KINETICS OF ELECTROCHEMICAL PROCESSES

I. SEMIPHENOMENOLOGICAL THEORY

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The microscopic Brönsted relation is used on the basis of highly general physical premises to obtain expressions for the volt-ampere characteristic of an electrochemical system with consideration of the continuous electron spectrum in the electrode. A generalized Brönsted relation that characterizes the electrochemical reaction as a whole is derived. The conditions under which it is possible to observe quasinonbarrier and quasinonactivation processes are discussed.

Considerable progress has been made in the theory of electrode processes during the last decade, both in understanding of the physical mechanism of the elementary event and in the acquisition of quantitative results in calculations of current and other kinetic parameters. We now have a quantum-mechanical theory covering a rather broad class of electrode processes that take place either with or without a change in reagent chemical bonds [1–3]. Nevertheless, it appears expedient to construct a consistent semiphenomenological theory of electrochemical reactions, on the one hand to broaden further the range of problems that can be treated and, on the other, to dispense to the extent possible with the model hypotheses of the quantum-mechanical theory.

The semiphenomenological theory to be set forth is based on a number of physical hypotheses, which will be enumerated below. Some of them are quite obvious; others have been confirmed by the results of quantum-mechanical calculations, some of which are published here, while others will be published in later articles of this series. The basic premises of the theory consist in the following: 1) the total current is composed of independent events in which ions are discharged with participation of electrons at various energy levels in the electrode;* 2) transport of charge to the electrode is the inhibited stage; 3) the probability of transition of the system in a unit of time from its initial state to its final state with fixed initial and final electron states and with fixed initial (m) and final (n) states of the quantum vibrational degrees of freedom [2] is given by the equation of the theory of absolute reaction rates (or the Arrhenius equation);

$$W_{mn}(\varepsilon)=\frac{kT}{h}\varkappa_{mn}\exp\left[-\frac{F_a^{mn}}{kT}\right]=\mathrm{const}\exp\left(-\frac{E_a^{mn}}{kT}\right), \tag{1}$$

where $\varkappa_{mn}$ is the transmission coefficient, F_a^{mn} and E_a^{mn} are the free energy and the activation energy, and ε is the energy of the electron in the electrode.

The general ideas of the semiphenomenological theory will be illustrated by the calculation for an electrochemical reaction in the course of which "free" electrons from the electrode pass to discrete isolated final-state levels (cathodic current) or vice versa (anodic current). This pertains to all possible electron-transport electrochemical processes, as well as to reactions that are accompanied by adsorption of

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*As was shown in [8], this hypothesis is valid for nonadiabatic electrochemical reactions.

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particles on the electrode. With these hypotheses, the general expression for the cathodic current takes the form [3]

$$\vec{i} = Av_m \sum_m \int \vec{i}^{mn}(\varepsilon)\,d\varepsilon = Av_m \sum_n \Phi_m(c_i)\, e\, \frac{kT}{h} \varkappa_{mn} \rho \int n(\varepsilon)\, e^{-\frac{F_a^{mn}(\varepsilon,\, e\eta)}{kT}}\, d\varepsilon, \tag{2}$$

where Av_m denotes averaging over the initial quantum vibrational states, $\Phi_m(c_i)$ is a concentration factor that characterizes the probability of entry of particles participating in one discharge event into the reaction zone, and $n(\varepsilon)$ and ρ are the Fermi electron distribution function and the density of the electron states in the metal.

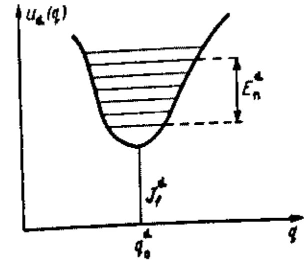

Fig. 1

The back current can be found by assuming that, despite the flow of current, the filling of the energy levels is of quasiequilibrium nature, and by using the principle of detailed balance. As a result, we obtain for the total current i

$$i = \vec{i} - \overleftarrow{i} = \vec{i}\left(1 - \exp\left[-\sum_\alpha \mu_\alpha \nu_\alpha / kT\right]\right), \tag{3}$$

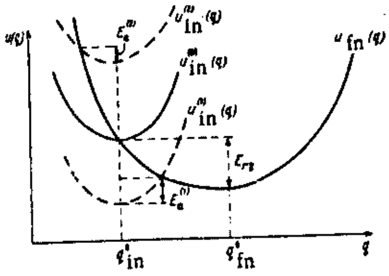

Fig. 2

where μ_α and ν_α are the quasiequilibrium electrochemical potentials of the substances participating in the reaction and the corresponding stoichiometric coefficients. If the adsorbed-particle coverages θ_a of the surface are small, we may, in view of the fact that in a steady-state process the electrochemical potentials of particles in the volume of the solution or in a gaseous phase are constant, while the electrochemical potential of the electron is $\mu_e = \mu_e^0 - e\eta$, where $\eta = \varphi_M - \varphi_M^0$ is the overvoltage, rewrite Eq. (3) in the form

$$i = \vec{i}\left[1 - \exp\left(\frac{\nu_e e\eta}{kT}\right) \prod_a (\theta_a^0/\theta_a)^{\nu_a}\right], \tag{4}$$

where θ_a^0 is the coverage of the surface at the equilibrium potential ($\varphi_M = \varphi_M^0$).

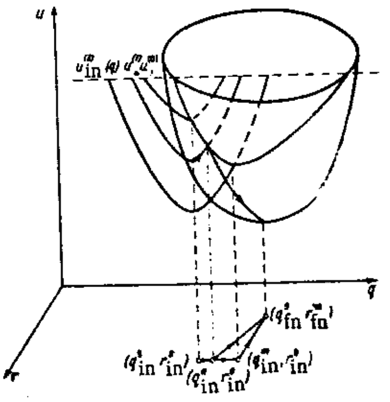

Fig. 3

The Brönsted relation, which established linearity between the logarithm of the reaction rate constant and the reaction heat Q_0 (or the standard free-energy change ΔF), plays an important role in construction of the semiphenomenological theory of electrode-process kinetics. The Brönsted relation is often written as a linear relation between the transition activation energy and Q_0 (or ΔF). As was shown in [3], the Arrhenius equation is, strictly speaking, valid only for the transition probability at fixed initial and final states of the quantum subsystem. Thus, if E_a is understood in the Brönsted relation as the activation energy determined by a saddle point on certain potential-energy surfaces, the Brönsted relation should be satisfied only for each partial process in the system's transition from its initial to its final state with fixed states of the entire quantum subsystem (ε, m, n). Numerous experimental studies made in recent years have shown that the linear Brönsted relation is approximate and is satisfied only in certain reaction-heat ranges. Therefore, we shall henceforth use the microscopic Brönsted relation (for the partial process) in its differential form

$$\alpha^{mn}(\varepsilon, \eta) = -\partial F_a^{mn}(\Delta F^{mn}(\varepsilon, \eta)) \,/\, \partial \Delta F^{mn}(\varepsilon, \eta), \tag{5}$$

where $\Delta F^{mn} = (F_i^m - F_f^n)$ is the free energy of the partial process. The nonequilibrium free energies of the initial and final states of the partial process, F^m and F_f^n, are

$$F_i^m = J_i^m + \mathcal{F}_i^m, \quad F_f^n = J_f^n + \mathcal{F}_f^n, \tag{6}$$

where J_i^m and J_f^n are the minimum potential energies of the classical subsystem for fixed states of the quantum subsystem (ε, m, n), $\mathcal{F}_i^m$ and $\mathcal{F}_f^n$ are the free energies of the classical subsystem at fixed (ε, m, n) and are determined by its energy spectrum E_m^i and E_n^f, which are read from J_i^m and J_i^n, respectively (Fig. 1).

Since the dependence of F_i^m on the electron energy ε and on the electrode potential φ_M will be important for what follows, it is convenient to separate in explicit form from J_i^m the energy of the electron in the metal $(\varepsilon - e\varphi_M)$ and the electrostatic energy of the ions in solution $\sum_i z_i e\varphi_i$, where φ_i is the potential at the position of the i-th ion: $J_i^m = (\varepsilon - e\varphi_M) + \sum_i z_i e\varphi_i + U_{i0}^m$. The quantity ε appears in F_i^m only as a summand. On the other hand, the dependence of F_i^m on φ_M is more complicated, since φ_i, U_{i0}^m, and $\mathcal{F}_i^m$ also generally depend on electrode potential. Physically, the dependence of U_{i0}^m on φ_M results from the fact that in first approximation, the action of the electric field is to polarize the solvent and stretch (or compress) certain intramolecular and intermolecular bonds without changing the corresponding elastic constants. If the field is strong enough, the elastic constants, i.e., the shape of the terms, also change in the second approximation. Quantitative calculation of the latter effect is made difficult by the need to know the detailed potential distribution in the electrolyte. To simplify the calculations, therefore, we shall henceforth assume that the potential at the location of the reacting ion remains constant on a change in φ_M. With these assumptions, F_f^n will not depend on φ_M, and $F_i^m(\varepsilon)$ can be written

$$F_i^m(\varepsilon, \eta) = (\varepsilon - \varepsilon_F) - e\eta + F_{0F}^m, \tag{7}$$

where F_{0F}^m is the free energy at the equilibrium potential $\varphi_M = \varphi_M^0$, provided that the electron energy equals the Fermi energy ε_F. It follows from (6) and (7) that the nonequilibrium free energy of the partial process

$$\Delta F^{mn}(\varepsilon, \eta) = F_i^m - F_f^n = \Delta J^{mn}(\varepsilon, \eta) + \Delta\mathcal{F}^{mn} = \Delta F_{0F}^{mn} + (\varepsilon - \varepsilon_F) - e\eta \tag{8}$$

contains ε and $e\eta$ only as summands. Hence the microscopic Brõnsted relation (5) can be written in the equivalent form

$$\alpha^{mn}(\varepsilon, \eta) = -\partial F_a^{mn} / \partial\varepsilon = \partial F_a^{mn} / \partial e\eta. \tag{9}$$

These equations permit a rather general qualitative analysis of the electrochemical-process kinetics. Let us examine the expression for the experimentally measured transport coefficient

$$\alpha_{\text{exp}} = -d \ln \vec{i} / d\frac{e\eta}{kT}. \tag{10}$$

If c_i and θ_a are small, the quantity $\Phi_m(c_i, \theta_a)$ in (2) will be proportional to $(\prod_i c_i^{\nu_i})(\prod_a \theta_a^{\nu_a})$. Thus, if the adsorbed particles are electrically neutral, the entire dependence of Φ_m on the overvoltage will be determined by the quantity

$$\gamma_a = -d \ln \Phi_m \Big/ d\frac{e\eta}{kT} = -\sum_a \nu_a d \ln \theta_a \Big/ d\frac{e\eta}{kT}. \tag{11}$$

Applying Eqs. (2), (10), and (11), it is easily shown that

$$\alpha_{\text{exp}} = \gamma_a + \frac{1}{\vec{i}} A v_m \sum_n \Phi_m(c_i) e \frac{kT}{h} \varkappa^{mn} \rho \int n(\varepsilon) e^{-\frac{F_a^{mn}(\varepsilon, \eta)}{kT}} \alpha^{mn}(\varepsilon, \eta) d\varepsilon. \tag{12}$$

The second term on the right side of this equation is the microscopic transport coefficient $\alpha^{mn}(\varepsilon, \eta)$ averaged over the partial currents $\vec{i}^{mn}(\varepsilon)$:

$$\alpha_{\text{exp}} = \gamma_a + \langle \alpha^{mn}(\varepsilon, \eta) \rangle. \tag{13}$$

Here the first term γ_a is determined by the potential dependence of adsorbed-particle concentration, and the second, $\alpha \equiv \langle \alpha^{mn}(\varepsilon, \eta) \rangle$, by the overvoltage dependence of the specific rate constant of the electrode reaction. We shall henceforth concern ourselves only with α, and assume $\gamma_a = 0$ to simplify the equations.

Thus far, we have used only the microscopic Brõnsted relation for the partial process, whose contribution to the total current equals $i^{mn}(\varepsilon) d\varepsilon$. It is possible to derive a generalized Brõnsted relation to characterize the electrochemical process as a whole. For this purpose, let us consider the contribution to the total cathodic current due to transition of the system from the initial vibrational state m of the quantum subsystem to the final state n with consideration of the entire energy spectrum of the electrons in the metal:

$$\vec{i}^{mn} = \int \vec{i}^{mn}(\varepsilon)\, d\varepsilon. \tag{14}$$

We shall assume that the activation energy has a minimum value $E^{mn}_{a\,\min}$ at a certain value of the partial heat effect $\Delta J^{mn} = \Delta\tilde{J}$ and increases monotonically as $\Delta J^{mn}(\varepsilon)$ varies in either direction from $\Delta\tilde{J}$. This assumption cannot be justified rigorously within the framework of the phenomenological theory, but it is physically quite obvious. Let us clarify it in the language of potential-energy surfaces (for simplicity, we shall for the time being omit the indices m and n). We shall first examine the elementary case in which the classical subsystem is characterized only by the single coordinate q, and the motion is of quantum nature in all other coordinates in both the initial and final states. Figure 2 gives a qualitative representation of the one-dimensional terms of the initial and final states corresponding to various "heats of reaction" $\Delta J = U_{in}(q_{in}{}^{0}) - U_{fn}(q_{fn}{}^{0})$. It shows that in the case considered, the minimum activation energy $E_{a\,\min} = 0$ [see the term $U_{in}(q)$], and that the corresponding "reaction heat" is determined from the equation

$$\Delta J = U_{\mathrm{fn}}(q^{0}_{\mathrm{in}}) - U_{\mathrm{fn}}(q^{0}_{\mathrm{fn}}) \equiv E_{r2}, \tag{15}$$

where we shall call E_{r2} the energy of reorganization for the reverse process. Accordingly, the forward-process reorganization energy will take the form

$$E_{r1} = U_{\mathrm{in}}(q_{\mathrm{fn}}) - U_{\mathrm{in}}(q_{\mathrm{in}}). \tag{16}$$

A monotonic increase in the activation energy as ΔJ deviates from $\Delta\tilde{J}$ proceeds directly from the monotonicity of the potential-energy functions $U_{in}(q)$ and $U_{fn}(q)$.

The above arguments extend automatically to the case of multi-dimensional terms. A more complicated situation arises when mutual transformation of quantum and classical degrees of freedom occurs in the course of the reaction [4, 5]. Here we give a qualitative analysis of the elementary variant in which one coordinate q remains classical during the course of the reaction, while the second coordinate r describes a quantum subsystem before the reaction, but the motion in this coordinate is classical after the reaction. Then the initial-state term will be represented by the curve of $U_{in}(q)$, and the final-state term by the surface $U_{fn}(q, r)$ (see Fig. 3). According to [3-5], the transition from the initial to the final state can be interpreted as preliminary stretching of the classical coordinate $q^{0}_{in} \to q^{*}$ on the initial term at a fixed quantum coordinate $r = r^{0}_{in}$. Here the transitional state corresponds to the point q^{*} at which the curve of $U_{in}(q)$ intersects the surface $U_{fn}(q, r)$:

$$U_{\mathrm{in}}(q^{*}) = U_{\mathrm{fn}}(q^{*}, r^{\bullet}_{\mathrm{in}}). \tag{17}$$

A quantum transition is made in the transitional state from the initial to the final terms, followed by classical motion in both coordinates r and q to the final state (r^{0}_{fn}, q^{0}_{fn}). As we see from Fig. 3, the activation energy has its minimum value $E_{a\,\min} = 0$ when the "reaction heat" reaches the value

$$\Delta J = U_{\mathrm{fn}}(q_{\mathrm{in}}, r_{\mathrm{in}}) - U_{\mathrm{fn}}(q_{\mathrm{fn}}, r_{\mathrm{fn}}). \tag{18}$$

For the reverse process, the activation-energy minimum corresponds to transition from the term $U_{fn}(q, r)$ to the term $U^{(3)}_{in}(q)$, which passes through the minimum of the curve of

$$U_{\mathrm{fn}}(q, r^{\bullet}_{\mathrm{in}}) \left(\frac{\partial}{\partial q} U_{\mathrm{fn}}(q^{\min}_{\mathrm{fn}}, r^{\bullet}_{\mathrm{fn}}) = 0\right):$$

$$\overleftarrow{E}_{a\,\min} \equiv \overleftarrow{E}_{\mathrm{nin}} = U_{\mathrm{fn}}(q^{\min}_{\mathrm{fn}}, r^{0}{}_{\mathrm{in}}) - U_{\mathrm{fn}}(q^{0}{}_{\mathrm{fn}}, r^{0}{}_{\mathrm{fn}}) \neq 0. \tag{19}$$

Here the presence of a nonzero minimum activation energy is explained physically by the fact that the coordinate r must of necessity equal r_{in} in the transient state; for any position of the term $U_{in}(q)$, therefore, it is first necessary to stretch (activate) the coordinate r from the value r^{0}_{fn} to the value $r^{0}_{in} (\neq r^{0}_{fn})$. It is easily seen that this is a general principle: if in the course of the reaction some classical coordinate becomes a quantum coordinate, the activation energy will be nonzero for any reaction heat. When the minimum activation energies $\overleftarrow{E}_{\min}$ and $\vec{E}_{\min}$ for the forward and reverse processes are nonzero, it is convenient to describe the transition process with simplified terms:

$$u_{\mathrm{in}}(q) = U_{\mathrm{in}}(q; r^{\bullet}_{\mathrm{fn}}); \quad u_{\mathrm{fn}}(q) = U_{\mathrm{fn}}(q; R^{\bullet}_{\mathrm{in}}), \tag{20}$$

where q is the ensemble of classical coordinates that do not change during the reaction, the r are the classical coordinates that become quantum coordinates, and the R are the quantum coordinates that become classical. For these terms, the "reaction heat" is the quantity

$$\Delta j = U_{\text{in}}\ (q_{\text{in}}^{\min};\ r_{\text{fn}}^{0}\ ) - U_{\text{fn}}\ (q_{\text{fn}}^{\min};\ R_{\text{in}}^{0}\ ) = \Delta J + (\overleftarrow{E}_{\min} - \overrightarrow{E}_{\min}). \tag{21}$$

It is with precisely these terms that the reorganization-energy notions are most conveniently generalized (see Eqs. (15) and (16)):

$$\begin{aligned} E_{r1} &= U_{\text{in}}\,(q_{\text{fn}}^{\min}\ ; r_{\text{fn}}^{0}) - U_{\text{in}}\,(q_{\text{in}}^{\min}\ ; r_{\text{fn}}^{0}), \\ E_{r2} &= U_{\text{fn}}\,(q_{\text{in}}^{\min}\ ; r_{\text{in}}^{0}) - U_{\text{fn}}\,(q_{\text{fn}}^{\min}\ ; r_{\text{in}}^{0}), \end{aligned} \tag{22}$$

It was shown in [3] on the basis of a quantum-statistical analysis that the activation entropy is a weak function of ΔJ, so that

$$\alpha^{mn}(\varepsilon,\eta) = -\frac{\partial F_a^{mn}}{\partial \Delta F^{mn}(\varepsilon)} \approx -\frac{\partial E_a^{mn}}{\partial \Delta J^{mn}(\varepsilon)} = -\frac{\partial E_a^{mn}}{\partial \Delta j^{mn}(\varepsilon)}, \tag{23}$$

where the indices (m, n, ε) have been restored. Since the activation energy has a minimum at $\Delta J^{mn}(\varepsilon) = E_{r2}$, it is readily seen that $\alpha^{mn}(\Delta j = E_{r2}) = 0$. Accordingly, $\beta^{mn} = 1 - \alpha^{mn}$ vanishes for the reverse reaction at $\Delta j^{mn} = -E_{r1}$, whence $\alpha^{mn}(\Delta j^{mn} = -E_{r1}) = 1$. Remembering that E_a^{mn} increases monotonically as Δ^{mn} deviates in either direction from $\Delta j^{mn} = E_{r2}$, we obtain the relations

$$\begin{gathered} \alpha^{mn}(\varepsilon) < 0, \text{ for } \quad E_{r2} < \Delta j^{mn}, \quad \text{or} \quad \Delta J^{mn} > E_{r2} + (\overleftarrow{E}_{\min} - \overrightarrow{E}_{\min}) \\ 0 < \alpha^{mn}(\varepsilon) < 1, \text{ for } E_{r2} > \Delta j^{mn} > -E_{r1}, \quad \text{or} \quad E_{r2} + \overleftarrow{E}_{\min} - \overrightarrow{F}_{\min} \\ > \Delta J^{mn} > -E_{r1} + (\overleftarrow{E}_{\min} - \overrightarrow{E}_{\min}) \\ \alpha^{mn}(\varepsilon) > 1, \text{ for } \quad \Delta j^{mn} < -E_{r1}, \quad \text{or} \quad \Delta J^{mn} < -E_{r1} + (\overleftarrow{E}_{\min} - \overrightarrow{E}_{\min}). \end{gathered} \tag{24}$$

The presence of an activation-energy (or free-energy) minimum indicates that the basic contribution to the total currents in electrochemical processes should be from transitions with participation of electrons at levels near a certain level $\varepsilon_{mn}{}^*$, whose position depends on the overvoltage. In this case, the transport coefficient $\langle\alpha^{mn}(\varepsilon, \eta)\rangle$ determined by Eqs. (12), (13) may be written

$$\alpha_{\exp} = \langle \alpha^{mn}(\varepsilon, \eta)\rangle \simeq Av_m \sum_n \alpha^{mn}(\varepsilon_{mn}^*, \eta)\, \vec{i}^{\,mn}/\vec{i}. \tag{25}$$

With Eqs. (8) and (9), it is easy to obtain the analog of the Brönsted relation for the m→ n transition process:

$$\partial F_a^{mn}(\Delta F_{mn}{}^*) \,/\, \partial \Delta F_{mn}{}^* = -\alpha^{mn}(\varepsilon_{mn}{}^*) \equiv -\alpha_{mn}{}^*, \tag{26}$$

where $\Delta F_{mn}{}^* = \Delta F^{mn}(\varepsilon_{mn}{}^*(\eta).\ e\eta)$. Equations (9) can be used to obtain one more important relationship. For this purpose, we substitute the corresponding expression from (9) for $\alpha^{mn}(\varepsilon, \eta)$ in (12) and integrate by parts. After simple transformations, we obtain

$$\alpha_{\exp} = \langle \alpha^{mn}(\varepsilon, \eta)\rangle \simeq Av_m \sum_n [1 - n\,(\varepsilon_{mn}^*)]\, \vec{i}^{\,mn}/\vec{i}. \tag{27}$$

Comparison of (25) with (27) gives

$$\alpha^{mn}(\varepsilon_{mn}{}^*) = 1 - n(\varepsilon_{mn}{}^*). \tag{28}$$

The phenomenological nature of (28) notwithstanding, it enables us to draw a number of important inferences as to the mechanism of the elementary event in the electrode reaction [3]. Since $n(\varepsilon) < 1$, it follows from (27) and (28), for example, that $\langle\alpha^{mn}(\varepsilon, \eta)\rangle$ is always included between zero and unity.

The dependence of the partial current $\vec{i}^{mn}$ on overvoltage was investigated in detail in [3], where it was shown that the curve of $\vec{i}^{mn}$ vs η has three regions that are characterized by different values of the the transport coefficient $\alpha_{\exp}$: (1) $\alpha_{\exp} \approx 1$, (2) $\alpha_{\exp} \approx 0$, and (3) $\alpha_{\exp} \sim 1/2$. Since the case in which $\overrightarrow{E}_{\min} =$ $\overleftarrow{E}_{\min} = 0$ was examined in [3], these regions were referred to respectively as the regions of nonbarrier [activation energy $E_a{}^{mn}$ equal (but opposite in sign) to the heat effect ΔJ^{mn} of the reaction], nonactivation ($E_a{}^{mn} = 0$), and normal discharge. The quantitative form of the dependence of $\vec{i}^{mn}$ on η that was obtained in [3] is also preserved when $\overleftarrow{E}_{\min} \neq 0$ and $\overrightarrow{E}_{\min} \neq 0$. In this case, however, it is more appropriate to refer to regions (1) and (2) on the volt-ampere curve as quasinonbarrier and quasinonactivation regions [6], since it is found in this case that the activation energy is larger than $-\Delta J^{mn}$ in region (1) by an amount

$\overleftarrow{E}_{\min}$ $(\vec{E}_a^{mn} \simeq \Delta J^{nm} + \vec{E}_{\min})$, and nonzero in region (2) $(E_a \simeq \overleftarrow{E}_{\min})$. Since the equations for the current $\overleftarrow{i}^{mn}$ differ formally in this case from the corresponding equations derived in [3] only in this change in the activation energy in the quasinonbarrier and quasinonactivation regions, we shall not present them here, but shall write out only the criteria that must be satisfied for the discharge to occur in the region in question. Considering that $0 < \alpha^{mn}(\varepsilon_{mn}^*) < 1$, the following relations are easily obtained from Eqs. (24):

$$e\eta_{n.a}^{mn} \equiv (\Delta F_{0F}^{mn} - \Delta F^{mn}) + \vec{E}_{\min} - \overleftarrow{E}_{\min} - E_{r2} < e\eta - (\varepsilon_{mn}^* - \varepsilon_F) < \Delta F_{0F}^{mn} - \Delta F^{mn} + \vec{E}_{\min} - \overleftarrow{E}_{\min} + E_{r1} \equiv e\eta_{n.b}^{mn} \quad (29)$$

The overvoltages that determine the boundaries of the normal region for a given partial current $\vec{i}^{mn}$ are denoted by $\eta_{n.a}^{mn}$ and $\eta_{n.b}^{mn}$ in (29). The condition for a quasinonbarrier partial process creating the cathodic current $\vec{i}^{mn}$ takes the form (given separately for the anodic $\eta = \eta_a > 0$ and the cathodic $\eta = \eta_c < 0$ overvoltages):

$$\eta_a > \eta_{n.a}^{mn}; \quad 0 < \eta_c < -\eta_{n.b}^{mn} \quad (30)$$

i.e., the cathodic current $\vec{i}^{mn}$ can correspond to a quasinonbarrier process only at high overvoltages in the anodic region and only at low overvoltages in the cathodic region. Similarly, for low anodic or high cathodic overvoltages

$$0 < 0\eta_a < e\eta_{n.a}^{mn}, \quad \eta_c > -\eta_{n.a}^{mn} \quad (31)$$

the cathodic current will be determined by a nonactivation process. The contrary conditions apply for the anodic current $\overleftarrow{i}^{mn}$.

Determining the analogous conditions for the process as a whole requires a detailed analysis of Eq. (2) for the total cathodic current $\vec{i}$. This equation is greatly simplified if it is assumed that the potential-energy surface of the classical subsystem is shifted only vertically upward, without a change in geometrical shape, on excitation of the quantum subsystem. It is easily seen that the transition from terms corresponding to unexcited states of the quantum subsystem to terms with m, n ≠ 0 is formally equivalent to applying an additional overvoltage $[(E_n - E_0^f) - (E_m - E_0^i)]$, so that the expression for $\vec{i}$ can be written

$$\vec{i} = \sum_{m,n} (\varkappa^{mn}/\varkappa^{00})\,\vec{i}^{00}[e\eta + (E_n - E_0^f) - (E_m - E_0^i)] \cdot \exp[-(E_m - E_0^i)/kT], \quad (32)$$

where $\vec{i}^{00}(e\eta)$ is the current without consideration of the excited states of the quantum subsystem and E_0^i and E_0^f are the energies of the initial and final ground states. Analysis of this formula shows that, depending on overvoltage, the basic contribution to the sum over m and n is from one or more terms with indices m and n close to certain m* and n*. In the range of overvoltages corresponding to the normal region for the current $\vec{i}^{00}$, the principal term in the sum is that with m* = n* = 0. In the overvoltage region corresponding to a quasinonbarrier process for the current $\vec{i}^{00}$ [Eq. (30) with m = n = 0], the process as a whole is also quasinonbarrier and the terms with n* = 0 and m* ≠ 0, which corresponds to transitions of the system from excited initial states to an unexcited final state, make an appreciable contribution to the sum. In the overvoltage region of (31) (with m = n = 0), the process as a whole is quasinonbarrier and m* = 0, n* ≠ 0. Thus, the conditions that determine the nature of the process as a whole are practically the same as the conditions that determine the nature of the transition between the unexcited states of the quantum subsystem.

In view of the above, the equation for $\alpha_{\exp}$ can be rewritten

$$\alpha_{\exp} = \alpha^* \equiv \alpha^{m^*,n^*}(\varepsilon_{m^*,n^*}^*, \eta). \quad (33)$$

Applying Eq. (9), we quickly find that

$$\partial F_a^* / \partial \Delta F^* = -\alpha^*, \quad (34)$$

where $F_a^* = F_a^{m^*n^*}(\Delta F^*)$, $\Delta F^* = \Delta F^{m^*n^*}(\varepsilon_{m^*n^*}^*(\eta), \eta)$.

This equation is a generalization of the microscropic Brönsted relation and signifies that the measured transport coefficient α^* is determined by the derivative of the free activation energy with respect to the free reaction energy for the partial process that makes the largest contribution to the total current at the particular overvoltage. The quantities $\varepsilon^*_{m^*n^*}$, m^*, n^*, which determine which partial current $i^{mn}(\varepsilon)$ is largest, depend on overvoltage.

In conclusion, let us discuss the possibilities of detecting nonbarrier and nonactivation (or quasinonbarrier and quasinonactivation) processes. Analysis of conditions (30) and (31) indicates that an extremely rigid condition is imposed on selection of electrochemical systems for which a nonactivation or nonbarrier process could be observed experimentally. For example, according to (30) and (31), a quasinonbarrier process can be detected only if the condition

$$(\overleftarrow{E}_{\min}-\vec{E}_{\min})-\Delta F_{0F}=kT\ln\frac{\prod\limits_i (c_0^i)^{\nu_i}}{\prod\limits_f (c_0^f)^{\nu_f}}+\overleftarrow{E}_{\min}-\vec{E}_{\min}>E_{r1} \tag{35}$$

is satisfied. As we noted previously, the reorganization energy E_{r1} of the forward process is usually a few electron volts, so that inequality (35) can be satisfied only if at least one of two physical conditions is met: a) the equilibrium concentration of one of the products is very low ($c_0^f \to 0$), and b) a quantum degree of freedom is transformed into a classical degree of freedom during the course of the reaction ($\vec{E}_{\min}=0$, $\overleftarrow{E}_{\min}\neq 0$). The first of these conditions may, for example, be satisfied for those particles that can be adsorbed on the electrode during the course of the reaction, in which case smallness of the adsorbed-particle concentration automatically requires that the desorption stage be very rapid. Thus, this case can be realized only for particles with very low adsorption-energy values. The second possible way to satisfy condition (35) is experimentally more attractive. In this case, the existence of the finite activation energy for the reverse process $\vec{E}_{\min}\neq 0$ may substantially lower the back current, with the result that the hypothesis of fast desorption becomes more realistic [4]. It was apparently this variant that was realized in Krishtalik's experiments [7].

For experimental detection of a nonactivation process, it will be convenient to select an electrochemical system such that the minimum activation $\vec{E}_{\min}$ is nonzero. This can be brought about physically if a quantum degree of freedom is transformed into a classical degree in the elementary discharge event, e.g., by rupture of a valence bond with a frequency $\omega \gg kT/\hbar$. The same conclusion results from the formal expression for the condition $\eta_c > -\eta_{n.a}$:

$$e\eta_c > E_{r2}-(\vec{E}_{\min}-\overleftarrow{E}_{\min})-kT\ln\prod_f (c_0^f)^{\nu_f}/\prod_i (c_0^i)^{\nu_i}=E_{r2}-(\vec{E}_{\min}-\overleftarrow{E}_{\min})-\Delta F_{0F}. \tag{36}$$

Since the reverse-process reorganization energy E_{r2} is of the order of several electron volts, it is necessary for satisfaction of inequality (36) that at least one of two conditions be met: a) $\vec{E}_{\min}\neq 0$, $\overleftarrow{E}_{\min}=0$ (see above); b) the equilibrium concentration of one of the particles participating in the reaction be small ($c_0^i \to 0$). The latter may be the case if an adsorbed particle with a small adsorption energy participates in the reaction.

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