KINETICS OF ELECTROCHEMICAL PROCESSES

IV. QUANTUM-MECHANICAL THEORY. CALCULATION OF THE PROBABILITY OF TRANSITION FOR NONADIABATIC REACTIONS WITHIN THE HARMONIC APPROXIMATION (GENERAL RELATIONSHIPS)

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Nonadiabatic transition between two multidimensional potential energy surfaces that have parabolic shapes is examined. General expressions for the probability of transition for an arbitrary form of the vibrational spectrum of the system in the initial and final states are obtained. All of the degrees of freedom of the system are divided into classical and quantum values in conformity with the magnitude of the vibrational quantum as compared with kT. The general expressions were analyzed for the case in which entanglement of the coordinates of the quantum and classical degrees of freedom as a result of the reaction is absent in the system. The transition in a system in which all of the vibrational degrees of freedom are classical is examined.

Introduction

The phenomenological theory of electrochemical processes was evolved in [1,2]. A number of qualitative assumptions regarding the form of the dependence of the probability (W) of an elementary act on the (microscopic) heat effect (ΔJ) of the process, namely, the Arrhenius law

$$W=Be^{-\beta E_a}\qquad(\beta=1/kT)\tag{1}$$

and the empirical Bronsted rule that the energy of activation (E_a) depends on the heat effect (ΔJ) of the process, in which the transition coefficient (the "symmetry factor," according to [3]) $\alpha(\Delta J)\equiv dE_a/d\Delta J$ is constant over a wide range of ΔJ, were used in the construction of the theory. Expressions for the form of these dependences for various models of the reacting system will be obtained in the present paper (and also in a number of subsequent papers) on the basis of a quantum-mechanical examination. In the present paper, this sort of examination will be made for the case of nonadiabatic reactions within the framework of the harmonic approximation for the description of the system. A correlation of these results for the case of adiabatic reactions and processes in which the harmonic approximation is inadequate will be given in subsequent papers.

The concept of reaction channels [4] should be introduced during the successive constructon of the quantum-mechanical theory of chemical reactions. For this, we will break down the complete Hamiltonian of the system (H) into the Hamiltonian of the initial (final) channel $H_i(H_f)$ and the perturbation $V_i(V_f)$, which leads to transition to the final (initial) state *:

$$H=H_i+V_i=H_f+V_f.\tag{2}$$

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*It should be noted that perturbation in the channels (V_i, for example) leads to two different effects: distortion of the structure of the reagents without transitions to the final state and transitions strictly to the final state. To a certain approximation, perturbation V_i can be broken down into "diagonal" part V_i^d (which

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For example, the states of Hamiltonian H_i for electron transfer reactions $A^{z_1} + B^{z_2} \rightarrow A^{z_1+1} + B^{z_2-1}$ correspond to the electron in the vicinity of ion A (with allowance for the polarizing field of ion B), while the state of H_f corresponds to the electron on ion B; the interaction of the transferring electron with ion B plays the role of interaction V_i in this case, while interaction with A (or, more precisely, the "nondiagonal" part of these interactions) plays the role of V_f. Hamiltonian H was similarly broken down for proton transfer reactions and more complex processes. As is shown in the general theory of collisions of particles with redistribution [4], the following general formula is valid for the probability (W) of transition from the initial state to the final state:

$$W=\frac{2\pi}{\hbar}Av_i\sum_f |\langle\Psi_f|\tau|\Psi_i\rangle|^2\cdot\delta(E_i-E_f), \tag{3}$$

where Ψ_i (Ψ_f) and E_i(E_f) are the wave functions and the energy levels for the initial (final) channels, and $H_i\Psi_i = E_i\Psi_i$, and $H_f\Psi_f = E_f\Psi_f$.

The summation in formula (3) is made over all of the final states Ψ_f and Gibbs averaging ($Av_iM_i = Q^{-1}\sum_i M_i\exp(-\beta E_i)$; Q is the statistical sum) is performed over all the initial states; finally,

$$\tau = V_i + V_f\frac{1}{E_i+i\delta-H}V_i. \tag{4}$$

For nonadiabatic reactions, when perturbations V_i and V_f are sufficiently small (the corresponding levels will be discussed in papers devoted to adiabatic reactions), one can replace τ in formula (3) by V_i.

Harmonic Approximation

In examining reactions in polar media, we find that the interaction of the reagents is strong and should be included in the channels of Hamiltonians H_i and H_f, such that $H_i = H_i^{(s)} + H_i^{(n)}$; $H_f = H_f^{(s)} + H_f^{(n)}$, where $H_i^{(n)}$ describes the state of the reagents [correspondingly, $H_f^{(n)}$ is the state of the products], and $H_i^{(s)}$ ($H_f^{(s)}$) is the Hamiltonian of the polar medium with allowance for the field of the reagents (reaction products) introduced into it. As shown in [5, 6], the polar medium can be described by an infinite set of harmonic oscillators, and in a number of cases it can be assumed that the normal coordinates of the oscillators ($q_\varkappa$) and the vibrational frequencies ($\omega_\varkappa$) of the polar medium are identical before and after the reaction:

$$H_i^{(s)}=\sum_\varkappa\frac{1}{2}\hbar\omega_\varkappa\left(q_\varkappa^2-\frac{\partial^2}{\partial q_\varkappa^2}\right);$$

$$H_f^{(s)}=\sum_\varkappa\frac{1}{2}\hbar\omega_\varkappa\left[(q_\varkappa-q_{\varkappa0})^2-\frac{\partial^2}{\partial q_\varkappa^2}\right]+\Delta J_0^{(s)}.$$

Here $q_{\varkappa0}$ is the shift in the equilibrium values of the normal coordinates of the medium as a result of the reaction (for the initial state, the equilibrium values are taken as the reference origin in order to simplify the formula). The harmonic approximation will be used to describe the intramolecular degrees of freedom of the reagents and products in the present paper:

$$H_i^{(n)}=-\sum_\xi\frac{\hbar^2}{2m_\xi}\frac{\partial^2}{\partial x_\xi^2}+\frac{1}{2}\sum_{\xi,\eta}g_{\xi\eta}x_\xi x_\eta,$$

$$H_f^{(n)}=-\sum_\xi\frac{\hbar^2}{2m_\xi}\frac{\partial^2}{\partial x_\xi^2}+\frac{1}{2}\sum_{\xi,\eta}g_{\xi\eta}'x_\xi x_\eta+\sum_\xi f_\xi x_\xi+\Delta J_0^{(n)}, \tag{6}$$

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is responsible for deformation of the structure of the reagents) and "nondiagonal" part V_i^{nd} (which leads to transitions between the distorted states in the channels): $V_i = V_i^d + V_i^{nd}$. Interaction V_i^d (the pronounced repulsion of the reagents at short distances, for example, is associated with it) will subsequently be included in channel Hamiltonian H_i, so that only "nondiagonal" portion V_i^{nd} is implied by V_i in all of the following formulas, while states with allowance for V_i^d are implied by the initial and final states. A similar procedure is known as "the method of distorted waves" in the case of gas reactions.

where $g_{\xi\eta}$ ($g_{\xi\eta}'$) are directly associated with the force constants for the corresponding valence and deformation bonds, x_ξ are the Cartesian coordinates of the nuclei of the reacting particles, and m_ξ is the mass of the corresponding nucleus. The f_ξ values characterize the shift in the equilibrium values of the coordinates as a result of the reaction (the initial equilibrium values of the coordinates are taken as the reference origin), while $\Delta J_0^{(n)}$ characterizes the difference between the final and initial equilibrium energies of the reacting particles. Hamiltonian (6) should be diagonalized for the subsequent analysis, i.e., one should introduce normal coordinates for the reagents and products. We will point out one of the possible methods for this introduction: after the substitutions $y_\xi = x_\xi \sqrt{m_\xi}$, one should effect the orthogonal transformation [7] of coordinates $z_\eta = \sum_\xi O_{\eta\xi} y_\xi$; in this case, for the kinetic energy operator we have $-\sum_\xi \frac{\hbar^2}{2m_\xi} \frac{\partial^2}{\partial x_\xi^2} = -\frac{\hbar^2}{2} \sum_\eta \frac{\partial^2}{\partial z_\eta^2}$. Matrix $\|O_{\eta\xi}\|$ is selected in such a way that the expression for the potential energy takes on a diagonal form: $\sum_{\xi,\eta} g_{\xi\eta} x_\xi x_\eta = \sum_{\xi,\eta} g_{\xi\eta} (m_\xi m_\eta)^{-1/2} y_\xi y_\eta = \sum_\eta \lambda_\eta z_\eta^2$, where λ_η are the eigenvalues of the matrix [7] $\|g_{\xi\eta}(m_\xi M_\eta)^{-1/2}\|$. Similarly, the orthogonal (but, generally speaking, a different one) transformation $z_\eta' = \sum_\xi O_{\eta\xi}' y_\xi$ diagonalizes form $\sum g_{\xi\eta}' x_\xi x_\eta$. Finally, substitutions $q_\eta = z_\eta \sqrt{\omega_\eta / \hbar}$ and $q_\eta' = z_\eta' \sqrt{\omega_\eta' / \hbar}$, where $\omega_\eta = \sqrt{\lambda_\eta}$, $\omega_\eta' = \sqrt{\lambda_\eta'}$, reduce Hamiltonians $H_i^{(n)}$ and $H_f^{(n)}$ to a form similar to (5):

$$H_i^{(n)} = \sum_\xi \frac{1}{2} \hbar \omega_\xi \left(q_\xi^2 - \frac{\partial^2}{\partial q_\xi^2} \right);$$

$$H_f^{(n)} = \sum_\eta \frac{1}{2} \hbar \omega_\eta' \left(q_\eta'^2 - \frac{\partial^2}{\partial q_\eta'^2} \right) + \sum_\eta \bar{f}_\eta q_\eta' + \Delta J_0^{(n)},$$

where the $\bar{f}_\eta$ values are linearly related to f_ξ in (6). Designating the equilibrium values of the dimensionless normal coordinates by means of $q_{\eta 0}' = -\bar{f}_\eta / \hbar \omega_\eta$ and considering (5), we have for H_i and H_f

$$H_i = \sum_\mu \frac{1}{2} \hbar \omega_\mu \left(q_\mu^2 - \frac{\partial^2}{\partial q_\mu^2} \right); \quad H_f = \sum_\mu \frac{1}{2} \hbar \omega_\mu' \left[(q_\mu' - q_{\mu 0}')^2 - \frac{\partial^2}{\partial q_\mu'^2} \right] + \Delta J_0, \tag{7}$$

in which the summation is made both with respect to the degrees of freedom of the medium ($\mu = \varkappa$) and with respect to the intramolecular degrees of freedom ($\mu = \xi$). In formula (7), ΔJ_0 is the difference in the equilibrium energies of the entire system (the polar medium and the reacting particles) for the final and initial states (for the ground electronic states). As seen from the derivation of formula (7), the normal coordinates of the initial and final states are interrelated by linear expressions:

$$q_\mu' = \sum_\nu \alpha_{\mu\nu} q_\nu, \text{ where } \alpha_{\mu\nu} = \tau_{\mu\nu} \sqrt{\frac{\omega_\mu'}{\omega_\nu}}; \quad \|\tau_{\mu\nu}\| = \left\| \begin{matrix} \|\delta_{\varkappa\varkappa'}\| & 0 \\ 0 & \|\tau_{\eta\xi}\| \end{matrix} \right\|, \tag{8}$$

in which $\tau_{\eta\xi} = \sum_\rho O_{\eta\rho}' O_{\xi\rho}$ is the orthogonal matrix ($\|\delta_{\varkappa\varkappa'}\|$ is the unit matrix). Thus matrix $\|\alpha_{\mu\nu}\|$ is known to be quasidiagonal [7], since the degrees of freedom of the solvent are not "entangled," in the process of reaction, with the intramolecular degrees of freedom, i.e., $q_\varkappa' = q_\varkappa$; $q_\eta' = \sum_\xi \alpha_{\eta\xi} q_\xi$. In addition, in many cases matrix $\|\tau_{\eta\xi}\|$ (and, consequently, matrix $\|\alpha_{\eta\xi}\|$) is quasi-diagonal, i.e., the set of expressions (8) can be broken down into several independent sets:

$$|\alpha_{\mu\nu}| = \left| \begin{array}{cccc|l} |\delta_{\varkappa\varkappa'}| & 0 & 0 & \ldots\ldots & q_\varkappa' = q_\varkappa \\ 0 & |\alpha_{\eta\xi}^{(1)}| & 0 & \ldots\ldots & q_\eta^{(1)'} = \Sigma \alpha_{\eta\xi}^{(1)} q_\xi^{(1)} \\ 0 & 0 & |\alpha_{\eta\xi}^{(2)}| & \ldots & q_\eta^{(2)'} = \Sigma \alpha_{\eta\xi}^{(2)} q_\xi^{(2)} \\ \ldots & \ldots & \ldots & \ldots & \ldots\ldots \end{array} \right. \tag{9}$$

[the term "independent sets" means that there is not even one q_ξ coordinate that would enter into more than one of the equations of expression (9)]. We will call the degrees of freedom $\{q_\xi^{(i)}\}$ that enter into one of the sets of expression (9) "interentangled."

General Expressions

In [8, 9] it was shown that for a system described by Hamiltonians of channels (7), expression (3) for the probability of transition can be transformed to

$$W = A \exp\{-\mathscr{H}[\theta^*(\Delta J),\ q_\nu^*(\Delta J);\ \Delta J]\}, \tag{10}$$

where A is only slightly dependent on heat effect ΔJ and reciprocal temperature $\beta = 1/kT$.

The index of the exponent in formula (10) has the form

$$\mathscr{H}(\theta, q_\nu, \Delta J) = \beta\theta\Delta J + \sum_\nu \left\{ q_\nu^2 \operatorname{th}\frac{1}{2}\beta\hbar\omega_\nu(1-\theta) + (q_\nu' - q_{\nu 0}')^2 \operatorname{th}\frac{1}{2}\beta\hbar\omega_\nu'\theta \right\}, \tag{11}$$

in which, in place of θ and q_ν, one must substitute $\theta^*(\Delta J)$ and $q_\nu^*(\Delta J)$, which are the solution of the system of the following equations:

$$\begin{cases} q_\nu^* \operatorname{th}\dfrac{1}{2}\beta\hbar\omega_\nu(1-\theta^*) + \sum\limits_\mu \alpha_{\mu\nu}(q_\mu' - q_{\mu 0}') \operatorname{th}\dfrac{1}{2}\beta\hbar\omega_\mu'\theta^* = 0 \quad \text{for all } \nu & (12a) \\ \Delta J = \sum \left[\dfrac{\frac{1}{2}\hbar\omega_\nu q_\nu^{*2}}{\operatorname{ch}^2 \frac{1}{2}\beta\hbar\omega_\nu(1-\theta^*)} - \dfrac{\frac{1}{2}\hbar\omega_\nu'(q_\nu'^* - q_{\nu 0}')^2}{\operatorname{ch}^2 \frac{1}{2}\beta\hbar\omega_\nu'\theta^*} \right] & (12b) \end{cases}$$

[the q_ν^* and $q_\mu'^*$ values are interrelated by expressions (8)]. The ΔJ value in formulas (11) and (12b), which is equal to $\Delta J_0 + \sum_\nu \left(\frac{1}{2}\hbar\omega_\nu' - \frac{1}{2}\hbar\omega_\nu\right)$ will subsequently be called the heat effect of the process.

An analysis of formulas (11) and (12) shows that in most cases of practical interest the index of the exponent in (10) is a linear function of reciprocal temperature β:

$$\mathscr{H}[\theta^*(\Delta J),\ q_\nu^*(\Delta J);\ \Delta J] = \beta E_a(\Delta J) + \sigma(\Delta J), \tag{13}$$

i.e., W depends on the temperature in accordance with the Arrhenius law with activation energy E_a. As will be seen from what follows, σ is associated with subbarrier crossing along several degrees of freedom and will therefore be called the "tunneling factor."

It is apparent from formulas (10) and (13) that there is a correlation between the principal kinetic parameters (E_a and σ) of the process and its thermodynamic characteristic – the heat effect of the process (ΔJ). It is convenient to use the transfer coefficient (the "symmetry factor" [13]) $\alpha(\Delta J) \equiv -d\ln W/\beta d\Delta J$ as the characteristic of this sort of correlation. It can be shown from expressions (10)-(12) that

$$\alpha(\Delta J) = -\frac{d\ln W}{\beta d\Delta J} \simeq \frac{d\mathscr{H}[\theta^*(\Delta J), q_\nu^*(\Delta J); \Delta J]}{\beta d\Delta J} = \theta^*(\Delta J). \tag{14}$$

So that below, the θ^* value will also be called the transfer coefficient.

In the general case, one can find the solution of equations (12) and obtain the expression for W for two values of the heat effect of the process (ΔJ), when† $\Delta J = -\sum_\nu \frac{1}{2}\hbar\omega_\nu' q_{\nu 0}'^2 = -E_r'$ and $\Delta J = \sum_\nu \frac{1}{2}\hbar\omega_\nu q_{\nu 0}^2 = E_r$ [$q_{\nu 0}$ and $q_{\nu 0}'$ are linked by expressions (8)]. In the first case, the minimum of the initial electronic term of system U(q) is found on the surface of the final electronic term U'(q):

$$U(q) = \sum_\nu \frac{1}{2}\hbar\omega_\nu q_\nu^2; \quad U'(q) = \sum_\nu \frac{1}{2}\hbar\omega_\nu'(q_\nu' - q_{\nu 0}')^2 + \Delta J. \tag{15}$$

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† The E_r and E_r' values will subsequently be called the energy of reorganization of the entire system for the forward (reverse) process.

In this case, $q_\nu^* = 0$, the transfer coefficient is θ^*, the activation energy (E_a) and the "tunneling" factor (σ) revert to zero, and the probability of the transition reaches a maximum value:

$$W=\frac{\beta|L|^2}{\hbar}\sqrt{\pi}\sum_{\nu}\left\{\left(\sum_{\mu}\frac{1}{2}\beta\hbar\omega_\mu'\alpha_{\mu\nu}q_{\mu 0}'\right)^2\operatorname{cth}\frac{1}{2}\beta\hbar\omega_\nu\right\}$$

(here L is the exchange integral [9]). In the second case, when the minimum of the final electronic term of system U'(q) is found on the surface of the initial term U(q), for all degrees of freedom $q_\nu'^* = q_{\nu 0}'$, transfer coefficient θ^* is one, σ reverts to zero, and the activation energy (E_a) coincides with the energy of reorganization of the forward process, i.e., $E_a = E_r = \Delta J$.

Using formulas (11), (12), and (14), one can show that transfer coefficient θ^* is a monotonically increasing function of heat effect ΔJ. When the change in ΔJ ranges from $-E_r'$ to E_r, the transfer coefficient therefore increases monotonically from zero to unity, while activation energy E_a increases monotonically from zero to E_r. In this case, because of the activation factor, the probability (W) of the transition changes by a factor of approximately $\exp\beta E_r$, i.e, by 17 orders of magnitude, when T = 300°K and $E_r = 1$ eV. For real processes, the condition $-E_r' < \Delta J < E_r$, i.e., $0 < \theta^* < 1$, is practically always satisfied. This circumstance is associated with the high total reorganization energies (E_r and E_r'), which usually amount to several electron volts. We note that all of the degrees of freedom of the system make a contribution to the total reorganization energies. If cleavage or the formation of rigid valence bonds occurs during the reaction, these degrees of freedom make a contribution of $^1/_2\hbar\omega_\nu q_{\nu 0}^2$ of the order of the dissociation energy for this bond to the reorganization energy, i.e., in this case E_r and E_r' will be particularly large. Violation of the conditions $-E_r' < \Delta J < E_r$ and $0 < \theta^* < 1$ should therefore be expected only for processes during which neither cleavage nor the formation of rigid valence bonds occur. In this connection, a broader range of heat effects (ΔJ)† than $-E_r' < \Delta J < E_r$ will be examined only for this class of reactions. In all of the remaining cases, we limited ourselves to an investigation of the interval $-E_r' < \Delta J < E_r$, when θ^* lies between zero and unity. The indicated result is in agreement with the experimental data for both chemical [10] and electrochemical [11] reactions.

Using formula (3), one can obtain the thermodynamic relationship between the rates of the forward (W) and reverse (W') processes:

$$W=W'e^{-\frac{\Delta F_0}{kT}}=W'e^{-\beta\Delta J}\prod_{\nu}\frac{1-e^{-\beta\hbar\omega_\nu}}{1-e^{-\beta\hbar\omega_\nu'}}, \tag{16}$$

where ΔF_0 is the free energy of the reaction. Then, according to (14), transfer coefficient α' for the reverse process is $1-\alpha$; from (16) and (13) it is also seen that $\sigma' = \sigma$ and $E_a' = E_a - \Delta J$ for the reverse process. The "reaction paths" are therefore identical for the forward and reverse processes, i.e., the same energy levels make the primary contribution to the transition probability (W and W').

We will now introduce the concept of "classical" and "quantum" degrees of freedom, which is important for the subsequent analysis. We will call degree of freedom q_ν classical if the vibrational frequency (ω_ν) for it is low enough that $^1/_2\beta\hbar\omega_\nu \ll 1$ ($\hbar\omega_\nu \ll 2kT$). The reverse condition $^1/_2\beta\hbar\omega_\nu \gg 1$ is satisfied for the quantum degrees of freedom. The breakdown into classical and quantum degrees of freedom in the final state is carried out in exactly the same way: $^1/_2\beta\hbar\omega_\nu' \ll 1$ or $^1/_2\beta\hbar\omega_\nu' \gg 1$. We note that, in the general case, expressions (8) link the classical degrees of freedom for the final state with both the classical and quantum degrees of freedom in the initial state; the same also applies to the quantum degrees of freedom.

Thus all of the sets of linear expressions (9) can be broken down into three groups: the "purely classical" sets‡ $q_j' = \sum_i \alpha_{ji}q_i$ (the vibrational frequencies for all of the degrees of freedom entering into this set

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† However, one should bear in mind that, according to [1, 2], for electrochemical reactions the "macroscopic" transfer coefficient $\alpha_{\exp} \equiv kT(d\ln i/de\eta)$ always lies between 0 and 1, even if $\alpha(\Delta J)$ may go beyond these limits. Physically speaking, this is associated with the presence of a continuous electronic spectrum in the electrode.

‡ Here and in what follows it is convenient for descriptive purposes to use the following symbols: subscripts i and j will always pertain to the "purely classical" sets, and $\|\alpha_{ji}\|$ is the corresponding matrix of

are sufficiently small in both the initial and final states: $^1/_2\beta\hbar\omega_i$, $^1/_2\beta\hbar\omega_j' \ll 1$ for all i, j); the "purely quantum" sets $q_t' = \sum_s \beta_{ts} q_s$ (all of the frequencies are sufficiently high: $^1/_2\beta\hbar\omega_s$, $^1/_2\beta\hbar\omega_t' \gg 1$ for all s, t), and the "mixed" sets $q_l' = \sum_k \gamma_{lk} q_k$ (there are both high and low vibrational frequencies). For the subsequent analysis it will not be particularly essential whether there are one or several "purely classical" sets in the system. All of the "purely classical" sets are therefore conveniently united into one "purely classical" subsystem with bond matrix $\|\alpha_{ji}\|$. The concept of a "purely quantum subsystem" with bond matrix $\|\beta_{ts}\|$ is similarly introduced. At the same time it will be essential for us whether we can break down the entire "mixed subsystem" into individual independent "mixed subsystems." In the general case, we will therefore isolate several independent mixed subsystems with bond matrices $\|\gamma^{(1)}_{lk}\|$ and $\|\gamma^{(2)}_{lk}\|$. Thus we will break down the entire set of linear expressions (8) as follows:

$$q_j' = \sum_i \alpha_{ji} q_i; \quad q_t' = \sum_s \beta_{ts} q_s; \quad q_l^{(1)'} = \sum_k \gamma_{lk}^{(1)} q_k^{(1)}; \quad q_l^{(2)'} = \sum_k \gamma_{lk}^{(2)} q_k^{(2)} \ldots \tag{17}$$

We note that a part of the subsystems may be absent in the general case. In the present paper we will examine only the particular case in which there are only purely classical and purely quantum subsystems, i.e., the case in which there is no "intermixing" of the classical and quantum degrees of freedom during the reaction. The general case is considered in our next paper.

Processes without "Intermixing" of Classical and Quantum Degrees of Freedom

As was pointed out above, in this case all of the degrees of freedom of the system can be broken down into classical (q_i, q_j') and quantum (q_s, q_t') values, and "entangling" of the classical and quantum degrees of freedom does not occur during the process:

$$q_j' = \sum_i \alpha_{ji} q_i; \quad q_t' = \sum_s \beta_{ts} q_s. \tag{18}$$

For example, redox reactions that proceed without cleavage of and formation of valence bonds with frequencies $\omega \gtrsim 2kT/\hbar$, and a considerable number of proton transfer reactions fall into this class of reactions. A large part of the degrees of freedom of the solvent [12] and the intramolecular degrees of freedom with low vibrational frequencies $\omega \ll 2kT/\hbar$ enter into the classical subsystem in this case, and low-frequency vibrations in complex ions [13] (including aquo complexes) also fall into this subsystem. The quantum subsystem includes a small part of the degrees of freedom of the solvent [12] and also the high-frequency valence and deformation vibrations in molecules and complex ions with frequencies $\omega \gg \frac{2kT}{\hbar}$ (in particular, the valence and deformation vibrations of the protons in molecules practically always satisfy this condition [14]).

Analysis of equations (12) [8, 9] shows that the entire range of heat effects of the process ($-E_r' < \Delta J < E_r$) is conveniently broken down into three ranges: "activationless" ($-E_r' < \Delta J < -E_c'$; transfer coefficient θ^* is practically zero over the entire range), "normal" ($-E_c' < \Delta J < E_c$; θ^* changes slowly from zero to unity), and "barrierless" ($E_c < \Delta J < E_r$; θ^* is practically constant and equal to unity). Here E_c(E_c') is the reorganization energy of the purely classical subsystem for the initial (final) state: $E_c = \sum_i \frac{1}{2}\hbar\omega_i q_{i0}^2$; $E_c' = \sum_j \frac{1}{2}\hbar\omega_j' q_{j0}'^2$. The E_c and E_c' values are usually much smaller than the total re-

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relationship (9); similarly, subscripts s and t and matrix $\|\beta_{ts}\|$ of relationship (9) will correspond to the "purely quantum" sets; finally, k, l, and matrix $\|\gamma_{lk}\|$ will always pertain to the "mixed" sets. In particular, $^1/_2\beta\hbar\omega_i$; $^1/_2\beta\hbar\omega_j' \ll 1$; $^1/_2\beta\hbar\omega_s$, $^1/_2\beta\hbar\omega_t' \gg 1$ therefore always hold true.

organization energies E_r and E_r' but nevertheless prove to be extremely large (from 0.5 to several electron volts) for real processes.† Most processes therefore actually occur in the normal range of heat effects. In this case, the following formula is valid for the transition probability (W):

$$W=Ae^{-\beta E_a-\sigma} \tag{19}$$

$$E_a=\sum_i \frac{1}{2}\hbar\omega_i q_i^{*2};\quad \sigma=\sum_s \{q_s^{*2}+(q_s'^{*}-q_{s0}')^2\}, \tag{20}$$

where the q_i^* and q_s^* values are determined from the system of equations

$$q_s^*+\sum_t \beta_{ts}(q_t'^{*}-q_{t0}')=0 \quad \text{for all } s \tag{21a}$$

$$\begin{cases} (1-\theta^*)\hbar\omega_i q_i^*+\theta^*\sum_j \alpha_{ji}\hbar\omega_j'(q_j'^{*}-q_{j0}')=0 \quad \text{for all } i \\ \Delta J=\sum_i \frac{1}{2}\hbar\omega_i q_i^{*2}-\sum_j \frac{1}{2}\hbar\omega_j'(q_j'^{*}-q_{j0}')^2. \end{cases} \tag{21b}$$

It is easy to show with (20) and (21b) that the activation energy coincides with the distance between the minimum of the initial term and the saddle point on the cross section of the surface of the potential energy of the purely classical subsystem‡ :

$$\tilde{U}(q_i)=\sum_i \frac{1}{2}\hbar\omega_i q_i^2;\quad \tilde{U}'(q_j')=\sum_j \frac{1}{2}\hbar\omega_j'(q_j'-q_{j0}')^2+\Delta J. \tag{22}$$

We note that the terms of (22) are obtained from the electronic terms of (15) if all of the quantum degrees of freedom are "frozen," i.e., if it is assumed that all q_s in the initial state are equal to zero and that in the final state $q_t'=q_{t0}'$. Tunneling factor σ is directly associated with the overlap integral of the wave functions of the unexcited states of the quantum subsystem $\Phi_0^{(i)}$ and $\Phi_0^{(f)}$:

$$|\langle\Phi_0^{(f)}|\Phi_0^{(i)}\rangle|^2=e^{-\sigma}\left\{\prod_s \sqrt{\frac{\omega_s}{4\omega_s'}}\cdot\det\left\|\delta_{st}+\sum_r \beta_{rs}\beta_{rt}\right\|\right\}^{-1}. \tag{23}$$

It is convenient to introduce the exchange integral for the entire quantum subsystem

$$L_{\text{quant}}=\langle\Phi_0^{(f)}|L|\Phi_0^{(i)}\rangle, \tag{24}$$

which is equal to the matrix element from the perturbation that leads to transitions and is calculated by means of the wave functions of the ground state of both the electrons and the quantum degrees of freedom of the vibrational subsystem. Equation (19) can then be rewritten as follows:

$$W=A_{\text{cl}}\cdot e^{-\beta E_a};$$
$$A_{\text{cl}}=|L_{\text{quant}}|^2\left(\frac{2\pi\beta}{\hbar^2}\frac{d\theta^*}{d\Delta J}\right)^{1/2}\left\{\det\left\|(1-\theta^*)\delta_{ij}+\theta^*\sum_k \alpha_{ki}\alpha_{kj}\frac{\omega_k'}{\omega_i}\right\|\right\}^{-1/2}. \tag{25}$$

The expression for W can also be written in a form similar to the formula of the theory of absolute reaction rates [15]:

$$W=\frac{2\pi\beta}{\hbar}|L_{\text{quant}}|^2\left[\int_{-\infty}^{+\infty}\prod_i dq_i e^{-\beta\tilde{U}}\right]^{-1}\int_{-\infty}^{+\infty}\prod_i dq_i e^{-\beta\tilde{U}}\delta(\tilde{U}-\tilde{U}'). \tag{26}$$

However, it should be emphasized that, in contrast to [15], the integration in formula (26) is performed only with respect to the classical degrees of freedom, while the transition along the degrees of freedom with frequencies $\omega \gg 2kT/\hbar$ is essentially a quantum transition.

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† We note that according to [12] almost all of the repolarization energy of the solvent enters as a term into E_c.

‡ The expressions for $E_a(\Delta J)$ in several concrete cases are presented below.

The transition process can be interpreted in the following way: owing to the heat fluctuation of the classical subsystem (with a probability proportional to $e^{-\beta E_a}$), there arises a transition state with configuration $q_i = q_i^*$, in which the energies of the electrons and quantum vibrational subsystem for the initial and final states prove to be equal; tunneling of the entire quantum subsystem from the unexcited initial state to the unexcited final state occurs in the transition state with a certain probability $\varkappa$ (the "transmission coefficient")†; if this transition has occurred, the classical subsystem relaxes (at a fixed state of the quantum subsystem) to the final equilibrium state. Thus, prior "classical" stretching of the bonds does not occur along the quantum degrees of freedom, so that the quantum vibrational subsystem in the normal range will behave precisely like the electronic subsystem; these subsystems determine only the transmission coefficient ($\varkappa$), while, according to (26), the expression for the activation energy (E_a) is determined only by the classical subsystem.

We will now examine strongly exothermic reactions, in which $-E_r' < \Delta J < -E_c'$, i.e., an activationless process. In this case, we will assume for simplicity that the vibrational frequencies in the classical subsystem do not change too markedly during the transition. In this case, the activation energy (E_a) is practically zero. The tunneling factor (σ), which was constant over the entire normal range, begins to gradually decrease (up to zero when $\Delta J = -E_r'$). The decrease in σ is a consequence of the fact that the transitions to the excited states of the quantum subsystem in the final state with energies approximately equal to the difference $E_c' - \Delta J$ begin to make the primary contribution in this range:

$$\sigma = \sum_s \left\{ q_s^{*2} + (q_s''^* - q_{s0}')^2 \operatorname{th} \frac{1}{2} \beta \hbar \omega_s' \theta^* \right\}, \tag{27}$$

where q_s* and * are determined from the system of equations

$$\begin{cases} q_s^* + \sum\limits_t \beta_{ts} (q_t''^* - q_{t0}') \operatorname{th} \dfrac{1}{2} \beta \hbar \omega_t' \theta^* = 0 \quad \text{for all } s, & (28\text{a}) \\ \Delta J = -E_c' - \sum\limits_t \dfrac{\frac{1}{2} \hbar \omega_t' (q_t''^* - q_{t0}')^2}{\operatorname{ch}^2 \frac{1}{2} \beta \hbar \omega_t' \theta^*}. & (28\text{b}) \end{cases}$$

We note that, although $\theta^* \ll 1$ over all of this range, nevertheless the substitution $\theta^* \to 0$ cannot be made in expressions (28) in view of $\frac{1}{2} \beta \hbar \omega_t' \gg 1$.

If all of the degrees of freedom do not "entangle" within the quantum subsystem, but the vibrational frequencies, generally speaking, change during the transition [i.e., bond matrix $\|\beta_{ts}\|$ in (18) is diagonal, and, according to (8), $\beta_{ts} = \delta_{ts} \sqrt{\omega_s' / \omega_s}$], then

$$\sigma = \sum_s \frac{q_{s0}^2}{1 + \frac{\omega_s}{\omega_s'} \operatorname{cth} \frac{1}{2} \beta \hbar \omega_s' \theta^*} = \sum_s \frac{m_s}{\hbar} x_{s0}^2 \left[\frac{1}{\omega_s} + \frac{\operatorname{cth} \frac{1}{2} \beta \hbar \omega_s' \theta^*}{\omega_s'} \right]^{-1}, \tag{29}$$

where $x_{s0} = q_{s0} \sqrt{\frac{\hbar}{m_s \omega_s}}$ is the shift in the s-th equilibrium Cartesian coordinate, m_s is the mass corresponding to this degree of freedom, and θ^* is determined from the equation

$$\Delta J = -E_c' - \sum_s \frac{1}{2} \hbar \omega_s q_{s0}^2 \cdot \frac{1 - \operatorname{th}^2 \frac{1}{2} \beta \hbar \omega_s' \theta^*}{\omega_s / \omega_s' + \operatorname{th} \frac{1}{2} \beta \hbar \omega_s' \theta^*}; \quad \frac{1}{2} \hbar \omega_s q_{s0}^2 = \frac{1}{2} m_s \omega_s^2 x_{s0}^2 \tag{30}$$

[the substitution coth $\frac{1}{2} \beta \hbar \omega_s' \theta^* \to 1$ should be made on passing to the normal range in (29)].

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† The expressions for $\varkappa$ in the more general case were obtained in [14, 16].

It is convenient to use formula (16) for the probability of the reverse process (W') in investigating the barrierless range of the process (large positive heat effects of the process: $E_c < \Delta J < E_r$), when the transfer coefficient (θ^*) is close to unity. Since $\alpha' = 1 - \alpha$, the process, which is the reverse of the barrierless process, occurs without activation. In this range, therefore, E_a coincides with ΔJ; the transitions of the quantum subsystem from the excited initial states to the ground final state make the primary contribution to probability W, so that σ gradually decreases as ΔJ increases. In this case, formulas (27)-(30) are valid if the following substitutions are made in them: $\Delta J \to -\Delta J$, $E_c' \to E_c$, $\omega_s' \to \omega_s$, $\theta^* \to 1 - \theta^*$, $q_s \rightleftharpoons q_s' - q_{s0}'$, and $\beta_{ts} \to \beta_{st}(\omega_t/\omega_s')$ (inverse matrix).

Transitions in a Purely Classical System

When all of the vibrational degrees of freedom are classical, i.e., $\omega_i, \omega_i' \ll 2kT/\hbar$ for all degrees of freedom, formulas (19), (20), (21b), (22), (25), and (26), in which one should set σ equal to zero and L_{quant} equal to L, prove to be valid not only in the range $0 < \theta^* < 1$ (i.e., $-E_r' = -E_c' < \Delta J < E_c = E_r$), but also outside of this range. One can obtain simpler expressions for the activation energy for some particular cases.

For some classes of reactions [12, 14], the degrees of freedom of the solvent do not become "entangled" during the reaction either with one another or with the degrees of freedom of the reagents, and for reactions in water one can assume [12] for qualitative examination that all of the degrees of freedom of the polar medium are classical (in a more accurate examination [12] part of the degree of freedom of the solvent proves to be quantum in nature, so that these degrees, according to (20), make a contribution to σ rather than to E_a). If there is no substantial change in the length and angles of the valence bonds of the reagents (extraspheral reactions) during the reaction, then

$$E_a = \frac{(E_c + \Delta J)^2}{4E_c}, \tag{31}$$

where E_c is the reorganization theory of the solvent† (or, more precisely, its classical part). Formula (31) remains valid if, in addition to the solvent, there are intramolecular degrees of freedom that do not become "entangled" during the transition, and $\omega_i = \omega_i'$; in this case, the reorganization energy of these degrees of freedom also enters into E_c. In the more general case, when the intramolecular classical degrees of freedom do not become "entangled" during the reaction but their frequencies change ($\omega_i \neq \omega_i'$), i.e., $\alpha_{ki} = \delta_{ki}\sqrt{\omega_i'/\omega_i}$, then

$$E_a = \theta^{*2} \sum \frac{\frac{1}{2}\hbar\omega_i^2\omega_i'^2 q_{i0}'^2}{[(1-\theta^*)\omega_i^2 + \theta^*\omega_i'^2]^2}, \tag{32}$$

where θ^* is determined from the expression

$$\Delta J = \sum_i \frac{1}{2}\hbar\omega_i^2\omega_i' q_{i0}'^2 \frac{(1-\theta^*)^2\omega_i^2 - \theta^{*2}\omega_i'^2}{[(1-\theta^*)\omega_i^2 + \theta^*\omega_i'^2]^2}. \tag{33}$$

Formulas (32) and (33) are simplified if all of the frequencies change only slightly ($|\omega_i - \omega_i'| \ll \omega_i$):

$$E_a = \left(\frac{1}{2} + \frac{\Delta J}{E_c + E_c'}\right)\left[E_c\left(\frac{1}{2} + \frac{\Delta J}{E_c + E_c'}\right) + (E_c' - E_c)\left\{\frac{1}{4} + \left(\frac{\Delta J}{E_c + E_c'}\right)^2\right\}\right]. \tag{34}$$

The expressions for $E_a(\Delta J)$ are also simplified in the case of a sharp change in vibrational frequencies during the transition: suppose that, in addition to the degrees of freedom with invariable vibrational frequencies (in particular, the solvent) with total reorganization energy E_s, there are another two independent subsystems. In the first of these, the frequencies increase sharply during transition to the final state ($\omega_{i_1} \ll \omega_{j_1}'$ for all i_1, j_1), while in the second, the reverse condition $\omega_{i_2} \gg \omega_{j_2}'$ for all i_2, j_2 is satisfied. In this case, the coordinates within each of these two subsystems may become "entangled" in an arbitrary manner. Then

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† According to (20), the dependence $E_a(\Delta J)$ in the normal range also has the form of (31) for proton transfer reactions.

$$E_a = E_1 + \frac{(E_s + E_2' - E_1 + \Delta J)^2}{4E_s}, \tag{35}$$

where

$$E_1 = \sum_{i_1} \frac{1}{2} \hbar \omega_{i_1} q_{i_1 0}^2 \left(E_2' = \sum_{k_2} \frac{1}{2} \hbar \omega_{k_2}' q_{k_2 0}'^2 \right)$$

is the reorganization energy for the first (second) subsystem in the initial (final) state. This situation is typical, for example, for dissociation or substitution reactions [13, 16]. In this case, low ω_{i_1} and ω_{j_2} frequencies correspond to the vibrations of "free" particles in the solution as a whole, while high frequencies (ω_{j_1}' and ω_{i_2}) correspond to vibrations along the valence bonds.

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