KINETICS OF ELECTROCHEMICAL PROCESSES

V. QUANTUM-MECHANICAL THEORY. CALCULATION OF THE PROBABILITY OF TRANSITION FOR NONADIABATIC REACTIONS WITHIN THE HARMONIC APPROXIMATION (ENTANGLEMENT OF THE QUANTUM AND CLASSICAL DEGREES OF FREEDOM)

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Nonadiabatic transition between two multidimensional potential energy surfaces is examined within the harmonic approximation in a system in which, as a result of a reaction, there is entanglement of the coordinates of the classical and quantum vibrational degrees of freedom. A method for the calculation of the activation energy of the process and the tunneling factor is described. Various cases corresponding to different ratios between the number of classical and quantum degrees of freedom that are entangled with one another are investigated.

Some general formulas for the probability (W) of the elementary act of a reaction, the activation energy (E_a), the tunneling factor (σ), and the transfer coefficient (θ^*) in the case of nonadiabatic reactions were obtained in [1] within the framework of the harmonic approximation for the description of both a polar medium and the intramolecular degrees of freedom of the reagents:

$$W = A \exp\{-\beta E_a(\Delta J) - \sigma(\Delta J)\} \qquad (1)$$

(ΔJ is the heat effect of the process). In a previous paper [1], we investigated expressions for $E_a(\Delta J)$ and $\sigma(\Delta J)$ in the particular case of processes that are not accompanied by "entanglement," during the reaction, of the classical and quantum degrees of freedom. In the present paper, we consider the general case, when this sort of "entanglement" does occur. It should be noted that precisely the latter case is typical for chemical reactions that are accompanied by cleavage or formation of valence bonds. If the mass of particle B undergoing transfer during the reaction

$$AB + C \rightarrow A + BC \qquad (2)$$

is of the same order of magnitude as the mass of particle A or C, it is not difficult to show that, generally speaking, all of the coordinates that characterize the degrees of freedom of molecules AB and C are "entangled" with all of the degrees of freedom of molecules of A and BC; since the frequencies of the valence vibrations of molecules AB and BC are usually quite high ($\beta\hbar\omega \gg 1$), while the vibrational frequencies of molecules A and C as a whole are low (as a rule, $\beta\hbar\omega \ll 1$), when such "entanglement" is present, the classical and quantum degrees of freedom become "entangled" [2]. A similar situation is encountered in dissociation (or bonding) reactions,* for example, in reactions involving substitution of ligands in complex ions that proceed via an S_{N1} mechanism [3]

$$AB \rightarrow A + B \qquad (3)$$

under the condition that the valence bond in molecule AB that is undergoing cleavage is a quantum bond.

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*In the case of reactions with proton transfer (B = H), entanglement of the classical and quantum degrees of freedom can be disregarded in many cases.

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As has been discussed in detail in [1], matrix $\|\alpha_{\xi n}\|$, which interlinks the dimensionless final (q_ξ') and initial (q_η) normal coordinates, in the general case is quasidiagonal, such that the entire vibrational system can be broken down into several "independent" subsystems:

$$q_j' = \sum_i \alpha_{ji} q_i, \quad q_t' = \sum_s \beta_{ts} q_s, \quad q_l^{(1)'} = \sum \gamma_{lk}^{(1)} q_k^{(1)}, \quad q_l^{(2)'} = \sum \gamma_{lk}^{(2)} q_k^{(2)} \ldots . \tag{4}$$

It is essential that in the first of these subsystems (the "purely classical" subsystem) all of the degrees of freedom in both the initial and final states are classical; i.e., $\frac{1}{2}\beta\hbar\omega_i$, $\frac{1}{2}\beta\hbar\omega_j' \ll 1$, for all i, j. Similarly, in the "purely quantum" subsystem, $\frac{1}{2}\beta\hbar\omega_s$, $\frac{1}{2}\beta\hbar\omega_t' \gg 1$ for all degrees of freedom of the subsystem. Within each of the subsequent subsystems there are both classical and quantum degrees of freedom (the "mixed" subsystems). For the following examination it is essential that, according to the condition, none of these mixed subsystems can be further broken down into several independent subsystems.

For reactions in a polar liquid that are accompanied by transfer or redistribution of charge, there is always a purely classical subsystem in the system: for example, a large part of the degrees of freedom of the solvent [4] enters into it (as a first approximation, one can suppose that all of the degrees of freedom of the polar medium are classical). A part of the intramolecular degrees of freedom with high vibrational frequencies may enter, along with some degrees of freedom of the solvent [4] (with a relatively low total reorganization energy), into the purely quantum subsystem. We note that in what follows the presence or absence of a purely quantum subsystem is not particularly important (in the latter case, one should only omit the terms pertaining to this subsystem in all of the expressions). At the same time, the presence of a purely classical subsystem is, generally speaking, a fundamental feature. The transitions in a system in which this subsystem is absent are examined at the end of this paper.

The analysis made in [5, 6] demonstrated that, just as in the case of systems without "entanglement" of the classical and quantum degrees of freedom [1], one can isolate, within the range $-E_r' < \Delta J < E_r$ (E_r and E_r' are the total reorganization energies of the system in the initial and final states), three subregions in which the process takes place: normal (transfer coefficient θ^* is not too close to 0 and 1), activationless ($\theta^* \simeq 1$), and barrierless ($\theta^* \simeq 0$). The heat effects (ΔJ) corresponding to each of the regions are presented below [formulas (17), (18), and (20)].

Let us consider the normal range in which the process occurs. To simplify the formulas, we will initially investigate the case in which there is only one " independent" mixed subsystem in the system with bond matrix $\|\gamma_{lk}\|$ (the general case is discussed below). It is convenient to introduce the following numbering of the degrees of freedom within the mixed subsystem: initially the classical degrees of freedom are numbered in both the initial and final states, after which the quantum degrees of freedom are numbered; i.e., $\frac{1}{2}\beta\hbar\omega_k$, $\frac{1}{2}\beta\hbar\omega_l' \ll 1$ when

$$k=1,2,\ldots,M; \quad l=1,2,\ldots,L \text{ and } \frac{1}{2}\beta\hbar\omega_k, \quad \frac{1}{2}\beta\hbar\omega_l' \gg 1$$

when k = M + 1, M + 2,..., P; l = L + 1, L + 2,..., P (P is the total number of degrees of freedom in the subsystem; the M and L values, in particular, may be equal to zero or P). When this is done, the following principles, which make it possible to find the energy of activation (E_a) of the process and the tunneling factor (σ), prove to be valid:

1) The magnitude of E_a is associated with the motion only along the classical degrees of freedom (in the initial state), while σ is due to subbarrier passage only along the quantum degrees of freedom (in the initial and final states). The unexcited states of the initial and final quantum degrees of freedom (in both the purely quantum and mixed subsystems) make the principal contribution to probability W. In particular, this means that none of the initial quantum degrees of freedom undergo prior activation; i.e., the corresponding bonds in the reagents remain unstretched up to the instant of the electron transition from the initial state to the final state. In other words, the system passes from the initial electronic term U to the final term U'

$$U = \sum_{\nu=(i,s,k)} \frac{1}{2}\hbar\omega_\nu q_\nu^2, \quad U' = \sum_{\mu=(j,t,l)} \frac{1}{2}\hbar\omega_\mu'(q_\mu' - q_{\mu 0}')^2 + \Delta J \tag{5}$$

such that up until the instant of the transition all of the initial "quantum" coordinates are equal to their equilibrium values (i.e., zero), but directly after the transition the coordinates for all of the final quantum degrees of freedom are equal to their equilibrium values for the final state. This means, in particular, that passage of the system from U to U' generally does not occur at the intersection of these surfaces (but the activation energy by no means always coincides with the energy at the corresponding saddle point).

2) Finding the tunneling factor (σ): for this, one must examine the index of the exponent that arises during remultiplication of the squares of the wave functions of the unexcited initial and final states ($\pi^{-1/4}e^{-q^2/2}$; $\pi^{-1/4}e^{-1/2(q'-q_0')^2}$) only for the quantum degrees of freedom:

$$\Sigma = \sum_s \{q_s^2 + (q_s' - q_{s0}')^2\} + \sum_{k=M+1}^{P} q_k^2 + \sum_{l=L+1}^{P} (q_l' - q_{l0}')^2. \tag{6}$$

In formula (6) the summation is made over all the quantum degrees of freedom both within the purely quantum subsystem ($\sum_s$), and within the mixed subsystems $\left(\sum_{k=M+1}^{P};\ \sum_{l=L+1}^{P}\right)$. The σ value is equal to the minimum Σ in formula (6) with allowance for the relationships (4) between the q' and q values; in minimizing Σ there is no imposition of any conditions whatsoever on the q_k and q_l' values ($1 \le k \le M$; $1 \le l \le L$) in (4), which correspond to the classical degrees of freedom. Thus to find σ it is sufficient to substitute the q^* and q'^* values found in the solution of the following system of equations into formula (6):

$$q_s^* + \sum_t \beta_{ts}(q_t'^* - q_{t0}') = 0 \quad \text{for all } s, \tag{7a}$$

$$\begin{cases} \sum\limits_{l=L+1}^{P} \gamma_{lk}(q_l'^* - q_{l0}') = 0 & \text{for} \quad 1 \leqslant k \leqslant M, \\ q_k^* + \sum\limits_{l=L+1}^{P} \gamma_{lk}(q_l'^* - q_{l0}') = 0 & \text{for} \quad M+1 \leqslant k \leqslant P \end{cases} \tag{7b}$$

with allowance for relationships (4).

It follows from formulas (6) and (7a) that in the presence of a purely quantum subsystem, tunneling factor σ is always some value other than zero (only if not all of the q_{j0}' shifts are simultaneously equal to zero); i.e., this subsystem in all cases makes the nonzero contribution $\sigma^{\text{quant}} = \sum_s \{q_s^{*2} + (q_s'^* - q_{s0}')^2\}$. to σ. At the same time, the mixed subsystem does not always make a contribution to σ (for greater detail, see below). It can also be shown [5, 6] that in the most general case tunneling factor σ is constant over the entire normal range; i.e., it is independent of the heat effect (ΔJ) of the process (and also independent of the temperature, only if in this case there is no change in the character of the motion along any of the classical or quantum degrees of freedom);

3) Finding the activation energy (E_a): let us introduce the effective potential energy surfaces for all of the classical degrees of freedom:

$$\begin{gathered} U = \sum_t \frac{1}{2}\hbar\omega_t q_t^2 + \sum_{k=1}^{M} \frac{1}{2}\hbar\omega_k q_k^2, \\ U' = \sum_j \frac{1}{2}\hbar\omega_j'(q_j' - q_{j0}')^2 + \sum_{l=1}^{L} \frac{1}{2}\hbar\omega_l'(q_l' - q_{l0}')^2 + \Delta J; \end{gathered} \tag{8}$$

these expressions are obtained from the electronic terms of (5), if all of the quantum degrees of freedom are "frozen," i.e., if $q_s = 0$; $q_k = 0$ ($M + 1 \le k \le P$); $q_t' = q_{t0}'$; $q_l' = q_{l0}'$ ($L + 1 \le l \le P$) (we note that when $M \ne L$ these surfaces have a different numbers of measurements). The activation energy is equal to the minimum energy on the intersection of these surfaces with allowance for the relationships that are imposed on the "quantum" variables q_k ($M + 1 \le k \le P$) and q_l' ($L + 1 \le l \le P$) during minimization of Σ in (6) [i.e., these values are equal to q_k^* ($M + 1 \le k \le P$) and $q_l'^*$ ($L + 1 \le l \le P$), found from (7b)].

Four cases, which differ in the values of the ranks of their Γ and Γ' matrixes [7], can occur in finding the σ and E_a values for concrete processes:

$$\begin{gathered} R = \operatorname{rank}\ \Gamma \equiv \operatorname{rank} \begin{Vmatrix} \gamma_{L+1,1} \cdots \gamma_{L+1,M} \\ \cdots\cdots\cdots \\ \gamma_{P,1} \cdots \gamma_{P,M} \end{Vmatrix}; \\ R' = \operatorname{rank}\ \Gamma' \equiv \operatorname{rank} \begin{Vmatrix} \gamma_{L+1,1} \cdots \gamma_{L+1,M}\ q'_{L+1,0} \\ \gamma_{P,1} \cdots \gamma_{P,M}\ q'_{P0} \end{Vmatrix}, \end{gathered} \tag{9}$$

namely: a) $R=M$, $R<R'$; b) $R=M$, $R=R'$; c) $R<M$, $R=R'$; d) $R<M$, $R<R'$ (it follows from the determination of the rank of the matrix that $R\le M$ and $R\le R'$ always). The ratio between R and R' determines the magnitude of the tunneling factor for mixed subsystem $\sigma^{\text{mixed}}=\sigma-\sigma^{\text{quant}}=\sum_{k=M+1}^{P} q_k^{*2}+\sum_{l=L+1}^{P}(q_l'^{*}-q_{l0}')^2$ when $R=R'$ $\sigma^{\text{mixed}}=0$, i.e.; the system of equations (7b) with allowance for (4) permits solutions of the form $q_k^*=0$ $(M+1\le k\le P)$, $q_l'^*=q_{l0}'$ $(L+1\le l\le P)$; if, however, $R<R'$, the σ^{mixed} factor differs from zero, $q_k^*\ne 0$, and $q_l'^*\ne q_{l0}'$. In satisfying the condition $R=M$, system of equations (7b) with allowance for (4) uniquely† determines all of the q_k^* and $q_l'^*$ $(1\le k,\ l\le P)$ coordinates in the mixed subsystem; this means, in particular, that all of the initial "classical" variables in the subsystem q_k^* $(1\le k\le M)$ and, consequently, the contribution of this subsystem to the activation energy $E_a^{\text{mixed}}=\sum_{k=1}^{M}\frac{1}{2}\hbar\omega_k q_k^{*2}$ [see (8)] are determined unambiguously in the process of finding σ^{mixed}. Therefore, when $R=M$, the activation energy for the mixed subsystem (E_a^{mixed}) is independent of ΔJ, so that to find the total activation energy [$E_a=E_a^{\text{class}}(\Delta J)+E_a^{\text{mixed}}$] one should find the energy at the saddle point on the intersection of the surfaces:

$$U=\sum_i\frac{1}{2}\hbar\omega_i q_i^2+E_m;\quad U'=\sum_j\frac{1}{2}\hbar\omega_j'(q_j'-q_{j0}')^2+E_m'+\Delta J, \tag{10}$$

in which $E_m=\sum_{k=1}^{M}\frac{1}{2}\hbar\omega_k q_k^{*2}$; $E_m'=\sum_{l=1}^{L}\frac{1}{2}\hbar\omega_l'(q_l'^{*}-q_{l0}')^2$ are independent of the heat effect of the process (ΔJ).

Let us now examine the indicated four classes of processes in greater detail.

a) $R=M<R'$. As a rule, these conditions are satisfied (although not always) when $P-L>M$, i.e., when the total number of classical degrees of freedom $M+L$ (in the initial and final states) within the mixed subsystem does not exceed the total number of quantum ($2P-M-L$) degrees of freedom. This case is apparently quite typical for chemical reactions, since most of the valence and deformation vibrations should be considered to be quantum values. As a simple example, one can cite the electrochemical removal of adsorbed atomic hydrogen from the electrode surface:

$$H_{ads}+H_2O\rightarrow H_2+OH^- \text{ or } H_{ads}+H_3O^+\rightarrow H_2+H_2O. \tag{11}$$

As the simplest model for this reaction, one should take into account the H_{ads} valence vibrations (along the bond with the metal; $\omega_a\sim 10^{14}\ \text{sec}^{-1}\gg 2kT/\hbar$) and the valence vibrations of the proton in H_2O or H_3O^+ ($\omega\sim 5\cdot 10^{14}\ \text{sec}^{-1}$); in the final state an H_2 molecule with a very rigid valence bond ($\omega\simeq 8\cdot 10^{14}\ \text{sec}^{-1}$), the vibrations of which as a whole are of very low frequency, is formed. In this case, $P=2$, $M=0$, and $L=1$, so that the condition $P-L>M$ is satisfied (consideration of the deformation vibrations for H_{ads} and the proton in H_2O and H_3O^+ and of the other valence bonds only reinforces this inequality).

In the case under consideration, system of equations (7b) with allowance for relations (4) $q_l'=\sum_{k=1}^{P}\gamma_{lk}q_k$ unambiguously determines all of the q_k^* and $q_l'^*$ values $(1\le k,\ l\le P)$, in which q_k^* and $q_l'^*-q_{l0}'$, generally speaking, differ from zero. As already indicated above, the tunneling factor for the mixed subsystem (σ^{mixed}) differs from zero; i.e., the system effects quantum subbarrier transition along tne coordinates of not only the electronic purely quantum subsystem but also those of the mixed subsystem. To find the activation energy (E_a), one should, in accordance with (10), examine the potential energy surfaces only for the purely classical subsystem for the "effective heat effect" ($\Delta j=\Delta J+E_m'-E_m$) and calculate the energy at the saddle point $\sum_i\frac{1}{2}\hbar\omega_i q_i^2$; E_m should be added to the value obtained. Thus the addition of the mixed subsystem, for which $R=M<R'$, leads to an increase in the tunneling factor by σ^{mixed} and an increase in the activation energy by E_m; in addition, E_a also changes due to "mixing" of the heat effect by $E_m'-E_m$. In the simplest case, in which neither the system of normal coordinates nor the vibrational frequencies change, the activation energy [see formula (31) in [1]) is

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† Using the methods of linear algebra [7], one can show that the system of equations (7b) and (4) has solutions for any $\|\gamma_{lk}\|$ and q_{l0}' values.

$$E_a = E_m + \frac{(E_c + \Delta J + E_m' - E_m)^2}{4E_c}. \tag{12}$$

b) $R = R' = M$. This case is typical for processes for which the condition $M + L = P$ is satisfied, i.e., the total number of classical degrees of freedom coincides with the total number of quantum degrees of freedom in the mixed subsystem. This sort of situation is also encountered extremely frequently in investigations of concrete processes. As typical examples, one can cite substitutions of ligands in complex metal ions that proceed via S_{N1} and S_{N2} mechanisms. In the first case (the simplest model is considered for these reactions), in both dissociation and bonding there is a degree of freedom (the distance between the ions and the ligand) that is converted from a quantum degree of freedom (ion–ligand bond) to a classical degree of freedom (vibrations of the ligand in solution) or vice versa; in this case, $P = 1$, $M = 0$, and $L = 1$, or $M = 1$, $L = 0$, so that the condition $M + L = P$ is satisfied. Similarly, in the second case (S_{N2} mechanism) there are two coordinates (the distances between the ion and the ligands), and at first one bond is very rigid (the ligand is bonded to the ion), while the low-frequency vibrations of the second ligand in solution as a whole correspond to the second coordinate; in the final state, the character of the motion along both coordinates is reversed. Therefore $P = 2$, $M = 1$, and $L = 1$, so that $M + L = P$ in this case.

In contrast to case (a), when the condition $R = R' = M$ is satisfied, the tunneling factor for the mixed subsystem (σ^{mixed}) reverts to zero; i.e., there is a classical superbarrier transition along the coordinates of this subsystem. However, in contrast to the purely classical subsystem, the trajectory of motion of the system along coordinates $q_k (1 \leq k \leq M)$ and $q_l' (1 \leq l \leq L)$ proves to be unambiguously determined, and in particular, is independent of the heat effect of the process. Coordinates $q_k^* = 0$ $(M + 1 \leq k \leq P)$ and $q_l'^* = q_{l0}'$ $(L + 1 \leq l \leq P)$, correspond to the transition state; i.e., to find the remaining q_k^* $(1 \leq k \leq M)$ values it is sufficient to solve the system of equations, among which there are exactly M linearly independent equations:

$$\sum_{k=1}^{M} \gamma_{lk} q_k^* = q_{l0}' \qquad (L+1 \leqslant l \leqslant P) \tag{13}$$

[the $q_l'^*$ $(1 \leq l \leq L)$ values are then found from $q_l'^* = \sum_{k=1}^{M} \gamma_{lk} q_k^*$]. Everything that was stated in case (a) is valid for finding the total activation energy (E_a) of the process; in this case, the solutions of Eqs. (13) should be substituted into formula (10) as the q_k^* and $q_l'^*$ values. We note that in both case (a) and (b) one of the E_m, E_m' values in formula (10) may be absent; for example, $E_m = 0$ if there is no classical degree of freedom in the initial state in the mixed subsystem.

c) $R = R' < M$. This case is usually realized when the condition $M + L > P$ is realized, i.e., when there are more classical than quantum degrees of freedom in the mixed subsystem.

In the case under consideration, the tunneling factor for the mixed subsystem (σ^{mixed}) proves to be zero; i.e., a classical superbarrier transition occurs along the coordinates of this system. The fundamental difference between this case and case (b) is the dependence of the "reaction path" along the coordinates of the mixed subsystem on the heat effect of the process (ΔJ); i.e., $E_a^{\mathrm{mixed}} = \sum_{k=1}^{M} \frac{1}{2} \hbar\omega_k q_k^{*2}$ proves to be a function of ΔJ. To find the total activation energy $E_a = \sum_i \frac{1}{2} \hbar\omega_i q_i^{*2} + \sum_{k=1}^{M} \frac{1}{2} \hbar\omega_k q_k^{*2}$ [see (8)], one should solve the system of equations.

$$(1-\theta^*)\hbar\omega_i q_i^* + \theta^* \sum_j \alpha_{ij} \hbar\omega_j' (q_j'^* - q_{j0}') = 0 \quad \text{for all } i, \tag{13a}$$

$$(1-\theta^*)\hbar\omega_k q_k^* + \theta^* \sum_{l=1}^{L} \gamma_{lk} \hbar\omega_l' (q_l'^* - q_{l0}') + \sum_{l=L+1}^{P} \nu_l \gamma_{lk} = 0 \quad \text{for } 1 \leqslant k \leqslant M, \tag{13b}$$

$$\Delta J = \sum_i \left\{ \frac{1}{2} \hbar\omega_i q_i^{*2} - \frac{1}{2} \hbar\omega_i' (q_i'^* - q_{i0}')^2 \right\} + \sum_{k=1}^{M} \frac{1}{2} \hbar\omega_k q_k^{*2} - \sum_{l=1}^{L} \frac{1}{2} \hbar\omega_l' (q_l'^* - q_{l0}')^2 \tag{13c}$$

(ν_l is the set of P–L auxiliary variables) with allowance for the bond equations:

$$q_j'^{*} = \sum_{i} \alpha_{ji} q_i; \quad q_l'^{*} = \sum_{k=1}^{M} \gamma_{lk} q_k^{*} \, (1 \leqslant l \leqslant L); \quad \sum_{k=1}^{M} \gamma_{lk} q_k^{*} = q_{l0}'$$
$$(L+1 \leqslant l \leqslant P). \tag{14}$$

This means that E_a is equal to the energy at the saddle point at the intersection of the effective terms of (8) with allowance for relationships (14). We note that in principle the case (when $R < P-L$) in which not all of the equations among the last $(P-L)$ equations of (14) are independent is possible. However, it can be shown [6] that system of equations (13-14) determines all of the q_k^* $(1 \le k \le M)$ and $q_l'^*$ $(1 \le l \le L)$ values in this case also. Thus when $R = R' < M$ the behavior of the mixed subsystem is similar to that of the purely classical subsystem.

d) $R < R'$; $R < M$. It should be expected that this case is realized extremely rarely, since $R' \le P-L$, so that $R < \min\{M, P-L\}$, which is unlikely. We will therefore only mention the results of the investigation in [6] (especially since the equations for $q_k{}^*$ and $q_l'^*$ prove to be most complex precisely in this case). Generally speaking, both the purely quantum (if there is one in the system) and the mixed subsystems make a nonzero contribution to the tunneling factor (σ), and, as always, σ is independent of ΔJ. As in case (c), the contribution to the activation energy from the mixed subsystem ($E_a{}^{\text{mixed}}$) depends on ΔJ.

We note that the $E_a{}^{\text{mixed}}$ value in cases (c) and (d) tends to other-than-zero limits of $\sum_{k=1}^{M} \frac{1}{2} \hbar\omega_k q_k^{*2}$ on approaching the boundaries of the normal region; in case (c) the q_k^* values for small θ^* (boundary of the normal and activationless regions) are determined from Eqs. (13) and (14) when $\theta^* = 0$, i.e.,

$$\left\{ \begin{array}{ll} \hbar\omega_k q_k^{*} + \sum\limits_{l=L+1}^{P} \gamma_{lk} v_l = 0 & \text{for} \quad 1 \leqslant k \leqslant M, \\ \sum\limits_{k=1}^{M} \gamma_{lk} q_k^{*} = q_{l0}' & \text{for} \quad L+1 \leqslant l \leqslant P. \end{array} \right. \tag{15}$$

Thus when a mixed subsystem is present in all cases (a), (b), (c), and (d) the activation energy generally remains finite, even when the transfer coefficient (θ^*) becomes very close to zero.

Up to this point we have examined processes in which there is only one "independent" mixed subsystem. In the general case [(4)], there is a set of mixed subsystems with bond matrixes $\|\gamma_{lk}^{(1)}\|, \|\gamma_{lk}^{(2)}\| \ldots$. In this case, the principles formulated above remain in force for finding E_a and σ with the obvious changes in (6), (7b), and (8). After this, one should, in accordance with (9), determine the ranks of all of the $\|\gamma_{lk}^{(n)}\|$ matrixes. The subsequent analysis (cases a, b, c, and d) is carried out separately for each of the mixed subsystems. In this case, the tunneling factors are found for all of the mixed subsystems, and the activation energies ($E_a{}^{\text{mixed}}$) are found for the mixed subsystems pertaining to cases (a) and (b). When there are mixed subsystems corresponding to cases (c) and (d), one should find [see case (c)] the saddle point at the intersection of the terms:

$$\tilde{U} = \sum_{i} \frac{1}{2} \hbar\omega_i q_i^2 + \sum_{\text{class}} \frac{1}{2} \hbar\omega_k q_k^2,$$
$$\tilde{U}' = \sum_{j} \frac{1}{2} \hbar\omega_j' (q_j' - q_{j0}')^2 + \sum_{\text{class}} \frac{1}{2} \hbar\omega_l' (q_l' - q_{l0}')^2 + \Delta J \tag{16}$$

with allowance for relationships (14) for mixed subsystems of the (c) and (d) type; the terms in $\tilde{U}$ and $\tilde{U}'$ pertaining to subsystems of the (a) and (b) types are independent of ΔJ and can be found beforehand by the methods indicated in (a) and (b).

Before passing to an examination of the activationless region of the process, we note that the heat effects (ΔJ) of the process in the range

$$-E_c' - E_M' + E_m < \Delta J < E_c + E_M - E_m', \tag{17}$$

where E_c (E_c') is the reorganization energy of the purely classical subsystem $\sum_i \frac{1}{2}\hbar\omega_i q_{i0}^2 \left(\sum_j \frac{1}{2}\hbar\omega_j' q_{j0}'^2\right)$ for the forward (reverse) process, and E_m (E_M) is the minimum (maximum) value $E_a^{\text{mixed}} = \sum_{k=1}^{M} \frac{1}{2}\hbar\omega_k q_k^{*2}$ in the normal region†: to find E_m one must solve Eqs. (15), while Eqs. (13b) and (14) must be solved for $\theta^* = 1$ to find E_M. Similarly, E_m' (E_M') is the minimum (maximum) value of the activation energy for mixed subsystems $E_a'^{\text{mixed}} = \sum_{l=1}^{L} \frac{1}{2}\hbar\omega_l'(q_l'^* - q_{l0}')^2$ for the reverse process; i.e., one must substitute solutions of (13b) and (14), respectively, for $\theta^* = 1$ and $\theta^* = 0$ in place of $q_l'^*$. In the activationless region, in which ΔJ lies in the range

$$-E_r' < \Delta J < -E_c' - E_M' + E_m \tag{18}$$

(E_r' is the total reorganization energy of the system for the reverse process [1]), transfer coefficient θ^* is always very small ($\theta^* \ll 1$). The activation energy of the process (E_a) is determined only by the mixed subsystem ($E_a = E_a^{\text{mixed}}$) and very slowly decreases from E_m to zero. The tunneling factor ($\sigma = \sigma^{\text{quant}} + \sigma^{\text{mixed}}$) also changes similarly. This effect is associated with excitation of the quantum degrees of freedom of the final state (in both the purely quantum and the mixed subsystems). To find

$$E_a = \sum_{k=1}^{M} \frac{1}{2}\hbar\omega_k q_k^{*2} \text{ and}$$

$$\sigma = \sum_s \left\{ q_s^{*2} + (q_s'^* - q_{s0}')^2 \operatorname{th} \frac{1}{2}\beta\hbar\omega_s'\theta^* \right\} + \sum_{k=M+1}^{P} q_k^{*2} + \sum_{l=L+1}^{P} (q_l'^* - q_{l0}')^2 \operatorname{th} \frac{1}{2}\beta\hbar\omega_l'\theta^*$$

one should solve the system of equations

$$q_s^* + \sum_l \beta_{ls}(q_l'^* - q_{l0}') \operatorname{th} \frac{1}{2}\beta\hbar\omega_l'\theta^* = 0 \quad \text{for all } s, \tag{19a}$$

$$\frac{1}{2}\beta\hbar\omega_k q_k^* + \sum_{l=L+1}^{P} \gamma_{lk}(q_l'^* - q_{l0}') \operatorname{th} \frac{1}{2}\beta\hbar\omega_l'\theta^* = 0 \quad \text{for} \quad 1 \leqslant k \leqslant M, \tag{19b}$$

$$q_k^* + \sum_{l=L+1}^{P} \gamma_{lk}(q_l'^* - q_{l0}') \operatorname{th} \frac{1}{2}\beta\hbar\omega_l'\theta^* = 0 \quad \text{for} \quad M+1 \leqslant k \leqslant P,$$

$$\begin{aligned} \Delta J = -E_c' &+ \sum_{k=1}^{M} \frac{1}{2}\hbar\omega_k q_k^{*2} - \sum_{l=1}^{L} \frac{1}{2}\hbar\omega_l'(q_l'^* - q_{l0}')^2 - \\ &- \sum_{l=L+1}^{P} \frac{\frac{1}{2}\hbar\omega_l'(q_l'^* - q_{l0}')^2}{\operatorname{ch}^2 \frac{1}{2}\beta\hbar\omega_l'\theta^*} - \sum_s \frac{\frac{1}{2}\hbar\omega_s'(q_s'^* - q_{s0}')^2}{\operatorname{ch}^2 \frac{1}{2}\beta\hbar\omega_s'\theta^*}. \end{aligned} \tag{19c}$$

Thus the purely classical subsystem effects an "activationless" transition to the final state, while the mixed subsystem undergoes prior activation up to energy $E_a = \sum_{k=1}^{M} \frac{1}{2}\hbar\omega_k q_k^{*2}$.

The range of barrierless transitions, in which

$$E_c + E_M - E_m' < \Delta J < E_r \tag{20}$$

and transfer coefficient θ^* is very close to unity, is readily investigated by means of the expression for the rates of the forward and reverse processes [1].

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*In cases (a) and (b), $E_m = E_M$ and $E_m' = E_M'$.

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