THEORY OF LOW-TEMPERATURE CHEMICAL REACTIONS

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During recent years a number of communications about experimental study of the kinetics of low-temperature chemical reactions have appeared in the literature [1, 2]. In the present work we give the results of a calculation of the probability of the elementary act of a chemical reaction taking place in the condensed phase in the low-temperature approximation. The calculation is based on the use of the general procedure developed in [3, 4]. According to [3, 4], the probability of transition in the first order of perturbation theory (nonadiabatic reactions) can be represented in the form

$$W_{ss'} = \frac{\beta L^2 e^{\beta F_s}}{i\hbar} \int_{-i\infty}^{i\infty} d\theta \, \mathrm{Sp}\{\rho_s(1-\theta)\rho_{s'}(\theta)\}, \quad \beta = 1/kT, \tag{1}$$

where L is the electron exchange integral, F_s is the free energy of the system in the initial state, $\rho_s(1-\theta)$ is the density matrix for the system in the initial state at the effective temperature $T/(1-\theta)$, and $\rho_{s'}(\theta)$ is the density matrix in the final state at the temperature T/θ.

The density matrices ρ_s and $\rho_{s'}$ can be represented in the form of a product of the density matrix of the medium $\rho_s^{(m)}$ and the density matrix $\rho_s^{(i)}$ which describes the intramolecular state of the reagents. As was shown in [4], the integral with respect to θ in Eq. (1) can be calculated by the steepest descent method, wherein the crossing point θ^* lies on a real axis and coincides with the symmetry factor in the Bronsted relationship

$$\theta^* = -\partial \ln W_{ss'}/\beta \partial \Delta F, \tag{2}$$

where ΔF is the free energy of the reaction. Equation (1) can be transformed into the form

$$W_{ss'} = \frac{\beta L^2}{i\hbar} \int_{-i\infty}^{i\infty} d\theta \left\langle\!\!\left\langle T_\tau \exp\left\{ -\int_0^{\beta\theta} d\tau [H_{s'}(\tau) - H_s(\tau)] \right\} \right\rangle\!\!\right\rangle_s ; \tag{3}$$

here $H_s(\tau)$ and $H_{s'}(\tau)$ are the Hamiltonians of the system in the initial and final states, taken in the interaction representation (the transition to the interaction representation is made with the aid of the operator $\exp(\tau H_s)$); T_τ denotes chronological ordering with respect to τ, and finally, $\ll \ldots \gg_s$ denotes quantum-statistical averaging with respect to the initial state. From here on we shall assume that the medium is linear and is described by some scalar field $\varphi(\mathbf{r})$. In polar medium the role of $\varphi(\mathbf{r})$ is played by the longitudinal component of the polarization vector, $P_{\parallel}(\mathbf{r})$; for nonpolar medium one may take the density of the medium as $\varphi(\mathbf{r})$ (generalization into vector fields presents no difficulties). We shall assume, moreover, that the interaction of reacting particles with the medium has a linear character:

$$V_s = -\int \varphi(\mathbf{r}) F_s(\mathbf{r}) d\mathbf{r}, \tag{4}$$

where $F_s(\mathbf{r})$ plays the role of a generalized force acting on the medium from the direction of the reagent particles.

Calculation of the expression under the integral in Eq. (3) for linear media is performed by the standard method of [5]. Omitting the cumbersome calculations, we give the final expression:

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$$W_{ss'}=\frac{\beta L^2}{i\hbar}\int_{-i\infty}^{i\infty}d\theta\,\Phi^{(i)}(\theta)\exp\left\{-\beta\theta\,\Delta F-\frac{1}{\pi\hbar}\sum_{\mathbf{k}}|\Delta F_{\mathbf{k}}|^2\int_{-\infty}^{\infty}\frac{d\omega}{\omega^2}\operatorname{Im}G(\mathbf{k},\omega)\frac{\operatorname{sh}\frac{\beta\hbar\omega\theta}{2}\operatorname{sh}\frac{\beta\hbar\omega(1-\theta)}{2}}{\operatorname{sh}\frac{\beta\hbar\omega}{2}}\right\},\quad(5a)$$

$$\Phi^{(i)}(\theta)=\exp(\beta F_s^{(i)})\,\mathrm{Sp}\{\rho_s^{(i)}(1-\theta)\rho_{s'}^{(i)}(\theta)\},\quad(5b)$$

where $F_s^{(i)}$ is the free energy of the reagents, measured from the energy of the free state (in $\rho_{s,s}^{(i)}$, the energies are also measured from zero levels); ΔF is the free energy of the reaction; ΔF_k is the difference of the Fourier transforms from $F_{s'}(\mathbf{r})$ and $F_s(\mathbf{r})$; and $G(\mathbf{k},\omega)$ is the time lag Green's function for operators of the $\varphi(\mathbf{r})$ field.

Initially we examine the limiting case $T\to 0$. According to Eq. (5), when $T\to 0$, the probability of transition is different from zero only when $\Delta F<0$, wherein the crossing point θ^* tends toward zero, but in such a way that $\beta\theta^*$ remains finite. This result is not hard to obtain if we represent $\ln W_{ss'}$ in Eq. (2) in the form of [3, 4]: $-\ln W_{ss'}=\beta E_a+\sigma$, where E_a is the activation energy for classical degrees of freedom and σ is the tunneling factor for quantum degrees of freedom. When $T\to 0$, classical degrees of freedom disappear in the system, that is, $E_a=0$, but $\ln W_{ss'}=-\sigma$ and $\beta\theta^*=\partial\sigma/\partial\Delta F$. Thus, the value of $\beta\theta^*$ determines the rate of change of the tunneling factor on change in ΔF.

As has already been noted, when $\Delta F>0$, according to Eq. (5), as was to be expected, $W_{ss'}\to 0$. It is of interest to find the asymptotic behavior of $W_{cc'}$ at low values of $|\Delta F|$. In this case practically all the degrees of freedom will make a transition from the base initial level to the base level of the final state, but compensation in the value of ΔF will take place due to excitation of a small number of low-frequency modes of the medium, which have frequencies $\omega\lesssim(\beta\hbar\theta^*)^{-1}$. The reorganization of low-frequency modes is determined by the asymptotic behavior of $\operatorname{Im}G(\mathbf{k},\omega)$ when $\omega\to 0$. As is well known, when $\omega\to 0$, $\operatorname{Im}G(\mathbf{k},\omega)\to a(\mathbf{k})\omega$. The value of $a(\mathbf{k})$ is determined by the properties of the medium and is connected with Green's function by the relationship

$$a(\mathbf{k})=\int_0^{\infty}G(\mathbf{k},t)\,t\,dt.\quad(6)$$

As calculation shows, at low values of $|\Delta F|$ the crossing point θ^* is determined from the condition

$$\beta\theta^*=\frac{1}{\pi\hbar|\Delta F|}\sum_{\mathbf{k}}a(\mathbf{k})|\Delta F_{\mathbf{k}}|^2\equiv\lambda/|\Delta F|,\quad(7)$$

and the probability of transition can be written in the form

$$W_{ss'}=\frac{2\pi}{\hbar}\tilde{L}^2\rho\frac{(\rho|\Delta F|)^{\lambda-1}}{(\lambda-1)!}\quad(8)$$

Here ρ is defined by the relationship

$$\ln\rho=\frac{1}{\pi\hbar\lambda}\sum_{\mathbf{k}}|\Delta F_{\mathbf{k}}|^2\int_0^{\infty}d\omega\ln(\gamma\hbar\omega)\frac{d}{d\omega}\left(\frac{\operatorname{Im}G(\mathbf{k},\omega)}{\omega}\right),\quad(9)$$

where $\ln\gamma=c\simeq 0.57$ is Euler's constant. In Eq. (8), by $\tilde{L}$ we imply the exchange integral calculated with use of the complete wave function for the reagents ($\Psi_{0s}^{(i)}$) and the products ($\Psi_{0s}^{(i)}$); that is, $\tilde{L}=\langle\Psi_{0s'}|L|\Psi_{0s}\rangle$. The applicability condition for Eq. (8) can be obtained from the requirement that all the characteristic frequencies of the medium ($\Omega^{(m)}$), as well as the frequencies of the intramolecular vibrations of the reaction products ($\Omega_s^{(i)}$), shall be appreciably larger than ($\beta\hbar\theta^*$), that is, $|\Delta F|\ll\lambda\hbar\Omega^{(m)},\ \lambda\hbar\Omega_s^{(i)}$. The magnitude of λ in the long wave approximation can easily be connected up with the reorganization energy of the medium $E_r^{(m)}$: $\lambda=(2a_0/\pi\hbar G_0)E_r^{m}\gg 1$. With rise in the value of $|\Delta F|$, successively more high-frequency modes of the medium will be excited, and also intramolecular vibrations of the reaction products. We now examine the second limiting case of larger values of $|\Delta F|$, where one can use the high-temperature approximation for $\rho_{s'}(\theta)$. In this case, in calculating $\Phi^{(i)}(\theta)$ for $\rho_s^{(i)}$ and $\rho_{s'}^{(i)}$ one can use the formulas

$$\rho_s^{(i)}(Q,Q';1-\theta)=\Psi_{0s}^{(i)}(Q)\,\Psi_{0s}^{*(i)}(Q');\quad(10a)$$

$$\rho_{s'}^{(i)}(Q,Q';\theta)=\exp\{-\beta\theta U_{s'}(Q)\}\cdot\delta(Q-Q'),\quad(10b)$$

where $\psi_{0s}^{(i)}$ is the wave function of the ground state of the reagents and $U_{s'}(Q)$ is the potential energy of the products. Since, in calculating the trace in Eq. (5b), the $Q = Q' \simeq 0$ will make the main contribution, then, with a good degree of accuracy, $\psi_{0s}^{(i)}(Q)$ can be approximated by the wave function of a set of oscillators having the frequencies Ω_n^s, and $U_{s'}(Q)$ can be expanded into a series close to the point $Q = 0$. As a result, for $\Phi^{(i)}(\theta)$ we obtain

$$\Phi^{(i)}(\theta) \simeq \exp\left\{-\beta\theta E_r^{(i)} + \frac{\beta^2\theta^2}{\varphi}\sum_n |\partial U_{s'}(0)/\partial Q_n|^2\right\}, \tag{11}$$

where $E_r^{(i)} = U_{s'}(0)$ is the energy of reorganization with respect to intramolecular degrees of freedom of the reaction products for the reverse reaction; and Q_n is a set of dimensionless normal coordinates for the reagents, $Q_n = x_n \cdot \sqrt{m_n \Omega_n^s/\hbar}$. In the case under study we obtain the following expression for the crossing point θ^*:

$$\beta\theta^* = \frac{E_r^{(m)} + E_r^{(i)} - |\Delta F|}{\hbar\Omega^{(m)} E_r^{(m)} + \hbar\Omega_{s'}^{(i)} E_r^{(i)}}; \tag{12}$$

where the reorganization energy of the medium $E_r^{(m)}$ and the characteristic frequencies of the medium $\Omega^{(m)}$ and of the products $\Omega_{s'}^{(i)}$ are determined from the equations

$$E_r^{(m)} = \frac{1}{2}\sum_k |\Delta F_k|^2 G(k, 0); \tag{13a}$$

$$\frac{1}{\pi}\sum_k |\Delta F_k|^2 \int_0^\infty d\omega \,\mathrm{Im}\, G(k, \omega) \equiv \Omega^{(m)} E_r^{(m)}; \quad \frac{1}{2}\sum_n |\partial U_{s'}(0)/\partial Q_n|^2 \equiv \Omega_{s'}^{(i)} E_r^{(i)}. \tag{13b}$$

Correspondingly, for the probability of transition we have

$$W_{s'} = \frac{\sqrt{2\pi}\, L^2}{\hbar} \frac{\exp\{-(E_r^{(m)} + E_r^{(i)} - |\Delta F|)^2/(2\hbar\Omega^{(m)} E_r^{(m)} + 2\hbar\Omega_{s'}^{(i)} E_r^{(i)})\}}{\sqrt{\hbar\Omega^{(m)} E_r^{(m)} + \hbar\Omega_{s'}^{(i)} E_r^{(i)}}}. \tag{14}$$

The limit of applicability of Eqs. (12) and (14) can be obtained from the condition $\beta\theta^* \hbar\Omega^{(m)} \leq 1$ and $\beta\theta^* \hbar\Omega_{s'}^{(i)} \ll 1$. Having made use of Eq. (12), we obtain

$$E_r - |\Delta F| \ll E_r^{(m)} + E_r^{(i)}\, \Omega_{s'}^{(i)}/\Omega^{(m)}, \quad E_r^{(i)} + E_r^{(m)}\, \Omega^{(m)}/\Omega_{s'}^{(i)}, \tag{15}$$

where by E_r we denote the total reorganization energy $E_r = E_r^{(m)} + E_r^{(i)}$. Thus, Eq. (14) is correct at large values of $|\Delta F|$, which are close to the total reorganization energy E_r. As was said above, the transitional configuration of the intramolecular degrees of freedom Q_n^* is determined by the condition that the term of the final state $U_{s'}(Q)$ intersects the term of the initial state $U_s(Q)$ close to the equilibrium configuration of the initial state $Q^* = Q_0^{(i)} = 0$. Thus, as a result of reaction when the conditions (15) are fulfilled, the products are obtained in a strongly excited vibrational state, a portion of the energy $|\Delta F|$ equal to $E_r^{(i)}$ being expended in excitation of the reaction products.

Moderate values of $|\Delta F|$ can be examined analogously. However, the specific expressions for $\beta\theta^*$ and $W_{ss'}$ depend considerably on the relationship between the basic parameters of the problem, such as $\Omega^{(m)}$, $\Omega^{(i)}$, $E_r^{(m)}$, and $E_r^{(i)}$. For example, if $\Omega^{(i)} \gg \Omega^{(m)}$ it is not hard to find an expression for $W_{ss'}$ at values of $|\Delta F|$ close to $E_r^{(m)}$ such that $E_r^{(m)} - |\Delta F| \ll E_r^{(m)}$. Since in this case $\beta\theta^*\hbar\Omega^{(i)} \gg 1$, then for ρ_s and $\rho_{s'}$ one can use the low-temperature approximation (10a). Therefore the expressions for $\beta\theta^*$ and $W_{ss'}$ can be obtained from Eqs. (12) and (14) if we formally set $E^{(i)} = 0$ in them and replace L by $\tilde{L}$.

It is not difficult to generalize the calculation method developed in the present work also for the case of low temperatures, not different from zero. Finally, it should be noted that in the case where one can use the low-temperature approximation (10a) for intramolecular degrees of freedom, $W_{ss'}$ can be calculated not only for nonadiabatic reactions, where L is small, but also in the case of partially nonadiabatic reactions, where L is large but $\tilde{L}$ is small. As was shown in [6], for this it is sufficient to replace L in Eq. (1) by $\Delta E/2$, where ΔE is the minimum splitting of the potential energy surfaces for the medium. If the intramolecular electronic terms $U_s(Q)$ and $U_{s'}(Q)$ can be approximated by one-dimensional terms, ΔE can be found by the use of the quasi-classical method of [7].

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