KINETICS OF ELECTROCHEMICAL PROCESSES.

II. PHENOMENOLOGICAL THEORY. GENERAL QUALITATIVE PROPERTIES OF POLARIZATION CURVES

M. A. Vorotyntsev, R. R. Dogonadze,
and A. M. Kuznetsov

UDC 541.138

The qualitative form of the polarization curve is derived, and some of its general properties are investigated, on the basis of the Arrhenius formula for the probability of the elementary event of an electrochemical reaction, with no model assumptions regarding the electronic subsystem in the electrode. The existence of regions of normal, nonbarrier, and nonactivation discharge is demonstrated with highly general assumptions as to the electronic subsystem in a metallic electrode. Polarization curves for semiconductor electrodes are examined.

Allowance for the effects of the continuous electrode-electron spectrum is an important factor in construction of a consistent theory of the elementary event of the electrochemical reaction. In the preceding paper [1], we took the electrode into account within the framework of concrete model assumptions regarding the spectrum of the electrons in the electrode. At first, we assumed a "single-electron" approximation, i.e., we introduced noninteracting quasiparticles corresponding to individual electrons in the self-consistent field of all other electrons (in a polarization "cloak"). It was also assumed that one of the quasiparticles vanishes (or appears) in the course of the reaction, and that the total current equals the sum of the currents flowing with participation of that quasiparticle. The quasiparticle energy distribution was assumed to be subject to the energy-distribution law of noninteracting electrons, i.e., to the Fermi distribution function $n(\varepsilon) = \left[\exp\left(\frac{\varepsilon - \varepsilon_F}{kT}\right) + 1\right]^{-1}$:

$$\vec{i} = e\int \rho n(\varepsilon) W(\varepsilon)\, d\varepsilon, \tag{1}$$

where ρ is the density of the quasiparticle spectrum and $W(\varepsilon)$ is the probability of transition of a quasiparticle from level ε to an ion in a unit time (for concreteness, the process in which an electron moves from the electrode to an ion is considered everywhere). Within the framework of these hypotheses, we also examined processes in which several electrons leave the electrode [2]. It was found that determination of the current again reduces to evaluation of an integral of the type (1)

$$\vec{i} = C\int M(\varepsilon) W(\varepsilon)\, d\varepsilon, \tag{2}$$

where ε is the sum of the energies of the electrons leaving the electrode, C is a constant, and $M(\varepsilon)$ is the probability that electrons with a given total energy ε will be in the electrode (the concrete form of the quantities C and $M(\varepsilon)$ for two-electron processes was found in [2]).

The correctness of the noninteracting-quasiparticle model for the electrons has been verified both theoretically and purely experimentally in a number of problems in solid state physics [3]. When it comes

---

Institute of Électrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 7, No. 3, pp. 306-312, March, 1971. Original article submitted May 28, 1969.

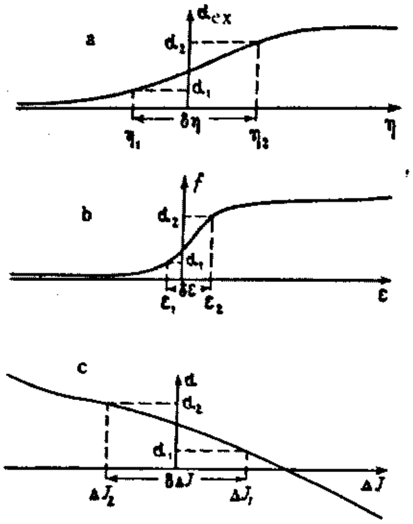

Fig. 1

to electrochemical processes, there are certain specifics that must be kept in mind in a theoretical study of the elementary event. In most homogeneous charge-transfer processes in solids, the electron emerges as a quasiparticle of the same species, i.e., the polarization "cloak" of the electron is the same at the beginning and end of scattering. Since the electron leaves the electrode in the elementary electrochemical-reaction event, it "throws off" all or part of its polarization "cloak" in the process, and this corresponds to a change in the species of the quasiparticles. Although this problem has not yet been solved theoretically, most of the experimental data obtained both for solids (thermal or photoionization of electrons captured by impurities, etc.) and for electrochemical processes nevertheless indicate that the single-particle approximation for the electrons is also valid in this case. However, it must be remembered that use of the Fermi distribution function for the electrons is a modelling device. Since the unit-time transition probability $W(\varepsilon)$ has been assigned purely phenomenologically on the basis of the Arrhenius law and Brönsted's rule in earlier papers, we shall dispense with model assumptions once and for all by proceeding from Eq. (2) for all electrochemical processes, taking $M(\varepsilon)$ to be a certain function that satisfies very weak and quite obvious conditions. In this sense, the theory to be set forth below will be fully phenomenological in nature. It is important to stress that this generalization permits a substantial expansion of the class of electrochemical reactions that can be examined. The absence of diffusion control of the reaction is practically the only limitation that we shall retain. We can easily satisfy ourselves of this by inspecting the formally written exact expression for the current:

$$\vec{i} = me\Phi(C_R)\, Av_i \sum_f \varkappa_{el}^{(if)} \langle W(\Delta J)\rangle_0, \tag{3}$$

where m is the number of transferred electrons, $\Phi(C_R)$ is the concentration factor [1], ΔJ is the microscopic heat effect of the reaction (i.e., the reaction heat effect for a fixed overvoltage η and assigned initial (i) and final (f) states of the electron subsystem), the operator Av_i signifies averaging over all initial states of the system of N interacting electrons in the electrode, $\sum_f$ indicates summation over all final states of the system of N − m electrons in the electrode, and $\langle W(\Delta J)\rangle_0$ is the probability of the elementary reaction event, averaged both over all classical and over all quantum degrees of freedom of the system for fixed initial and final states of the entire electron subsystem. For convenience, we have factored $\varkappa_{el}^{(if)}$ out of the total probability $\langle W(\Delta J)\rangle$, since it is determined solely by the electronic wave function. Equation (3) for the current can then be written

$$\vec{i} = me\Phi(C_R) \int M(\varepsilon) \langle W(\Delta J)\rangle_0\, d\varepsilon, \tag{4}$$

with

$$\Delta J = \varepsilon - m\varepsilon_F - me\eta + \Delta J_{0F}, \tag{5}$$

where $\varepsilon = E_N^{(i)} - E_{N-m}^{(f)}$ is the energy change of the electron subsystem in the electrodes in the course of the reaction (less the electrostatic part $me\eta$), ΔJ_{0F} is the equilibrium reaction heat provided that the energy of the electron subsystem in the electrode changes by $m\varepsilon_F$ on transition of m electrons, and the function $M(\varepsilon)$ is determined by the expression

$$M(\varepsilon) = Av_i \sum_f \varkappa_{el}^{(if)} \delta(E_N^{(i)} - E_{N-m}^{(f)} - \varepsilon). \tag{6}$$

Since the summation in Eq. (6) extends over the entire energy spectrum of the electrons in both the initial and final states, this analysis covers, among other things, the case of electrodeposition for solutions of metals. In addition, this approach avoids the difficulties associated with the use of the single-particle Fermi distribution function for liquid electrodes (on mercury, gallium, etc.).

We should note that the question as to whether a reaction is adiabatic or nonadiabatic is nontrivial in electrochemical kinetics [4, 5]. Thus, the transition to the adiabatic case cannot be made by setting

$\varkappa_{el}^{(if)}$ formally equal to unity in (3). This problem will be analyzed in detail in one of the forthcoming articles when we expound the quantum theory of electrode processes. The method developed below is formally applicable in the case of either nonadiabatic or adiabatic reactions, but we shall confine ourselves in the present paper to the case of nonadiabatic reactions, for which it can be assumed that the total current equals the sum of independent partial currents $i(\varepsilon) = me\Phi(C_R)\varkappa_{el}^{(if)}\langle W(\Delta J)\rangle_0$.

The objective of the present paper is to investigate the integral in Eq. (4) for metallic and semiconductor electrodes with quite general assumptions regarding the properties of the functions $\langle W(\Delta J)\rangle_0$ and $M(\varepsilon)$. As previously [1], we shall assume that $\langle W(\Delta J)\rangle_0$ satisfies the Arrhenius law

$$\langle W(\Delta J)\rangle_0 = Ae^{-E_a/kT}, \tag{7}$$

where the basic dependence of $\langle W(\Delta J)\rangle_0$ on ε and the overvoltage η is connected with the dependence of the activation energy E_a on the microscopic reaction heat ΔJ: $E_a = E_a(\Delta J)$. To simplify the formulas that follow, we consider only the case in which $m = 1$; the general case is obtained by the simple substitutions $e \to me$; $e\eta \to me\eta$; $\varepsilon_F \to m\varepsilon_F$. No assumptions will be made regarding the concrete form of E_a as a function of ΔJ for the time being.

In the nonadiabatic-reaction case under consideration, the function $M(\varepsilon)$ does not depend on overvoltage; this follows directly from the derivation of Eq. (4). For that which follows, it will be helpful to replace $M(\varepsilon)$ by the new function $f(\varepsilon)$ in accordance with

$$M(\varepsilon) = \exp\left\{-1/kT\int f(\varepsilon)\,d\varepsilon\right\} \text{ or } f(\varepsilon) = -kT\frac{d\ln M(\varepsilon)}{d\varepsilon}. \tag{8}$$

We shall assume that a small group of levels around a certain level ε^* makes the basic contribution to the integral in (4). This assumption is quite natural, since the "concentration" factor (fill factor) $M(\varepsilon)$ usually decreases with increasing ε, while the "activation" factor $W(\varepsilon)$ increases owing to the decrease in the activation energy E_a as the reaction heat rises (at least within certain limits [6, 7]). The equation for ε^* and the expression for the current i are easily found [4] by the Laplace method:

$$\begin{gathered}\alpha(\Delta J) = f(\varepsilon)\\ \vec{i} = AC\Delta\varepsilon^* M(\varepsilon^*)\exp\{-E_a(\Delta J^*)/kT\},\end{gathered} \tag{9}$$

where $\alpha(\Delta J) \equiv (dE_a/d\Delta J)$ is the microscopic transfer coefficient and $\Delta\varepsilon^*$ is the width of the level interval contributing to the current. For the macroscopic transfer coefficient [1] $\alpha_{ex}(\eta) \equiv -kT\,d\ln i/de\eta$, Eq. (9) readily yields the simple relationship

$$\alpha_{ex}(\eta) = \alpha(\Delta J^*) = f(\varepsilon^*), \tag{10}$$

where $\Delta J^* = \varepsilon^* - \varepsilon_F - e\eta + \Delta J_{0F}$. Equations (10) indicate that to find $\varepsilon^*(\eta)$ and $\alpha_{ex}(\eta)$, it is necessary to plot diagrams of $\alpha(\Delta J)$ and $f(\varepsilon)$ against ε for a fixed η. If the curves of $\alpha(\Delta J)\,|_{\eta=\mathrm{const}}$ and $f(\varepsilon)$ intersect at only one point, the abscissa of that point determines the level ε^*, and its ordinate α_{ex}. The form of the polarization curve will naturally depend on the concrete form of the functions $f(\varepsilon)$ and $\alpha(\Delta J)$, which can be found only under model assumptions.

The inverse problem, that of finding $\alpha(\Delta J)$ and $f(\varepsilon)$ from a known function $\alpha_{ex}(\eta)$, might also be stated. Two problems are possible here: 1) find $\alpha(\Delta J)$ from known functions $f(\varepsilon)$ and $\alpha_{ex}(\eta)$; 2) find $f(\varepsilon)$ from $\alpha(\Delta J)$ and $\alpha_{ex}(\eta)$. Figure 1 illustrates the graphical method of solving these problems. The procedure used to construct, for example, the function $\alpha(\Delta J)$ consists in the following: find $\alpha_{ex}(\eta_1) = \alpha_1$ from diagram (1a) for a given overvoltage η_1; then find ε_1 from the $f(\varepsilon)$ diagram; the result is the value α_1 of the function $\alpha(\Delta J)$ at the point $\Delta J_1 = \varepsilon_1 - \varepsilon_F - e\eta_1 + \Delta J_{0F}$. Values of the function $\alpha(\Delta J)$ for all other points are found similarly. The analytical expression for the function $\alpha(\Delta J)$ can be written in the form $\alpha(\Delta J) = \alpha_{ex}[\eta(\Delta J)]$, where the function $\eta(\Delta J)$ is found by solving the equation $\alpha_{ex}(\eta) = f(\Delta J + \varepsilon_F + e\eta - \Delta J_{0F}$. This problem is solved in similar fashion.

We note that it is impossible to reconstruct the form of the terms even from a known $\alpha(\Delta J)$ relationship (i.e., a known $E_a(\Delta J)$). This becomes especially clear when we note that the terms of the classical subsystem are usually multidimensional. Moreover, the form of the terms cannot be reconstructed even in the one-dimensional case, owing to the possible difference between the forms of the terms in the initial and final states. Thus, the form of one-dimensional terms can be determined only, for example, on the assumption that the initial and final terms are the same.

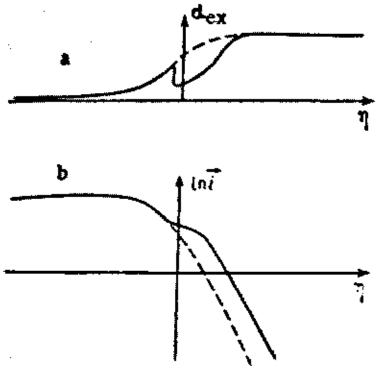

Fig. 2

Although it is impossible to find the two functions $\alpha(\Delta J)$ and $f(\varepsilon)$ from a single known $\alpha_{ex}(\eta)$ relationship, it is possible, with certain highly general assumptions, to draw certain important qualitative inferences as to the kinetics of electrochemical processes. First, let us consider the case in which $1 - f(\varepsilon)$ and $\alpha(\Delta J)$ are nonincreasing functions. The results obtained for nonmonotonic $\alpha(\Delta J)$ and $f(\varepsilon)$ will be set forth at the end of this paper. It follows directly from (10) that

$$\frac{d\varepsilon^*}{de\eta} = \frac{d\alpha(\Delta J^*)/d\Delta J}{(d\alpha(\Delta J^*)/d\Delta J) - (df(\varepsilon^*)/d\varepsilon^*)} \cdot \tag{11}$$

Thus,

$$0 \leqslant \frac{d\varepsilon^*}{de\eta} \leqslant 1; \quad 0 \leqslant -\frac{d\Delta J^*}{de\eta} \leqslant 1. \tag{12}$$

In this case, $\alpha_{ex}(\eta)$ is naturally a monotonically increasing function. The physical significance of inequalities (12) is quite simple: for example, the first means that ε^* is a monotonically increasing function of η, with ε^* increasing more slowly then $e\eta$. The second inequality has a similar sense. Let us now examine an arbitrary overvoltage interval $\delta e\eta \equiv e\eta_2 - e\eta_1$. The quantities $\delta\Delta J$ and $\delta\varepsilon$ (see Fig. 1) can be compared to this interval. We obtain for these quantities from inequalities (12)

$$\begin{gathered} 0 \leqslant \delta\varepsilon \leqslant \delta e\eta; \\ 0 \leqslant \delta\Delta J \leqslant \delta e\eta. \end{gathered} \tag{13}$$

An important general conclusion may be drawn from inequalities (13): the curve of $\alpha_{ex}(\eta)$ is no less "distended" than the curves of $\alpha(\Delta J)$ and $f(\varepsilon)$ in the corresponding region. In other words, the characteristic scale of the variation of $\alpha_{ex}(\eta)$ is no smaller than those of the variations of the functions $\alpha(\Delta J)$ and $f(\varepsilon)$.

Let us now consider the character of the $f(\varepsilon)$ and $\alpha(\Delta J)$ relationships in greater detail. When a reaction takes place at a metallic electrode, a number of natural physical assumptions may be adopted regarding $M(\varepsilon)$: 1) around $m\varepsilon_F$, the function $M(\varepsilon)$ varies on scales of order kT; 2) for $\varepsilon - m\varepsilon_F \gg kT$, the fill factor $M(\varepsilon)$ diminishes in accordance with the Boltzmann law $M(\varepsilon) \sim e^{-\varepsilon/kT}$; 3) for $m\varepsilon_F - \varepsilon \gg kT$ the function $M(\varepsilon)$ is either constant or varies no more rapidly than a power function. These conditions are, for example, satisfied by all of the functions that we considered earlier [1, 2]. In particular, it is easily verified by the method of [2] that for the transfer processes of m electrons, the function $M(\varepsilon)$ behaves in the noninteracting-electron approximation as $(\varepsilon - m\varepsilon_F)^{m-1} \exp(-\varepsilon - m\varepsilon_F/kT)$ for large ε and as $(m\varepsilon_F - \varepsilon)^{m-1}$ for small ε, with a transitional region of the order of several kT. Thus, $f(\varepsilon)$ has two characteristic scales of variation: the scale kT for ε around $m\varepsilon_F$ and an infinitely large scale as ε moves away from $m\varepsilon_F$, with $f(\varepsilon)$ tending to zero or unity for $m\varepsilon_F - \varepsilon \gg kT$ or $\varepsilon - m\varepsilon_F \gg kT$, respectively.

The following remark is in order before we discuss the characteristic scales of variation of $\alpha(\Delta J)$. In Eq. (4), the current i is the current with consideration of all excited states of the quantum subsystem. It was shown in [7] that for large $|\Delta J|$ (of the order of the reorganization energy), consideration of excited quantum states results in vanishing (nonactivation region) or unity (nonbarrier region) $\alpha(\Delta J)$. Physically, this result is perfectly analogous to the appearance of regions of nonbarrier and nonactivation discharge when excited states of the electron (in the electrode), which is also a quantum particle, are considered. A rigorous defense of this statement will be given in one of the forthcoming articles. Thus, for values of $|\Delta J|$ exceeding the reorganization energy, the function $\alpha(\Delta J)$ has an infinitely large scale of variation. According to (13), this implies that the $\alpha_{ex}(\eta)$ curve has two regions with infinitely large scales of variation, where α_{ex} equals zero (nonactivation region) and unity (nonbarrier region).

The width of the transitional region for $\alpha(\Delta J) \simeq 0$ to $\alpha(\Delta J) \approx 1$ is of the order of the reorganization energy; hence the width of the normal region on the $\alpha_{ex}(\eta)$ curve (i.e., the transition from $\alpha_{ex} \simeq 0$ to $\alpha_{ex} \simeq 1$) is also of the order of E_r. The concrete behavior of the $\alpha_{ex}(\eta)$ curve in the normal range depends on the forms of the functions $\alpha(\Delta J)$ and $f(\varepsilon)$. If the terms are smooth enough, E_r is the characteristic scale of $\alpha(\Delta J)$. In this case, the form of the $\alpha_{ex}(\eta)$ curve in the middle of the normal range (where the characteristic scale of $f(\varepsilon)$ is of the order of kT) is determined only by the function $\alpha(\Delta J)$, i.e.,

$$\alpha_{ex}(\eta) = \alpha(-e\eta + \Delta J_{er}). \tag{14}$$

With increasing distance from the middle of the normal range, the characteristic scale of the $f(\varepsilon)$ curve increases rapidly, and the form of the $\alpha_{ex}(\eta)$ curve begins to depend also on the form of the $f(\varepsilon)$ curve.

However, if there are sharp inflections on the potential terms, discontinuities may appear on the curve. A simple example is found in the linear terms [8] that are sometimes examined in electrochemical-reaction theory. However, it is a purely speculative approximation to use them near the minimum. Actually, it would be more reasonable to use a potential of the Morse type, which has a characteristic scale of the order of the dissociation energy, for the intramolecular degrees of freedom. As for the solvent, it will be shown in the next article that the corresponding terms are parabolic in a rather broad range around the minimum.

Let us now consider an electrochemical reaction taking place on a semiconductor electrode (see [9] for details). If the surface of the semiconductor is degenerate, i.e., if the Fermi level intersects the conduction or valence band, the $M(\varepsilon)$ relation takes the same form as in the case of a metal electrode. A more interesting case is that of a semiconductor with a nondegenerate surface, in which the Fermi level lies in the forbidden band quite far (several kT) from its edges.

The current $\vec{i}$ on the semiconductor equals the sum of electronic (levels in conduction band) $\vec{i}^e$ and hole (levels in valence band) $\vec{i}^p$ currents. Below we shall investigate the volt–ampere characteristic only for the electronic component $\vec{i}^e$ of the current. An expression similar to (4) can be written for i^e, but with the integration extended over the energy levels in the conduction band:

$$\vec{i}^e = e\Phi(C_R)\int_{\Delta_k+\varepsilon_F}^{\infty}\rho(\varepsilon-\varepsilon_F-\Delta_k)\,e^{-\frac{\varepsilon-\varepsilon_F}{kT}}\varkappa_{el}\langle W(\Delta J)\rangle_0\,d\varepsilon. \tag{15}$$

This equation is valid for both the single-electron and the multielectron approximations [10]. In it, $\varkappa_{el} \simeq$ const, the surface of the semiconductor is nondegenerate, the reaction heat ΔJ equals, as before

$$\Delta J = \varepsilon - \varepsilon_F - e\eta + \Delta J_{0F} \tag{16}$$

(here we consider only reactions with transfer of a single electron), and Δ_k is the distance from the bottom of the conduction band on the electrode surface to the Fermi level, Δ_k depending on the difference between the overvoltages inside the electrode (η) and at the contact (η_k):

$$\Delta_k = e(\eta - \eta_k) + \Delta_0 .$$

Here Δ_0 is the distance from the bottom of the conduction band in the electrode to the Fermi level. The contact overvoltage η_k is a function of the overvoltage η, with the form of the relationship determined by the properties of the semiconductor. Below we shall examine two limiting cases in which η_k undergoes practically no change on a change in η ($d\eta_k/d\eta \ll 1$) and $d\eta_k/d\eta \simeq 1$. Semiconductors with low surface-state concentrations correspond to the former case. In it, the role of $M(\varepsilon)$ is taken by $\exp\left(-\frac{\varepsilon-\varepsilon_F}{kT}\right)$ $(f(\varepsilon) \equiv 1)$, and that of $< W(\Delta J) >_0$ by the product $\rho(\Delta J - \Delta_0 + e\eta_k - \Delta J_{0F} \cdot < W(\Delta J) >_0$. Thus, Eq. (10) has a unique solution in this case, with $\alpha_{ex}(\eta) \equiv 1$. Let us now consider the kinetics of electrochemical processes on a semiconductor electrode with a large number of surface states. Then $d\eta_k/d\eta \simeq 1$ and Δ_k does not depend on overvoltage. In this case, $M(\varepsilon) = \rho(\varepsilon - \Delta_k - \varepsilon_F)\,e^{-\frac{\varepsilon-\varepsilon_F}{kT}}$, and $< W(\Delta J) >_0$ is, as before, determined by the Arrhenius equation (7). In this case, Eq. (10) for ε^* assumes the form

$$\alpha_{ex}(\eta) = \alpha(\Delta J^*) = 1 - kT\frac{d\ln\rho}{d\varepsilon}.$$

The specifics of the semiconductor electrodes are manifested in the fact that the level density ρ vanishes in accordance with a power law at the edge of the band. Thus, $f(\varepsilon)$ varies in this case from $-\infty$ at $\varepsilon = \Delta_k + \varepsilon_F$ to 1 at $\varepsilon - \varepsilon_F - \Delta_k \ll kT$, with two characteristic regions of variation: a region with an infinite scale of variation at $f(\varepsilon) \simeq 1$ and a region with a small scale (smaller than kT) for $f(\varepsilon) < 1$. It then follows from the inequalities (13) that $\alpha_{ex}(\eta)$ has a region with an infinite scale of variation in which $\alpha_{ex}(\eta) = 1$ (region of nonbarrier discharge). Since the scale of variation of the function $\alpha(\Delta J)$ is at least kT in all cases, the characteristic scale of variation of this function for $\alpha_{ex}(\eta) < 1$ is determined basically by the function $\alpha(\Delta J)$. Therefore, in contrast to the case of reactions at metallic electrodes, α_{ex} could become negative in the absence of quantum degrees of freedom (apart from the electrons). However, if a change in the state of the quantum degrees of freedom takes place during the reaction, then we have, as in the case of metal electrodes, $0 \leq \alpha_{ex} \leq 1$, and both nonbarrier ($\alpha_{ex} \simeq 1$) and nonactivation ($\alpha_{ex} \simeq 0$) discharge regions exist.

We have thus far considered the course of only one reaction at the electrode. In the case of more complex processes, it is possible in principle for the limiting stage to change; this might result in a stepwise change of α_{ex} (on distances of the order of a few kT).

In conclusion, we present the results obtained for the case in which the functions $f(\varepsilon)$ and $\alpha(\Delta J)$ are nonmonotonic: 1) the dependence of α_{ex} on the overvoltage η may, like the $\varepsilon^*(\eta)$ and $\Delta J^*(\eta)$ relationships, be nonmonotonic; 2) sharp inflections may appear on the volt-ampere characteristic (in an overvoltage range of the order of a few kT) owing to a nonmonotonic stepwise change in α_{ex} (see Fig. 2, where the dashed curves correspond to the "normal" monotonic function $\alpha_{ex}(\eta)$ and the solid curves to nonmonotonic α_{ex}).

The authors are profoundly grateful to L. I. Krishtalik for discussion of the work.

LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, Élektrokhimiya 7, 172 (1971).
2. M. A. Vorotyntsev and A. M. Kuznetsov, Élektrokhimiya 6, 208 (1970).
3. W. Harrison, Pseudopotentials in the Theory of Metals, Benjamin (1968).
4. R. R. Dogonadze and A. M. Kuznetsov, in: Advances in Science: Electrochemistry (1967) [in Russian] All-Union Institute of Scientific and Technical Information, Moscow (1969).
5. M. A. Vorotyntsev and A. M. Kuznetsov, No. 1233-69 dep. All-Union Institute of Scientific and Technical Information.
6. R. R. Dogonadze, A. M. Kuznetsov, and V. G. Levich, Electrochim. Acta 13, 1025 (1968).
7. M. A. Vorotyntsev and A. M. Kuznetsov, Vestn. MGU, Fizika, No. 2, 146 (1970).
8. J. O'M. Bockris, in: Certain Problems of Contemporary Electrochemistry [Russian translation], IIL, Moscow (1958).
9. R. R. Dogonadze, A. M. Kuznetsov, and A. A. Chernenko, Uspekhi Khimii, 34, 1179 (1965). V. G. Levich, in: Advances in Science: Electrochemistry, 1965 [in Russian], All-Union Institute of Scientific and Technical Information, Moscow (1967).
10. V. L. Bonch-Bruevich and S. V. Tyablikov, The Method of Green's Functions in Statistical Mechanics [in Russian], Fizmatgiz, Moscow (1961).