Low-temperature chemical reactions considered as dissipative tunnel systems

Yu. I. Dakhanovskiĭ, A. A. Ovchinnikov, and M. B. Semenov

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow
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An analysis is made of low-temperature chemical reactions occurring in condensed media. The reaction constants of elementary events are calculated in the semiclassical (instanton) approximation. It is shown that in the case of specific types of vibrational spectra of a medium a reaction may slow down, and for symmetric reactions complete stoppage may occur. The semiclassical action (argument of the exponential function) and the preexponential factor in the rate constant are calculated exactly for a two-well potential in the form of two parabolas along the reaction coordinate. The condition for validity of the theory which guarantees quasistatic occurrence of the kinetic process (exponential decay of the tunneling probability with time) is found.

1. INTRODUCTION

Low-temperature chemical reactions in condensed phases have been demonstrated convincingly for the majority of reaction systems.[1,2] The reaction rates are characterized by a low-temperature plateau, whereas at high temperatures the temperature dependence is of the activated type. Conventionally a chemical reaction is understood to be the transfer of a particle from one reaction center to another. A necessary condition for a chemical reaction is the breaking of old chemical bonds and formation of new ones. We shall extend somewhat the range of physical and chemical kinetic processes of interest. In particular, we shall understand a chemical reaction to be also the transfer of an electron which does not alter chemical bonds of the reaction centers, a transition between left- and right-hand optically active isomers characterized by chiral symmetry, an inversion transition between symmetric positions of tetrahedral molecules (NH_3, CH_4,...) in a condensed medium, and similar processes.

We shall be interested in adiabatic chemical reactions, i.e., the reactions for which the Landau-Zener parameter is large:

$$\Delta^2/\hbar u|F_2-F_1| \gg 1,$$

where Δ is the electron matrix element of the interaction between the initial and final states; u is the velocity of the particle being transported; $F_{1,2}$ are the forces at the term-crossing point. In this case the repulsion of the electron terms is large, the reaction system is characterized by a single potential surface, and transitions to the upper branch are negligible.

Our purpose is to determine the influence of the medium on the tunneling rate. We shall select the simplest form of a two-well potential: $U(x) = \frac{1}{2}m\omega^2(|x| - x_0)^2$. In the case of tunnel processes this selection is justified if the duration of motion below the vertex part of the potential is short, i.e., if

$$\Omega_{\text{vert}}^{-1} \ll \omega^{-1},$$

where Ω_{vert} is the "frequency" of the vertex part of the potential and ω is the frequency of the well in the initial (final) state. However, in spite of such model selection of the tunneling potential, we hope to reproduce all the main features of the influence of the medium on the tunneling rate.

Low-frequency motion of the medium, which cannot be described on the basis of the Einstein model, plays a special role in the tunnel process. The nature of this process may be modified greatly by low-frequency vibrations which in the limit of high temperatures are responsible for the Brownian motion of the transported particle.

The low-temperature motion of a Brownian particle was first discussed in Refs. 3 and 4 for the tunneling of the superconducting phase at Josephson contacts. The generalization to arbitrary temperatures is given in Refs. 5–7. An important conclusion which follows from these investigations is the slowing down of the tunneling rate in the presence of a medium, but one should allow here for renormalization of the one-dimensional potential in which a particle is moving along the tunneling coordinate. The total probability of decay is governed by the sum of the contributions of the probabilities of quantum tunneling and classical above-barrier motion (the range of temperatures where these contributions are approximately the same is considered in Ref. 5). We shall be interested only in the quantum tunneling mechanism, i.e., we shall consider only low temperatures.

One should point out the difference between meta-stable decay in Josephson contacts and in chemical reactions. In the former case we are concerned mainly with a potential in the form of a cubic parabola so that the final state of the system is described by a continuous spectrum. In the case of chemical reactions the tunneling potential is of the two-well type and the final state is not always of the decay type. We shall show below that this feature imposes restrictions on the temperature, viscosity, and other parameters of the system.

In the next section we shall consider the formulation of the problem of the tunneling of a particle in chemical kinetics and show how the initial Hamiltonian of the reaction system can be reduced to the usual Hamiltonian describing tunnel transitions subject to dissipation. In Sec. 3 we shall find the argument of the exponential function in the tunneling rate (semiclassical action), determine the preexponential factor, and provide the criterion for validity of the quasi-steady approximation. In Sec. 4 we shall discuss several

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important special cases of the vibrational spectrum of molecules in the medium. The conclusions will be presented in Sec. 5.

2. INTRODUCTION OF A TUNNELING COORDINATE

The state of a reaction system in a medium can be described by a multidimensional potential surface. In considering the low-temperature kinetics a good approximation for this surface is provided by two paraboloids:

$$U_i=\sum_{i=1}^{N}\omega_{0i}^2(x_i+x_{0i})^2/2, \qquad U_j=\sum_{i=1}^{N}\omega_{0i}^2(x_i-x_{0i})^2/2-\Delta I. \tag{1}$$

We shall assume that at low temperatures the terms of the initial and final states can be represented by a set of oscillators with frequencies ω_{0i} shifted relative to one another by $2x_{0i}$ and we shall assume that the oscillator masses are 1, which renormalizes the coordinate to the root of the relevant mass. The final-state term is located below the initial term and the difference is ΔI (heat of reaction). The surface of intersection of two paraboloids is a plane described by

$$2\lambda\sum_{i=1}^{N}\gamma_i x_i=-\Delta I, \tag{2}$$

where

$$\gamma_i=x_{0i}\omega_{0i}^2/\lambda, \tag{3}$$

$$\lambda^2=\sum_{i=1}^{N}\omega_{0i}^4x_{0i}^2 \tag{4}$$

and the following normalization condition is obeyed:

$$\sum_{i=1}^{N}\gamma_i^2=1. \tag{5}$$

The spatial coordinate perpendicular to the plane (2) will be called the tunneling coordinate. We shall select it from all possible coordinates and choose the coordinates in the plane (2) in such a way that the remaining $N-1$ oscillators do not interact with one another and are only linearly related to the tunneling coordinate. We shall consider an orthogonal rotation of the coordinate system as a result of which one coordinate coincides with the tunneling coordinate

$$y_1=\sum_{i=1}^{N}\gamma_i x_i, \tag{6}$$

whereas the remaining $N-1$ coordinates reduce the potential energy in the plane (2) to the diagonal form:

$$y_j=\sum_{i=1}^{N}U_{ji}x_i, \tag{7}$$

where $U_{1i}=\gamma_i$. Then the quadratic form $\sum_{i=1}^{N}\omega_{0i}^2x_i^2$ can be reduced to

$$\omega_1^2y_1^2+2y_1\sum_{\alpha=2}^{N}C_\alpha y_\alpha+\sum_{\alpha=2}^{N}\omega_\alpha^2y_\alpha^2, \tag{8}$$

where ω_α^2 satisfies the following eigenvalue equation (this equation is derived in the Appendix):

$$\sum_{i=1}^{N}\frac{\gamma_i^2}{\omega_{0i}^2-\omega_\alpha^2}=0, \tag{9}$$

whereas

$$\omega_1^2=\sum_{i=1}^{N}\omega_{0i}^2\gamma_i^2, \tag{10}$$

$$C_\alpha=\left[\sum_{i=1}^{N}\frac{\gamma_i^2}{(\omega_{0i}^2-\omega_\alpha^2)^2}\right]^{-1/2}. \tag{11}$$

Using Eqs. (8)–(11), the Hamiltonian of the system can be written as follows:

$$\hat{H}=\frac{p_1^2}{2}+v_1(y_1)+y_1\sum_{\alpha=2}^{N}C_\alpha y_\alpha+\frac{1}{2}\sum_{\alpha=2}^{N}(p_\alpha^2+\omega_\alpha^2y_\alpha^2), \tag{12}$$

where

$$v_1(y_1)=(^1/_2\omega_1^2y_1^2+\lambda y_1)\theta(-\Delta I/2\lambda-y_1)+(^1/_2\omega_1^2y_1^2-\lambda y_1-\Delta I)\theta(\Delta I/2\lambda+y_1). \tag{13}$$

The probability of tunneling of a particle per unit time can be found in the semiclassical approximation. It is essential to ensure that the de Broglie wavelength of the particle is much less than the characteristic linear scale of the potential. This is done simply by making the barrier height much greater than the energy of zero-point vibrations in the well of the initial state.[8] In addition to the semiclassical approximation, we have to assume that the decay is quasisteady (for details see Refs. 9 and 10), i.e., that the width of the level Γ from which a particle is tunneling should be much less than the energy of zero-point vibrations. In the case of a finite temperature the probability of decay per unit time is defined as follows:

$$\Gamma=2T\,\mathrm{Im}\,Z/\mathrm{Re}\,Z. \tag{14}$$

Here, Z is the partition function of the system which, because of decay, is a complex variable. A discussion of the validity of generalizations of this expression to the multidimensional case can be found in Refs. 9 and 10. In calculating Γ it is convenient to represent Z as a path integral[11]:

$$Z=\prod_{\alpha}\int Dy_1\int Dy_\alpha\exp[-S\{y_1;y_\alpha\}]. \tag{15}$$

Since we are interested in the oscillator states in the initial and final states, we can integrate with respect to paths $y_\alpha(\tau)$ and with respect to the initial conditions $y_\alpha(-\beta/2)=y_\alpha(\beta/2)$ (here, $\beta=T^{-1}$).[4,12] The action functional depends only on the path $y_1(\tau)$:

$$S\{y_1\}=\int_{-\beta/2}^{\beta/2}d\tau\left[\frac{1}{2}\dot{y}_1^2+v(y_1)+\frac{1}{2}\int_{-\beta/2}^{\beta/2}d\tau'K(\tau-\tau')y_1(\tau)y_1(\tau')\right], \tag{16}$$

where

$$v(y_1)=v_1(y_1)-\frac{1}{2}\sum_{\alpha=2}^{N}\frac{C_\alpha^2}{\omega_\alpha^2}y_1^2. \tag{17}$$

This potential is renormalized, i.e., the adiabatic potential is introduced (for a discussion of this topic see Ref. 4). The kernal of the integral term in Eq. (16) depends only on the oscillator parameters. The Fourier coefficients ζ_n in the expansion of the kernal $K(\tau)$ as a Fourier series are defined as follows:

$$\zeta_n = \nu_n^2 \sum_{\alpha=2}^{N} \frac{C_\alpha^2}{\omega_\alpha^2(\omega_\alpha^2+\nu_n^2)}. \tag{18}$$

Here, $\nu_n \equiv 2\pi n T$ is the Matsubara frequency. For convenience in the calculations we shall now shift the coordinate y_1 in such a way that the maximum of the potential $v(y_1)$ is located at the point $q = 0$, i.e., that

$$q = y_1 + \Delta I/2\lambda. \tag{19}$$

Then,

$$v(q) = {}^1/_2\omega_0^2(q+q_0)^2\theta(-q) + [{}^1/_2\omega_0^2(q-q_1)^2 - \Delta I]\theta(q), \tag{20}$$

where

$$\omega_0^2 = \omega_1^2 - \sum_{\alpha=2}^{N} \frac{C_\alpha^2}{\omega_\alpha^2}, \tag{21}$$

$$q_0 = \lambda/\omega_0^2 - \Delta I/2\lambda, \quad q_1 = \lambda/\omega_0^2 + \Delta I/2\lambda.$$

3. CALCULATION OF THE TUNNELING RATE IN THE ONE-INSTANTON APPROXIMATION

The partition function Z can be calculated in the semiclassical approximation. It is assumed that the action $S\{q\}$ is dominated by the path $q_B(\tau)$ (instanton) which minimizes the action functional (16) and obeys the Euler-Lagrange equation:

$$-\ddot{q}_B(\tau) + \frac{\partial v(q_B)}{\partial q_B} + \int_{-\beta/2}^{\beta/2} d\tau' K(\tau-\tau') q_B(\tau') = 0, \tag{22}$$

where the path $q_B(\tau)$ is sought in the class of periodic functions

$$q_B(\tau) = q_B(\tau+\beta).$$

The path $q_B(\tau)$ is shown in Fig. 1. The nature of $q_B(\tau)$ is determined from the nature of motion of a particle in the potential $-v(q)$. The particle begins its motion (at zero temperature) at the vertex of the potential $-v(q)$, i.e., at the point $-q_0$, then passes through a minimum ($q_B = 0$) at time $\tau = -\tau_0$ and reaches the value $q_B = q_0$ (in the case of a symmetric potential) at time $\tau = 0$. Then, the particle repeats the path in the opposite direction. Such a path is called an instanton.[13-15] It is remarkable that the action for the path $q_B(\tau)$ is independent of the position of the center of the instanton. The time τ_0 is found from the condition

$$q_B(\tau_0) = 0. \tag{23}$$

Introduction of the time τ_0 makes it much easier to solve Eq. (22) because step functions of the coordinate can be replaced with corresponding functions of time.

The path $q_B(\tau)$ will be sought as a Fourier series:

$$q_B(\tau) = \beta^{-1} \sum_{n=-\infty}^{\infty} q_n \exp(i\nu_n\tau). \tag{24}$$

Expanding also the θ functions and the kernal $K(\tau)$ as Fourier series, we obtain equations for the Fourier coefficients q_n, which can be solved exactly. We then have

$$q_B(\tau) = -q_1 + \frac{2(q_0+q_1)\tau_0}{\beta} + \frac{2\omega_0^2(q_1+q_0)}{\beta} \sum_{n=1}^{\infty} \frac{\sin\nu_n\tau_0 \cos\nu_n\tau}{\nu_n(\nu_n^2+\omega_0^2+\zeta_n)}, \tag{25}$$

where ζ_n is found from Eq. (18). We shall substitute next Eq. (25) in the expression for the action. We then find that

$$S_B = 2\omega_0^2(q_0+q_1)q_1\tau_0 - 2\omega_0^2(q_0+q_1)^2\tau_0^2/\beta - \frac{4\omega_0^4(q_0+q_1)^2}{\beta} \sum_{n=1}^{\infty} \frac{\sin^2\nu_n\tau_0}{\nu_n^2(\nu_n^2+\omega_0^2+\zeta_n)}. \tag{26}$$

Therefore, the quasiclassical action is defined exactly in the one-instanton approximation.

We shall now calculate the preexponential factor. Its value is governed by the contribution of the paths located close to the instanton. We can do this by expanding the action up to the term quadratic in deviations $q - q_B$ and integrating in the functional space.[13-15] The tunneling probability per unit time can then be written in the form

$$\Gamma = B\exp(-S_B), \tag{27}$$

where

$$B = \left[\frac{S_0}{2\pi} \frac{\det(\delta^2 S/\delta q^2)_{q=-q_0}}{\det'(\delta^2 S/\delta q^2)_{q=q_B(\tau)}}\right]^{1/2}, \tag{28}$$

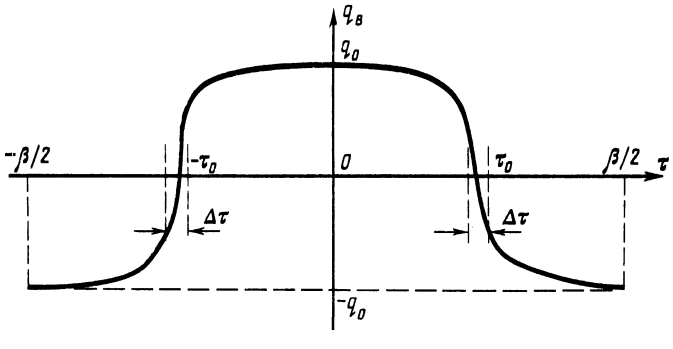

FIG. 1. Path of an instanton $q_B(\tau)$. Here, τ_0 is the center of the instanton and $\Delta\tau$ is its width.

$$S_0 = \int_{-\beta/2}^{\beta/2} \dot{q}_B^2(\tau)\, d\tau, \tag{29}$$

and det' means that the zero eigenvalue corresponding to the zeroth instanton mode is omitted. It should be pointed out that the derivation of this formula is based on the approximation of an ideal instanton gas[14,15]

$$\Gamma \ll (\Delta\tau)^{-1}, \tag{30}$$

where $\Delta\tau$ is the width of the transition from the initial value of the path to the negatve value (see Fig. 1). Strictly speaking, the path $q_B(\tau)$ is a sum of two paths: an instanton and an antiinstanton. If τ_0 is large, we can assume that the interaction between an instanton and an antiinstanton is weak. However, the approximation is invalid at low values of τ_0. We shall therefore consider not an ideal instanton gas but a rarefied gas of instanton-antiinstanton pairs. The width $(\Delta\tau)^{-1}$ will be defined as follows:

$$(\Delta\tau)^{-1} = |\dot{q}_B(\tau_0)|/q_0. \tag{31}$$

In Eq. (28) the expression $\det(\delta^2 S/\delta q^2)$ represents calculation of the product of the eigenvalues of the following equation[13-15]:

$$\left[-\frac{\partial^2}{\partial\tau^2} + \frac{\partial^2 v}{\partial q^2} - \lambda\right] q(\tau) + \int_{-\beta/2}^{\beta/2} d\tau'\, K(\tau-\tau')\, q(\tau') = 0. \tag{32}$$

The second derivative of the potential with respect to position is taken either for the instanton or at the point of the minimum of the metastable potential. In the case of our potential we have

$$\partial^2 v/\partial q^2 = \omega_0^2 - \omega_0^2(q_0+q_1)\delta(q), \tag{33}$$

where we shall use the condition

$$\omega_0^2(q_1^2 - q_0^2)/2 = \Delta I.$$

We shall first calculate the eigenvalues of Eq. (32) for $q = -q_0$. As in the case of an instanton, the eigenfunctions will be sought in the class of periodic functions. Expanding the path and the kernal $K(\tau)$ as Fourier series, we obtain the eigenvalues λ_{0n} of Eq. (32):

$$\lambda_{0n} = \nu_n^2 + \omega_0^2 + \zeta_n. \tag{34}$$

We shall now find the product of the eigenvalues of Eq. (32) in the instanton path. The eigenvalue equation then becomes

$$\left[-\frac{\partial^2}{\partial\tau^2} + \omega_0^2 - \lambda\right] q(\tau) - \frac{\omega_0^2(q_0+q_1)}{|\dot{q}_B(\tau_0)|}\left[\delta(\tau+\tau_0) + \delta(\tau-\tau_0)\right] + \int_{-\beta/2}^{\beta/2} d\tau'\, K(\tau-\tau')\, q(\tau') = 0. \tag{35}$$

The solution of this equation will also be sought in the class of periodic functions. Expanding $q(\tau)$, δ functions, and $K(\tau)$ as Fourier series and integrating with respect to τ using a factor $\exp(-i\nu_l\tau)$, we find that

$$(\nu_l^2 + \omega_0^2 + \zeta_l - \lambda)\, q_l = \frac{2\omega_0^2(q_0+q_1)}{\beta|\dot{q}_B(\tau_0)|}\left[A\sin\nu_l\tau_0 + B\cos\nu_l\tau_0\right], \tag{36}$$

where

$$A = \sum_{n=-\infty}^{\infty} q_n \sin\nu_n\tau_0, \qquad B = \sum_{n=-\infty}^{\infty} q_n \cos\nu_n\tau_0.$$

Equation (36) can be used to find q_l; substitution of q_l into A and B gives two eigenvalue equations:

$$\sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}} = \sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n} - \lambda^{(1)}}, \tag{37a}$$

$$\sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}} = \sum_{n=-\infty}^{\infty} \frac{\cos^2\nu_n\tau_0}{\lambda_{0n} - \lambda^{(2)}}. \tag{37b}$$

We are assuming here that

$$|\dot{q}_B(\tau_0)| = \frac{2\omega_0^2(q_0+q_1)}{\beta} \sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}}.$$

In the first of the above equations there is an eigenvalue $\lambda = 0$ corresponding to the zeroth mode which has to be excluded from the product of roots. According to the Viet theorem, the product of roots in the first equation (in the absence of $\lambda = 0$) can be found exactly:

$$\lambda_1^{(1)} \ldots \lambda_n^{(1)} \ldots = \lambda_{01} \ldots \lambda_{0n} \ldots \sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}^2} \left(\sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}}\right)^{-1}. \tag{38}$$

We shall similarly determine the product of the second series of roots:

$$\lambda_0^{(2)} \ldots \lambda_n^{(2)} \ldots = \lambda_{00} \ldots \lambda_{0n} \ldots \sum_{n=-\infty}^{\infty} \frac{\cos 2\nu_n\tau_0}{\lambda_{0n}} \left(\sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}}\right)^{-1}. \tag{39}$$

We can finally find the preexponential factor by normalization of the zeroth mode S_0 described in Eq. (29):

$$S_0 = \frac{4\omega_0^4(q_0+q_1)^2}{\beta} \sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}^2}. \tag{40}$$

Using Eqs. (38)–(40), we now obtain the preexponential factor:

$$B = \frac{2\omega_0^2(q_0+q_1)^2}{(2\pi\beta)^{1/2}} \sum_{n=-\infty}^{\infty} \frac{\sin^2\nu_n\tau_0}{\lambda_{0n}} \left(\sum_{n=-\infty}^{\infty} \frac{\cos 2\nu_n\tau_0}{\lambda_{0n}}\right)^{-1/2}. \tag{41}$$

The problem of tunneling of a particle in the model potential of Eq. (1) is thus solved exactly in the one-instanton approximation. The argument of the exponential function is determined by the semiclassical action of Eq. (26) and the preexponential function B is described by Eq. (41). The quasisteady condition (30) (for an ideal gas of instanton-antiinstanton pairs) imposes restrictions on temperature and other parameters of the system.

4. SPECIAL CASES FOR ζ_n and ΔI

1. The important case of the spectral density of phonons is the ohmic damping approximation, i.e., $\zeta_n = \gamma|\nu_n|$. This case corresponds to viscous motion of a particle in the classical limit when the probability of transition per unit time is that calculated by Kramers.[16] At low temperatures the series

in the expression for the action can be summed by the Euler-MacLaurin method which gives

$$S_B \approx \omega_0^2(q_1^2-q_0^2)\tau_0 + \frac{(q_1+q_0)^2}{\pi}\frac{\Lambda_2^2\ln(\Lambda_1/\omega_0)-\Lambda_1^2\ln(\Lambda_2/\omega_0)}{\Lambda_2-\Lambda_1}$$

$$+\frac{\gamma(q_1+q_0)^2}{\pi}(C+2\ln 2)$$

$$+\frac{\gamma(q_1+q_0)^2}{\pi}\ln\left(\frac{\omega_0\beta}{4}\sin^2\frac{\pi\tau_0}{\beta}\right)+O(\beta^{-2}). \qquad (42)$$

Here, C is the Euler constant and $\Lambda_1\tau_0, \Lambda_2\tau_0 \gg 1$. We can similarly calculate the preexponential factor

$$B=\frac{2\omega_0^2(q_0+q_1)\ln(\Lambda_2/\Lambda_1)\sin(2\pi\tau_0/\beta)}{\pi^2(2\gamma)^{1/2}(\Lambda_2-\Lambda_1)}. \qquad (43)$$

The case of a symmetric potential ($\tau_0=\beta/4, q_1=q_0$) is of special interest. The action of Eq. (42) then diverges at low temperature

$$S_B \approx \frac{4q_0^2}{\pi}\frac{\Lambda_2^2\ln(\Lambda_1/\omega_0)-\Lambda_1^2\ln(\Lambda_2/\omega_0)}{\Lambda_2-\Lambda_1}$$

$$+\frac{4\gamma q_0^2}{\pi}(C+2\ln 2)+\frac{4\gamma q_0^2}{\pi}\ln\left(\frac{\omega_0\beta}{4\pi}\right)+O(\beta^{-2}), \qquad (44)$$

and the preexponential factor is

$$B\approx 4\omega_0^4 q_0 \ln(\Lambda_2/\Lambda_1)/\pi^2(\Lambda_2-\Lambda_1)(2\gamma)^{1/2}. \qquad (45)$$

We shall consider the complete expression for the tunneling rate:

$$\Gamma=B_0(2\gamma)^{-1/2}(\beta\omega_0/4\pi)^{1-4\gamma q_0^2/\pi}\exp(-S_B'), \qquad (46)$$

where

$$B_0=16\omega_0^3 q_0 \ln(\Lambda_2/\Lambda_1)/\pi(\Lambda_2-\Lambda_1),$$

$$S_B'=\frac{4q_0^2}{\pi}\frac{\Lambda_2^2\ln(\Lambda_1/\omega_0)-\Lambda_1^2\ln(\Lambda_2/\omega_0)}{\Lambda_2-\Lambda_1}+\frac{4\gamma q_0^2}{\pi}(C+2\ln 2).$$

It is clear from Eq. (46) that, depending on the sign of the power exponent in front of the factor $\beta\omega_0$, we can have three cases discussed below.

a) If we assume that

$$4\gamma q_0^2/\pi > 1, \qquad (47)$$

then in the case of sufficiently strong damping a particle becomes localized in the well of the initial state. This effect is not observed if the reaction is simulated by a two-frequency model.[1] Localization of a particle means breaking of the symmetry for the right and left positions. A similar temperature dependence is obtained in a two-level model in Ref. 17.

b) When the inequality of Eq. (47) is reversed, it is found that the quasisteady condition is disobeyed at low temperatures and temperature is limited by the inequality of Eq. (30).

c) If $4\gamma q_0^2/\pi = 1$, the tunneling rate is independent of temperature.

The condition of validity of the theory of the ohmic damping case is

$$\frac{4q_0\omega_0^2}{\pi(2\gamma)^{1/2}}\left(\frac{\beta\omega_0}{4\pi}\right)^{1-4\gamma q_0^2/\pi}\exp(-S_B')\ll 1. \qquad (48)$$

It should be pointed out that the semiclassical action and the preexponential factor in the case of a symmetric potential can be found at arbitrary temperatures. We shall give only the expression for the action (the preexponential factor is far too complicated to reproduce):

$$S_B=\frac{4\gamma q_0^2}{\pi}(C+2\ln 2)+\frac{4q_0^2}{\pi}\left[\Lambda_2^2\psi\left(\frac{1}{2}+\frac{\Lambda_1\beta}{4\pi}\right)\right.$$

$$\left.-\Lambda_1^2\psi\left(\frac{1}{2}+\frac{\Lambda_2\beta}{4\pi}\right)\right]\Big/(\Lambda_2-\Lambda_1), \qquad (49)$$

where ψ is the logarithmic derivative of the Γ function.[18]

2. In the case of a symmetric potential the instanton action can be calculated exactly if ζ_n is selected in the form of the Drude approximation[4]:

$$\zeta_n=\gamma\omega_c|\nu_n|/(|\nu_n|+\omega_c),$$

where ω_c is the boundary value of the frequency in the vibrational spectrum. In this case, we have

$$S_B=\frac{4\gamma q_0^2}{\pi}(C+2\ln 2)+\frac{4\omega_0^4 q_0^2}{\pi}\left[\frac{(\omega_c-\lambda_1)\psi(1/2+\lambda_1\beta/4\pi)}{\lambda_1^2(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)}\right.$$

$$\left.+\frac{(\omega_c-\lambda_2)\psi(1/2+\lambda_2\beta/4\pi)}{\lambda_2^2(\lambda_1-\lambda_2)(\lambda_3-\lambda_2)}+\frac{(\omega_c-\lambda_3)\psi(1/2+\lambda_3\beta/4\pi)}{\lambda_3^2(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)}\right], \qquad (50)$$

where λ_1, λ_2, and λ_3 are the roots of the following algebraic equation:

$$\lambda^3-\omega_c\lambda^2+(\omega_0^2+\gamma\omega_c)\lambda-\omega_0^2\omega_c=0.$$

At low temperatures ($\lambda_i\beta \gg 1$, where $i=1, 2, 3$), we find that

$$S_B \approx \frac{4\gamma q_0^2}{\pi}(C+2\ln 2)+\frac{4\omega_0^4 q_0^2}{\pi}\left[\frac{(\omega_c-\lambda_1)\ln(\lambda_1/\omega_c)}{\lambda_1^2(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)}\right.$$

$$\left.+\frac{(\omega_c-\lambda_2)\ln(\lambda_2/\omega_c)}{\lambda_2^2(\lambda_1-\lambda_2)(\lambda_3-\lambda_2)}+\frac{(\omega_c-\lambda_3)\ln(\lambda_3/\omega_c)}{\lambda_3^2(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)}\right]$$

$$+\frac{4\gamma q_0^2}{\pi}\ln\frac{\beta\omega_c}{4\pi}+O(\beta^{-2}). \qquad (51)$$

As in the preceding case the action diverges at low temperatures. This divergence is related to the linear dependence $\zeta(\nu_n)$ in the limit $\nu_n \to 0$, i.e., the divergence determines low frequencies.

The preexponential factor can also be calculated exactly but we shall not give the full expression for B, but simply point out that the temperature dependence of the decay probability is exactly the same as in the optical damping case. Moreover, the dependence on the viscosity remains the same.

3. We shall now assume that

$$\zeta_n=\gamma\nu_n^2/(|\nu_n|+\omega_c).$$

This model is of interest in the theory of tunneling of color centers[19] in solids. Once again the action can be calculated exactly for a symmetric potential. We shall give only its low-temperature asymptote:

$$S_B \approx \frac{4\omega_0^4 q_0^2}{\pi}\left[\frac{(\omega_c-\Lambda_1)\ln(\Lambda_1/\omega_c)}{\Lambda_1^2(\Lambda_2-\Lambda_1)(\Lambda_3-\Lambda_1)}\right.$$

$$+\frac{(\omega_c-\Lambda_2)\ln(\Lambda_2/\omega_c)}{\Lambda_2^2(\Lambda_1-\Lambda_2)(\Lambda_3-\Lambda_2)}+\frac{(\omega_c-\Lambda_3)\ln(\Lambda_3/\omega_c)}{\Lambda_3^2(\Lambda_2-\Lambda_3)(\Lambda_1-\Lambda_3)}\Big]+O(\beta^{-2}), \tag{52}$$

where Λ_i $(i=1, 2, 3)$ satisfies the algebraic equation

$$\Lambda^3-(\omega_c+\gamma)\Lambda^2+\omega_0^2\Lambda-\omega_0^2\omega_c=0.$$

In this case the action is finite at low temperatures.

The preexponential factor becomes

$$B\approx B_0'\gamma^{-1/2}\beta^2, \tag{53}$$

Where B_0' is a coefficient independent of temperature (we shall not give the expression for this coefficient because it is rather cumbersome). It follows from Eq. (53) that the preexponential factor diverges at low temperatures as β^2, but in contrast to the exponential divergence in the one-dimensional case, the divergence in the present case is weakened to a power law because of the viscous motion of the oscillators in the medium. In fact, the divergence is removed by the condition that the inequality (30) hold, i.e., by the approximation that the kinetic process be quasisteady.

4. It is particularly interesting to calculate the action in the limit $\tau_0\to 0$. The potential then has the form shown in Fig. 2. Expanding Eqs. (25) and (26) as a series in small values of τ_0, we obtain

$$S_B=2\omega_0^2(q_0+q_1)q_1\tau_0-\frac{2\omega_0^2(q_0+q_1)^2\tau_0^2}{\beta}$$
$$-\frac{4\omega_0^4(q_0+q_1)^2\tau_0^2}{\beta}\sum_{n=1}^{\infty}(\nu_n^2+\omega_0^2+\zeta_n)^{-1}. \tag{54}$$

The value of τ_0 is found from Eq. (23):

$$\frac{2\tau_0}{\beta}=\frac{q_0}{q_0+q_i}\Big[\omega_0^2\sum_{n=1}^{\infty}(\nu_n^2+\omega_0^2+\zeta_n)^{-1}\Big]^{-1}. \tag{55}$$

Substituting τ_0 from Eq. (55) into the expression for the action (54), we obtain

$$S_B=\frac{\beta q_0^2}{2}\Big[\sum_{n=1}^{\infty}(\nu_n^2+\omega_0^2+\zeta_n)^{-1}\Big]^{-1}. \tag{56}$$

The above is exactly the same as the analogous relation derived in Ref. 20. It should be pointed out that the sum in Eq. (56) never diverges; and it is calculated for different types of spectra in Ref. 20. The action in the case of tunneling of a particle in such a potential is not equal to half the action in the case of a symmetric potential, in contrast to one-dimensional tunneling.

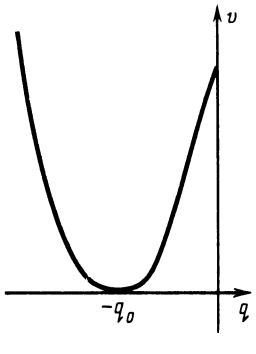

FIG. 2. Potential energy of a particle corresponding to the case when $\tau_0=0$.

We shall now express the above results in terms of the initial parameters of the problem defined by the potential energy terms of Eq. (1). We shall do this by applying the following theorem from the theory of analytic functions:

$$\int_C g(z)\frac{f'(z)}{f(z)}dz=2\pi i\sum_{k=1}^{n}g(a_k)-2\pi i\sum_{k=1}^{m}g(b_k), \tag{57}$$

where $f(z)$ and $g(z)$ are regular functions on a contour C, a_k are zeros of the function $f(z)$, and b_k are the poles of this function in a region D bounded by the contour C. Therefore,

$$\sum_{\alpha=2}^{N}\frac{C_\alpha^2}{\omega_\alpha^2}=\sum_{\alpha=2}^{N}\Big[\omega_\alpha^2\sum_{i=1}^{N}\frac{\gamma_i^2}{(\omega_{0i}^2-\omega_\alpha^2)^2}\Big]^{-1}$$
$$=\frac{1}{\pi i}\int_C dz\Big[z\sum_{i=1}^{N}\frac{\gamma_i^2}{\omega_{0i}^2-z^2}\Big]^{-1}, \tag{58}$$

where the contour C surrounds the poles $z_1, z_2,\ldots$ and is separated from the real axis by a distance $\pm\varepsilon$. We can similarly calculate the kernel of the integral term

$$\zeta_n=\frac{\nu_n^2}{\pi i}\int_C\frac{dz}{z(z^2+\nu_n^2)}\Big[\sum_{n=1}^{N}\frac{\gamma_i^2}{\omega_{0i}^2-z^2}\Big]^{-1}. \tag{59}$$

We shall express the viscosity in terms of the initial parameters of the problem. We shall do this by introducing the spectral density function[4]:

$$J(\omega)=\frac{\pi}{2}\sum_{i=1}^{N}\frac{C_i^2}{\omega_i}\delta(\omega-\omega_i). \tag{60}$$

In the Ohmic damping case, we have

$$J(\omega)=\gamma\omega\theta(\omega_c-\omega).$$

Then, the sum of Eq. (58) can be readily calculated and we find that

$$\gamma=\frac{1}{2i\omega_c}\int_C dz\Big[z\sum_{i=1}^{N}\frac{\gamma_i^2}{\omega_{0i}^2-z^2}\Big]^{-1}. \tag{61}$$

We shall now express the frequency ω_0 in terms of the initial parameters of the problem [see Eq. (21)]:

$$\omega_0^2=\sum_{i=1}^{N}\omega_{0i}^2\gamma_i^2-\frac{2\gamma\omega_c}{\pi}. \tag{62}$$

Therefore, the problem of calculating the probability of tunneling of a particle in parabolic terms of the potential energy (1) has been solved exactly in the semiclassical approximation.

5. CONCLUSIONS

As pointed out in the Introduction, tunnel chemical reactions have been observed in condensed phases. The kinetics of the tunnel transport is discussed above in the semiclassical approximation. This is done using the instanton method,[13-15] which for the potential energy terms of Eq. (1) can be used to calculate exactly the tunneling rate constant.

It is shown that for a specific type of the spectrum (ohmic damping) of vibrations of the medium and for symmetric reactions there is a zero quantum limit, i.e., a particle is always localized in the well of the initial state. In the case of such "viscous" tunneling it is essential to ensure that there are many low-frequency vibrational modes of the medium. This condition is fully justified in the case of viscous polymer particles. Such localization of a particle represents the principle of symmetry breaking. This is entirely a many-body effect and is characterized by a fairly large viscosity [see the inequality of Eq. (47)]; it is completely absent in the case of ordinary one-dimensional tunneling, in which case the quantum-mechanical parameter is not always zero (although it is small).

The condition of validity of the theory [Eqs (30) and (31)] is obtained for the multdimensional case. Violation of this condition is related to departure from the quasisteady nature of the probability flux (exponential decay of the tunneling probability). The temperature need not be very low in the case of one-dimensional tunneling and symmetric potential; otherwise oscillations are possible between the wells. It therefore follows that the influence of the medium does not always accelerate a chemical reaction. The situation depends on the spectrum of vibrations of the medium and on the initial parameters of the problem.

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APPENDIX

We consider diagonalization of the quadratic form

$$\sum_{i=1}^{N} \omega_{0i}^2 x_i^2, \tag{A.1}$$

on condition that the tunneling coordinate is given by Eq. (6) and other coordinates of the oscillators are selected in such a way that there are no terms of the $y_i y_j$ type $(i, j \geqslant 2)$ and there are terms representing the interaction of the coordinate y_1 with the coordinates y_i $(i \geqslant 2)$. We do this by diagonalization of the quadratic form

$$\sum_{i=1}^{N} \omega_{0i}^2 U_{ji} U_{j'i} = \omega_i^2 \delta_{jj'}, \tag{A.2}$$

where U_{ji} are elements of an orthogonal matrix. We multiply both sides of this equation by $U_{j'i}$ and sum with respect to j' between 2 and N allowing for the orthogonality of the transformation matrix:

$$U_{jk} = \gamma_k C_j / (\omega_{0k}^2 - \omega_j^2), \tag{A.3}$$

where

$$C_j = \sum_{i=1}^{N} \omega_{0i}^2 \gamma_i U_{ji}. \tag{A.4}$$

Substituting U_{jk} from Eq. (A.3) into Eq. (A.4), we obtain the following equation for the eigenvalues ω_j^2

$$\sum_{i=1}^{N} \frac{\omega_{0i}^2 \gamma_i^2}{\omega_{0i}^2 - \omega_j^2} = 1. \tag{A.5}$$

Hence, we can see there is one eigenvalue $\omega_1^2 = 0$, which should be ignored. Using Eq. (5), we can transform Eq. (A.5) to

$$\sum_{i=1}^{N} \frac{\gamma_i^2}{\omega_{0i}^2 - \omega_j^2} = 0. \tag{A.6}$$

We shall now determine the coefficients C_j from Eq. (A.4) and the condition of orthogonality of the transformation matrix:

$$C_j = \left[\sum_{i=1}^{N} \frac{\gamma_i^2}{(\omega_{0i}^2 - \omega_j^2)^2} \right]^{-1/2}. \tag{A.7}$$

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