the equations for the moments M_0 and M_1. For time $t > \gamma^{-1}$, the dynamics for establishing equilibrium are simplified, since the velocity probability distribution function is close to Maxwellian. This permits, first of all, solving the stationary equation for the moment M_1 and, second, expressing the moment M_2 in terms of M_0, using their equilibrium ratio:

$$M_2/M_0 \simeq (M_2/M_0)_e = T/\mu.$$

Expressing the moment M_1 in terms of M_0 and assuming that the coefficient of friction does not depend on the reaction coordinate x, we arrive at the Smoluchowski equation

$$\frac{\partial M_0}{\partial t} = (\mu\gamma)^{-1}\frac{\partial}{\partial x}\left(T\frac{\partial M_0}{\partial x} - KM_0\right). \qquad (1.2)$$

The rate of the chemical reaction is the probability that the system per unit time will turn out to be in a state with the coordinate greater than some fixed value x. This quantity is numerically equal to the flux of the probability density or the moment

$$M_1 = (\mu\gamma)^{-1}(KM_0 - T\partial M_0/\partial x).$$

Thus, the moment of the distribution M_1 is the basic quantity sought.

We will solve Eq. (1.2) over a finite segment $[0, l]$ with initial and boundary conditions of the form

$$M_0|_{t=0} = \delta(x - x_0); \qquad (1.3)$$

$$M_1|_{x=0} = 0, \; M_0|_{x=l} = 0. \qquad (1.4)$$

The first boundary condition causes the probability density flux to vanish at the point x = 0, since at this point the repulsive force between the reacting particles increases indefinitely. As the reacting particles move apart to a distance of the order of the mean free path length, they themselves become particles in the surrounding medium. For this reason, the second boundary condition corresponds to an absorbing boundary at the point $x = l$

$$l = l_1 + l_2 = (\sigma N)^{-1}, \; \sigma = \sigma_1\sigma_2/(\sigma_1 + \sigma_2),$$

where l_1 and l_2 are the mean free path lengths for the reacting particles; σ_1 and σ_2 are their collision cross sections; and N is the particle density in the medium.

2. Solution of Smoluchowski's Equation. Kramers' Equations.

Let us make the substitution

$$M_0 = f\exp(-U/T). \qquad (2.1)$$

Substituting (2.1) into (1.2) leads to the equation

$$\exp\left(-\frac{U}{T}\right)\frac{\partial f}{\partial t} = \frac{T}{\mu\gamma}\frac{\partial}{\partial x}\left[\exp\left(-\frac{U}{T}\right)\frac{\partial f}{\partial x}\right]. \qquad (2.2)$$

Integrating (2.2) twice with respect to the coordinate taking into account the first boundary condition (1.4), we obtain

$$f = f_0 + \hat{E}f, \qquad (2.3)$$

where $f_0 = f(x_0, t)$, while the evolution operator is defined by the equation

$$\hat{E} = \frac{\mu\gamma}{T}\int\limits_{x_0}^{x} dx' \exp\left(\frac{U}{T}\right)\int\limits_{0}^{x'} dx'' \exp\left(-\frac{U}{T}\right)\frac{\partial}{\partial t}.$$

We solve Eq. (2.3) by the method of successive approximations, at the first step of which we operate on the function f_0 by the operator $\hat{E}$. As a result, we represent the solution as a series in powers of the operator $\hat{E}$ or a series in terms of the derivatives of the parameter f_0

$$f = f_0 + \hat{E}f_0 + \hat{E}^2 f_0 + \ldots = f_0 + \beta_1(x)\frac{df_0}{dt} + \beta_2(x)\frac{d^2 f_0}{dt^2} + \ldots, \tag{2.4}$$

where

$$\beta_n = \frac{\mu\gamma}{T}\int\limits_{x_0}^{x} dx' \exp\left(\frac{U}{T}\right)\int\limits_{0}^{x'} dx'' \exp\left(-\frac{U}{T}\right)\beta_{n-1}, \quad \beta_0 \equiv 1. \tag{2.5}$$

Terms with high order derivatives are important initially. Then, they decrease in importance and, beginning at some time, in (2.4) it is possible to consider only a finite number of terms [6, 7]. The distribution function, obtained by truncating the series (2.4) and including the n-th order time derivative, has been named the n-th order quasistationary distribution function (QDF). The time variation of the parameter f_0 is determined by substituting the QDF into the second boundary condition (1.4). As a result, an ordinary differential equation for f_0 with constant coefficients arises

$$f_0 + \beta_1(l)\frac{df_0}{dt} + \ldots + \beta_n(l)\frac{d^n f_0}{dt^n} = 0. \tag{2.6}$$

The general solution of (2.6) contains n integration constants. We now substitute the n-th order QDF into the equation for the moments of the initial distribution function (1.3)

$$\int\limits_0^l M_0 |_{t=0} x^m dx = x_0^m. \tag{2.7}$$

Setting m = 0, 1, . . . , (n − 1), we arrive at a system of linear algebraic equations, from whose solution we find the values of the integration constants.

We limit ourselves to examining the first order QDF; integrating (2.6) taking into account (2.7) gives

$$f_0 = c\exp\left(-\frac{t}{\tau}\right); \tag{2.8}$$

$$f(x,t) = \frac{\beta_1(l) - \beta_1(x)}{\int\limits_0^l \exp\left(-\frac{U}{T}\right)[\beta_1(l) - \beta_1(x)]\,dx}\exp\left(-\frac{t}{\tau}\right), \tag{2.9}$$

where the characteristic time for the variation of the distribution function is

$$\tau = \beta_1(l). \tag{2.10}$$

For times $t \ll \tau$, the distribution function does not depend on time and gives a stationary flux M_1 of the probability density, determining the rate of the chemical reaction. Changing the order of integration in the denominator of Eq. (2.9) we have

$$M_1 = -\frac{T}{\mu\gamma}\exp\left(-\frac{U}{T}\right)\frac{\partial f}{\partial x} = \frac{T}{\mu\gamma}\,\frac{g(x)}{\int\limits_0^l \exp\left(\frac{U}{T}\right)g^2(x)\,dx}, \tag{2.11}$$

where $g(x) = \int\limits_0^x \exp\left(-\frac{U}{T}\right)dx'$.

Equation (2.11) was obtained within the scope of the diffusion model and requires that the time τ_{col} between successive collisions, which the reacting system undergoes, is short compared to the characteristic time for the change in the distribution function [3], i.e.,

$$\tau_{\text{col}} \ll \tau. \tag{2.12}$$

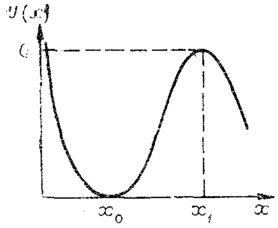

Fig. 1

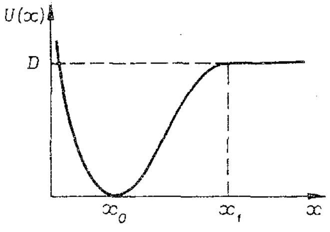

Fig. 2

In addition, Eq. (2.11) is limited by the limits of applicability of the first order QDF. Substituting (2.8) into (2.4), it is evident that in the given series the signs alternate and the terms decrease in absolute magnitude and, therefore, the series converges. The error arising in replacing the exact sum of the series by its partial sum in the corresponding first order QDF is small if the inequality

$$\beta_1(l)[\beta_1(l) - \beta_1(x)] \gg \beta_2(x) \tag{2.13}$$

is satisfied.

It is evident that (2.13) is satisfied for values of the coordinates that are not very close to the boundary $x = l$. Inequalities (2.12) and (2.13) will be discussed below for a specific interaction potential.

We will now examine the problem in which the state of the system of reacting particles passes over the potential barrier and we will show that Eq. (2.11) for gas temperatures T much less than the height of the barrier Q goes over into Kramers' equation [8]. Let the interaction energy U(x) have the form shown in Fig. 1 and let the system be found initially in a state with coordinate x_0. We set $x = x_1$ in (2.11). The main contribution to the integral in the numerator in (2.11) comes from the region near the point x_0, while in the denominator it comes from near the point x_1. Representing the potential in the vicinity of these points in the form

$$U(x) = \frac{1}{2}\mu\omega^2(x - x_0)^2, \quad U(x) = Q - \frac{\mu\omega'^2}{2}(x - x_1)^2,$$

we obtain

$$g(x_1) \simeq \int\limits_{-\infty}^{\infty} \exp\left[-\frac{\mu\omega^2}{2T}(x - x_0)^2\right] dx = \omega^{-1}\left(\frac{2\pi T}{\mu}\right)^{1/2},$$

$$\int\limits_0^l \exp\left(\frac{U}{T}\right) g^2(x)\, dx \simeq g^2(x_1) \int\limits_{-\infty}^{\infty} \exp\left[\frac{Q}{T} - \frac{\mu\omega'^2}{2T}(x - x_1)^2\right] dx = g^2(x_1) \exp\left(\frac{Q}{T}\right)(\omega')^{-1}\left(\frac{2\pi T}{\mu}\right)^{1/2}.$$

From here the probabilities sought equal

$$M_1 = (\omega\omega'/2\pi\gamma)\exp(-Q/T), \quad T \ll Q. \tag{2.14}$$

For the potential which is symmetric relative to the point x_1

$$U(x) = \begin{cases} \frac{1}{2}\mu\omega^2(x - x_0)^2, & x \leqslant x_1, \\ \frac{1}{2}\mu\omega^2(x + x_0 - 2x_1)^2, & x \geqslant x_1, \end{cases}$$

the calculation of the probability for passing over the potential barrier is similar to the preceding case. The numerator in (2.11) retains its previous form. The main contribution to the integral in the denominator in (2.11) again comes from the region near the point x_1. Carrying out the integration, we obtain

$$\begin{gathered} \int\limits_0^l \exp\left(\frac{U}{T}\right) g^2(x)\, dx \simeq \frac{2Tg^2(x_1)}{\omega(2\mu Q)^{1/2}} \exp\left(\frac{Q}{T}\right), \quad Q = U(x_1), \\ M_1 = \frac{\omega^2}{2\gamma}\left(\frac{Q}{\pi T}\right)^{1/2} \exp\left(-\frac{Q}{T}\right), \quad T \ll Q. \end{gathered} \tag{2.15}$$

Equations (2.14) and (2.15) exactly coincide with Kramers' results [8].

3. Dissociation of Diatomic Molecules. Within the scope of the diffusion model, it is possible to examine as well the problem of the dissociation of molecules. We will solve this problem for the interaction potential illustrated in Fig. 2. Let the system be initially found at the bottom of the potential well with coordinate x_0.

As a result of the action of the surrounding medium on the molecule, it dissociates. We will assume that the dissociation process is complete if the distance between the reacting particles becomes of order of the mean free path length in the surrounding medium. For this reason, in Eq. (2.11), we set $x = l$.

Let us first examine the case of relatively low gas temperatures, satisfying the inequality

$$\exp(-D/T)l \ll x_1, \tag{3.1}$$

where D is the dissociation energy of the molecules; x_1 is the characteristic distance beginning with which the interaction potential is practically constant and equals the dissociation energy. We note that for gaseous media, $x_1 \ll l$.

The main contribution to the integral in the numerator in (2.11) in view of inequality (3.1) comes from the region of integration from zero to x_1, while that in the denominator comes from the region from x_1 to l. For this reason,

$$g(l) = g(x_1) \simeq \int\limits_{-\infty}^{\infty} \exp\left[-\frac{\mu\omega^2}{2T}(x - x_0)^2\right] dx = \omega^{-1}\left(\frac{2\pi T}{\mu}\right)^{1/2}, \qquad \int\limits_0^l \exp\left(\frac{U}{T}\right) g^2(x)\, dx = \exp\left(\frac{D}{T}\right) g^2(x_1)\, l,$$

where ω is the vibrational frequency of the molecule near the equilibrium position.

From here, the equation for the dissociation rate constant has the form

$$K = \frac{M_1(l)}{N} = \frac{\sigma\nu}{\gamma}\left(\frac{2\pi T}{\mu}\right)^{1/2} \exp\left(-\frac{D}{T}\right), \quad \omega = 2\pi\nu. \tag{3.2}$$

The dissociation constant, as in the model of single-quantum step-like excitations [3], is proportional to the vibrational frequency of the molecule ν in the ground electronic state, as well as to the gas kinetic number of collisions $z_0 = \sigma(2\pi T/\mu)^{1/2}$. The temperature dependence of the pre-exponential factor in (3.2) is determined by the function $\gamma = \gamma(T)$ and can vary for different temperature intervals.

An estimate of the characteristic dissociation time according to Eq. (2.10) gives

$$\tau = (KN)^{-1}.$$

The diffusion approximation is applicable to the calculation of the dissociation constant, if (2.12) is satisfied. Assuming that

$$\tau_{\text{col}} \sim (\sigma_0 \bar{v} N)^{-1}, \quad \bar{v} \sim (T/m)^{1/2},$$

where σ_0 is the cross section for a collision between the dissociating molecule and a particle in the medium, and m is their reduced mass, we obtain from (2.12)

$$\frac{\sigma}{\sigma_0}\,\frac{\nu}{\gamma}\left(\frac{2\pi m}{\mu}\right)^{1/2} \exp\left(-\frac{D}{T}\right) \ll 1. \tag{3.3}$$

Inequality (3.3) imposes an upper limit on the temperature of the medium.

We will now study the condition (2.13) for the applicability of the first order QDF. For this, to within a factor $\mu\gamma/T$, we present the following estimates:

$$\beta_1(l) \sim \int\limits_{x_0}^{l} \exp\left(\frac{U}{T}\right) g(x)\, dx = \exp\left(\frac{D}{T}\right) g(x_1)\, l,$$

$$\beta_1(x) \sim \int\limits_{x_0}^{x} \exp\left(\frac{U}{T}\right) g(x')\, dx' < \exp\left(\frac{U}{T}\right) x g(x); \quad \exp\left(\frac{U}{T}\right)\frac{x^2}{2},$$

$$\beta_2(x) \sim \int\limits_{x_0}^{x} dx' \exp\left(\frac{U}{T}\right) \int\limits_0^{x'} dx'' \exp\left(-\frac{U}{T}\right) \beta_1(x'') < \int\limits_{x_0}^{x} dx' \exp\left(\frac{U}{T}\right) \int^{x'} dx'' \frac{(x'')^2}{2} < \exp\left(\frac{U}{T}\right)\frac{x^4}{24}.$$

Substituting in (2.13) for $\beta_1(x)$ and $\beta_2(x)$ their highest values, we will thereby investigate the stronger inequality

$$\exp\left(\frac{D}{T}\right) g(x_1)\, l \left[\exp\left(\frac{D-U}{T}\right) g(x_1)\, l - g(x)\, x\right] \gg \frac{1}{24} x^4.$$

For $x \simeq x_1$, this inequality is obviously satisfied and is violated only for values of the coordinates close to the boundary value. For $x > x_1$, we once again make the inequality stronger, setting on the right side $x = l$:

$$\exp(D/T)g^2(x_1)l\,\Delta x \gg (1/24)l^4,$$

where $\Delta x = l - x$.

From here, we find the size of the region near the boundary for which (2.13) is violated:

$$\Delta x \simeq (l^3/g^2(x_1))\exp(-D/T).$$

Since the dissociation rate is equal to the flux of the probability density through the boundary $x = l$, the error in determining the constant from Eq. (3.2) will not be large if $\Delta x \ll l$ or

$$(2\pi\mu v^2/\sigma^2 N^2 T)\exp(-D/T) \ll 1. \tag{3.4}$$

Inequality (3.4), in contrast to (3.3), imposes limitations on the density of the surrounding medium as well.

Let us now turn to the case of high gas temperatures, satisfying the condition

$$\exp(-D/T)l \gg x_1. \tag{3.5}$$

On the strength of inequality (3.5), the numerator in Eq. (2.11) at $x = l$ equals

$$g(l) = \exp(-D/T)\,l.$$

Estimates show that just as for low temperatures, the main contribution to the integral in the denominator in (2.11) comes from the region of integration over the segment $[x_1, l]$. For this reason

$$\int_0^l \exp\left(\frac{U}{T}\right) g^2(x)\,dx = \exp\left(\frac{D}{T}\right)\int_{x_1}^{l}\left[g(x_1) + \exp\left(-\frac{D}{T}\right)(x - x_1)\right]^2 dx = \frac{l^3}{3}\exp\left(-\frac{D}{T}\right).$$

In this case, we use the obvious inequality $g(x_1) < x_1$ and (3.5). Substituting these expressions into (2.11), we obtain an equation for the dissociation rate constant

$$K = 3T\sigma^2 N/\mu\gamma. \tag{3.6}$$

In contrast to the low-temperature case, here the constant is proportional to the density of particles in the medium and does not depend on the vibrational frequency of the molecule near the equilibrium position. The temperature dependence is also determined by the form of the function $\gamma = \gamma(T)$.

A calculation of the characteristic dissociation time (2.10) leads to the equation

$$\tau = \left(\frac{2}{3}KN\right)^{-1}.$$

Let us now discuss the limits of applicability of Eq. (3.6). Condition (2.12) for the correctness of using the diffusion approximation gives

$$(2\sigma^2/\gamma\sigma_0)(mT/\mu^2)^{1/2}N \ll 1. \tag{3.7}$$

For gaseous media, inequality (3.7) is almost always satisfied.

Let us examine condition (2.13) for applicability of the first order QDF. For high temperatures (3.5), estimates of $\beta_1(x)$ and $\beta_2(x)$ are the same as for low temperatures. Only the value of $\beta_1(l)$, in the integral for which the region x_1 to l gives the main contribution, will change:

$$\beta_1(l) \sim \exp\left(\frac{D}{T}\right)\int_{x_1}^{l}\left[g(x_1) + \exp\left(-\frac{D}{T}\right)(x - x_1)\right]dx = \frac{l^2}{2}.$$

Substituting into (2.13) leads to the stronger condition

$$l^2[\exp(-U/T)l^2 - x^2] \gg (1/6)x^4. \tag{3.8}$$

For $x \simeq x_1$, (3.8) is satisfied. For $x > x_1$, we have

$$\exp(-D/T) - z \gg (1/6)z^2,\quad z = (x/l)^2. \tag{3.9}$$

We now require that the left part of (3.9) be at least six times greater than the right side. Then, we arrive at the inequality

$$z^2 + z - \exp(-D/T) < 0,$$

whose solution gives

$$z < [1/4 + \exp(-D/T)]^{1/2} - 1/2 \simeq \exp(-D/T)$$

or

$$x < \exp(-D/2T)l.$$

The size of the region nearest the boundary where condition (2.13) breaks down equals

$$\Delta x = l[1 - \exp(-D/2T)].$$

Equation (3.6) will correctly determine the order of magnitude of the constant, if $\Delta x \lesssim l/2$. From here, we obtain the condition for the temperature of the medium

$$T \geqslant D/2\ln 2 = 0{,}72\, D.$$

In calculating the integral $g(x_1)$ in the problem of dissociation with relatively low temperatures of the medium, a parabolic interaction potential $U(x)$ was used near the equilibrium position. This approximation corresponds to independent harmonic vibrations and rotation of the molecule in the center of mass system of the reacting particles. Deviations from the parabolic law arise as a result of taking into account anharmonicity of the vibrations and their interactions with rotation. In this case, the interaction potential near the equilibrium position can be represented in the form [14]

$$U(x) = \frac{1}{2}\mu\omega^2 x_0^2(\xi^2 - \alpha\xi^3 + \beta\xi^4), \tag{3.10}$$

where $\xi = x/x_0 - 1$; α and β are some molecular constants, related to the rotational constant of the molecule, anharmonicity, and the vibrational–rotational coupling constants [14].

We will calculate the integral $g(x_1)$ for the potential (3.10) and find corrections to the dissociation rate constant (3.2). Substituting (3.10) into the equation for $g(x_1)$, we obtain

$$g(x_1) = \int_0^{x_1} \exp\left[-\frac{\mu\omega^2 x_0^2}{2T}(\xi^2 - \alpha\xi^3 + \beta\xi^4)\right]dx \simeq \int_{-\infty}^{\infty} \exp\left(-\frac{\mu\omega^2}{2T}x^2\right)$$
$$\times\left(1 + Ax^3 + \frac{1}{2}A^2x^6\right)(1 - Bx^4)\,dx = \int_{-\infty}^{\infty} \exp\left(-\frac{\mu\omega^2}{2T}x^2\right)$$
$$\times\left(1 - Bx^4 + \frac{1}{2}A^2x^6\right)dx = \omega^{-1}\left(\frac{2\pi T}{\mu}\right)^{1/2}\left[1 + \frac{T}{\mu\omega^2 x_0^2}\left(\frac{15}{8}\alpha^2 - \frac{3}{2}\beta\right)\right].$$

From here, Eq. (3.2), taking into account the anharmonicity of the vibrations and their interactions with rotation, takes the form

$$K = \frac{\sigma v(2\pi T/\mu)^{1/2}}{\gamma\left[1 + \frac{T}{\mu\omega^2 x_0^2}\left(\frac{15}{8}\alpha^2 - \frac{3}{2}\beta\right)\right]}\exp\left(-\frac{D}{T}\right).$$

4. Calculation of the Constants of Specific Reactions and Comparison with Experimental Results.

Let us calculate the constants of some dissociation reactions, estimating the frictional coefficient from Stokes' equation

$$\gamma_i = 6\pi a_i\eta/m_i \quad (i = 1,\ 2),$$

where a_i is the radius of the i-th reacting particle; m_i is its mass; and η is the temperature-dependent coefficient of viscosity of the medium.

We will assume that the cross sections for collisions between the reacting particles and particles in the surrounding medium equal the geometric values

$$\sigma_i = \pi(a_i + a)^2 \quad (i = 1,\ 2),$$

where a is the radius of a particle in the surrounding medium.

We first examine the dissociation reaction for oxygen in argon

$$O_2 + Ar = O + O + Ar$$

with the temperature of the surrounding medium T = 1000°K and the viscosity coefficient for argon at the temperature indicated $\eta = 5.5 \cdot 10^{-4}$ g·cm^{-1}·sec^{-1} [15]. For the calculation, we used the following data: $a_1 = a_2 =$ 0.06 nm [16], $a = 0.15$ nm [16], $\nu = 1580$ cm^{-1} [16] (for the ground electronic term of the oxygen molecule). As a result of calculations using Eq. (3.2), the theoretical value of the pre-exponential factor equals $2.2 \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1}. The experimental value is $(1\text{-}2.4) \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1} [17].

For the dissociation of a hydrogen molecule in argon

$$H_2 + Ar = H + H + Ar$$

with parameters T = 1300°K, $\eta = 6.16 \cdot 10^{-4}$ g·cm^{-1}·sec^{-1} [15], $a_1 = a_2 = 0.04$ nm [16], $a = 0.15$ nm, $\nu = 4400$ cm^{-1} [16], the theoretical value of the pre-exponential factor in (3.2) is $1.9 \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1} and the experimental value is $2.3 \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1} [17].

For the reaction

$$H_2 + H_2 = H + H + H_2$$

with parameters T = 1300°K, $\eta = 2.35 \cdot 10^{-4}$ g·cm^{-1}·sec^{-1} [15], $a_1 = a_2 = 0.04$ nm, $a = 0.11$ nm [16], $\nu = 4400$ cm^{-1}, the theoretical value of the pre-exponential factor in (3.2) is $3.1 \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1} and the experimental value is $8.2 \cdot 10^{15}$ cm^3·mole^{-1}·sec^{-1} [17].

Exchange reactions such as

$$A + BC = AB + C$$

can also be investigated within the scope of the diffusion model.

In the general case, the calculation of the constant for this reaction must depend on the results of the problem of the interaction of three particles in the presence of a random force. In this case, it is necessary to integrate a higher order Fokker–Planck equation in contrast to (1.2). The problem can be simplified if it is assumed that the exchange reaction proceeds with the formation of a bound complex ABC. Then, the exchange reaction can be viewed as the association of particles A and BC in the molecule ABC and, then, the dissociation of the molecule ABC into particles AB and C. Thus, for a number of types of chemical reactions, the approach examined here gives the practical possibility of calculating the constants.

We note that the limits of applicability of the diffusion model are also determined by the classical nature of the approach. In particular, the de Broglie wavelength must be small compared to the characteristic distance over which the interaction varies. In this sense, the equations obtained are not applicable to calculating the reaction constants for reactions that occur with a change in the electronic state of the reacting particles. Such reactions must be described using a quantum mechanical analysis.

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DETERMINATION OF THE DIMENSIONS OF THE SATURATION ZONE FOR INFILTRATION FROM A CHANNEL WITH A SHALLOW WATER DEPTH

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A hydrodynamic solution has been considered [1-4] for the planar stationary case of a freshwater lens established by infiltration in accordance with Darcy's law from a channel involving the displacement of saline groundwater from the channel zone. It is assumed that the depth of water in the channel is infinitely shallow and that the flow factor that compensates for the loss from the channel is evaporation from the free surface. Here we examine infiltration from a channel into a layer of homogeneous isotropic soil of thickness T with a horizontal impermeable layer underneath. This case is a limiting one for the above problem when the density of the saline water increases without limit. The solution is found as in [1-4] by the method of [5], which is based on the analytical theory of ordinary differential equations. The canonical region is taken as the region for which the characteristics of the filtration flow can be derived in closed form in terms of certain special functions.

In view of the symmetry of the infiltration region we restrict consideration to the right-hand half, which is shown schematically in Fig. 1. The bottom of the channel is represented by a horizontal line of length $2l$. With the coordinate system shown in Fig. 1, we locate the plane of potential comparison in the plane $y = 0$, and then the following conditions are obeyed at the boundary of the infiltration region:

$$\begin{gathered} y = 0,\ \varphi_r = 0 \ \text{on } AD,\ x = 0,\ \psi_r = 0 \ \text{on } AB,\ y = T,\ \psi_r = 0 \ \text{on } BC, \\ \varphi_r + y = 0,\ \psi_r + \varepsilon_r x = \varepsilon_r L \ \text{on } CD, \end{gathered} \tag{1}$$

where $\omega_r = \varphi_r + i\psi_r$ is the complex filtration potential referred to the filtration coefficient, with φ_r the reduced potential for the filtration rate and ψ_r the reduced current function, while $z = x + iy$ is the complex coordinate in the infiltration region and ε_r is the reduced evaporation rate.

As the auxiliary region we take half the plane of w in Fig. 2. In the method used here, the functions $d\omega/dw$ and dz/dw are unknowns to be determined as the solutions to a certain linear differential equation of the Fuchs class with regular singular points. We first consider the behavior of the functions $d\omega/d\zeta$ and $dz/d\zeta$, where ζ is the upper half-plane, and we find that the characteristic parameters of these functions near the singular points have the following values: near point A $(\zeta = -a)(-1/2, -1/2)$, near point B $(\zeta = 0)(-1/2, 0)$, near point C $(\zeta = 1)(\nu/2 - 1/2, -\nu/2 - 1/2)$, and near point D $(\zeta = \infty)(3/2, 2)$, where $\nu = 1 - (2/\pi)\arctan\sqrt{\varepsilon_r}$, and the singularity at point $\zeta = -a$ can be eliminated.

The solution that satisfies the conditions of (1) takes the form

$$\frac{d\omega}{dw} = A\frac{\sqrt{\varepsilon_r}\,\operatorname{sh}\nu w}{\sqrt{\operatorname{sh}^2 w + a\operatorname{ch}^2 w}},\quad \frac{dz}{dw} = A\frac{\operatorname{ch}\nu w}{\sqrt{\operatorname{sh}^2 w + a\operatorname{ch}^2 w}}, \tag{2}$$

where A is some real constant.

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