BRIEF COMMUNICATIONS

THE EQUATION OF ELECTROCHEMICAL KINETICS FOR THE DISCHARGE OF A METAL CATION TO FORM A SOLUTION IN ANOTHER METAL

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In a previous report [1] we discussed the form of the equation of electrochemical kinetics in the case when the discharge of a transitional reaction group differs from the discharge of a reacting particle (e. g., the discharge of a hydrogen ion to form an adsorbed atom). It is interesting to consider a reaction for which this assumption is not necessary. For example, the discharge of a metal cation can be treated as the transition of a cation from the electrolyte into the metal lattice, taking the atoms in the solid metal as being completely ionized. The hypothesis has also been put forward that the primary product of discharge of a hydrogen ion on iron is not an adsorbed atom but a proton dissolved in the metal.

For simplicity, let us consider the case of a singly charged cation Me^+ which, as a result of the electrode process, crosses into the metal phase and forms a solution (for example, an amalgam). Regardless of any assumptions on the mechanism of the process, the overall result of the reaction can be expressed by the equation

$$\mathrm{Me}^+ + e^- \rightleftarrows \mathrm{Me}. \tag{1}$$

The equilibrium potential, φ_r of reaction (1) is given by

$$\varphi_r = \frac{RT}{F}\ln\frac{[\mathrm{Me}^+]}{[\mathrm{Me}]} + g_{\mathrm{Me}} + \mathrm{const} \tag{2}$$

where $[Me^+]$ is the concentration of the cation in the electrolyte,[Me] the concentration of dissolved metal in the solvent metal (ignoring any assumption on the degree of ionization of its atoms), and g_{Me} is the standard free energy of the transport of a dissolved atom of metal Me from the solvent metal to a vacuum,

$$(\mathrm{Me})_{\mathrm{solv}} \rightarrow (\mathrm{Me})_{\mathrm{vac}}, \tag{3}$$

expressed in electrical units; φ_r is referred to a constant comparison electrode and the constant is independent of the nature of the metal solvent.

Let us consider the conditions which (2) imposes on the expression for the rates of discharge v and ionization v. Let us assume that ln $\overrightarrow{v}$ and ln $\overleftarrow{v}$ depend linearly on the potential φ, but let us leave open the question of how they depend on the zero charge potential φ_0 of the solvent metal. In accordance with our assumption (stated at the beginning of this paper) that the cation Me^+ crosses directly from the electrolyte to the metallic phase, we shall also assume that ln $\overrightarrow{v}$ and ln $\overleftarrow{v}$ depend linearly on g_{Me} (or on the analogous quantity g_{Me^+} which refers not to the atom but to the ion Me^+—see below). Then in the general case we can write

$$\ln\overrightarrow{v} = -\frac{\alpha F}{RT}\varphi + \frac{F}{RT}f_1(\varphi_0) + \frac{F}{RT}\alpha' g_{\mathrm{Me}} + \ln[\mathrm{Me}^+] + \mathrm{const}' \tag{4}$$

$$\ln\overleftarrow{v}=\frac{\beta F}{RT}\varphi+\frac{F}{RT}f_2(\varphi_0)-\frac{F}{RT}\beta' g_{\mathrm{Me}}+\ln[\mathrm{Me}]+\mathrm{const}'' \tag{4a}$$

where α, β, α', and β' are unknown constants and $f_1(\varphi_0)$ and $f_2(\varphi_0)$ are unknown functions of φ_0. From the condition of equilibrium $\overrightarrow{v}=\overleftarrow{v}$ and (2), we get

$$\alpha+\beta=1 \tag{5}$$

$$\alpha'+\beta'=1 \tag{6}$$

$$f_1(\varphi_0)=f_2(\varphi_0) \tag{7}$$

Condition (7) is satisfied by the ordinary form of the equation of electrochemical kinetics, as it is assumed that

$$f_1(\varphi_0)=f_2(\underset{\rightarrow}{\varphi_0})=-(1-\alpha)\psi_1 \tag{8}$$

If we wanted to express in $\ln\overrightarrow{v}$ as a function of $(\varphi-\varphi_0)$, instead of φ with a correction for ψ_1, we should have to put

$$f_1(\varphi_0)=\alpha\varphi_0-(1-\underset{\rightarrow}{\alpha})\psi_1 \tag{9}$$

as in this case we should get for $\ln\overrightarrow{v}$ the expression

$$\ln\overrightarrow{v}=-\frac{\alpha F}{RT}(\varphi-\varphi_0)-\frac{F}{RT}(1-\alpha)\psi_1+\frac{F}{RT}\alpha' g_{\mathrm{Me}}+\ln[\mathrm{Me}^+]+\mathrm{const}'. \tag{10}$$

By (4), (5), (6), and (7), the equation for $\ln\overleftarrow{v}$

$$\begin{aligned}\ln\overleftarrow{v}={}&\frac{(1-\alpha)F}{RT}\varphi+\frac{\alpha F}{RT}\varphi_0-\frac{F}{RT}(1-\alpha)\psi_1\\&-\frac{F}{RT}(1-\alpha')g_{\mathrm{Me}}+\ln[\mathrm{Me}]+\mathrm{const}''.\end{aligned} \tag{10a}$$

Thus, whatever the value of α, we cannot express the rates of the forward and reverse reactions in terms of functions of $(\varphi-\varphi_0)$.

To find out what effect may be exerted by φ_0 on the process rate, it is useful to consider the case when the electrical center of the transitional complex is located inside a dense layer, while the diffuseness of the electrical double layer can be neglected. Then

$$\psi_1=\gamma(\varphi-\varphi_0) \tag{11}$$

where $0<\gamma<1$, and

$$\begin{aligned}\ln\overrightarrow{v}={}&\frac{F}{RT}(-\alpha+\alpha\gamma-\gamma)\varphi+\frac{F}{RT}(1-\alpha)\gamma\varphi_0\\&+\frac{F}{RT}\alpha' g_{\mathrm{Me}}+\ln[\mathrm{Me}^+]+\mathrm{const}'\end{aligned} \tag{12}$$

$$\begin{aligned}\ln\overleftarrow{v}={}&\frac{F}{RT}(1-\alpha)(1-\gamma)\varphi+\frac{F}{RT}(1-\alpha)\gamma\varphi\\&-\frac{F}{RT}(1-\alpha')g_{\mathrm{Me}}+\ln[\mathrm{Me}]+\mathrm{const}''.\end{aligned} \tag{12a}$$

If γ is not very small, the effect of φ_0 will be comparable with that of φ. For example, if $\alpha = {}^1/_2$, then in (12) the coefficient of $\varphi F/RT$ will be $-{}^3/_4$ and that of $\varphi_0 F/RT$ will be $+{}^1/_4$.

The electronic work function We does not come into the kinetic equations compatible with (2). It can be brought into (2) if, instead of the process free energy of (3), we introduce a similar quantity g_{Me^+} which refers to the transport of a Me^+ cation from the solvent metal to a vacuum,

$$(Me^+)_{solv} \rightarrow (Me^+)_{vac}. \tag{13}$$

Since

$$g_{Me} = g_{Me^+} + W_e - I_{Me} \tag{14}$$

where I_{Me} is the ionization potential of Me, from (2) and (14) we get

$$\varphi_r = \frac{RT}{F}\ln\frac{[Me^+]}{[Me]} + g_{Me^+} + W_e + \text{const.} \tag{15}$$

where the constant is different from that in (2). In the theory of delayed discharge, the corresponding expressions for $\ln \overrightarrow{v}$ and $\ln \overleftarrow{v}$ (putting $\alpha = \alpha'$) are:

$$\ln v = -\frac{\alpha F}{RT}\varphi - \frac{F}{RT}(1-\alpha)\psi_1 + \frac{F}{RT}\alpha(g_{Me^+} + W_e) + \ln[Me^+] + \text{const}_1' \tag{16}$$

$$\ln \overleftarrow{v} = \frac{(1-\alpha)F}{RT}\varphi - \frac{F}{RT}(1-\alpha)\psi_1 - \frac{F}{RT}(1-\alpha)(g_{Me^+} + W_e) + \ln[Me] + \text{const}_1''. \tag{16a}$$

From the approximate relation

$$W_e - \varphi_0 = 4.71 \tag{17}$$

we get from (16) and (16a)

$$\ln \overrightarrow{v} = -\frac{\alpha F}{RT}(\varphi - \varphi_0) - \frac{F}{RT}(1-\alpha)\psi_1 + \frac{F\alpha}{RT}\cdot g_{Me^+} + \ln[Me^+] + \text{const}_2' \tag{18}$$

$$\ln \overleftarrow{v} = \frac{(1-\alpha)F}{RT}(\varphi - \varphi_0) - \frac{F}{RT}(1-\alpha)\psi_1 - \frac{F(1-\alpha)}{RT}\cdot g_{Me^+} + \ln[Me] + \text{const}_2''. \tag{18a}$$

In this case, $\overrightarrow{v}$ and $\overleftarrow{v}$ are actually expressed as functions of $(\varphi - \varphi_0)$. However, this expression does not vouchsafe any new result on how φ_0 affects the kinetics, because, when φ_0 is changed by any surface reaction and the bulk properties of the solvent metal remain the same (so that the values of g_{Me} remain constant), g_{Me^+} obviously changes in the opposite sense, compensating for the change in φ_0. Thus variations in φ_0 can affect the process kinetics only via the value of ψ_1.

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LITERATURE CITED

1. A. N. Frumkin, Élektrokhimiya, 1, 394 (1965); J. Electroanalyt. Chem., 9, 173 (1965).