BRØNSTED RELATIONSHIPS IN THE KINETICS OF COMPLEX ELECTRODE PROCESSES

B. M. Grafov and A. N. Frumkin

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The phenomenological theory of the kinetics of electrode processes [1] is built upon the following three basic conditions:

1. The rate of individual, elementary steps of a complex electrochemical reaction is activational in nature.

2. The activation energies of forward and reverse processes of elementary steps are connected with the reaction heats by linear Brønsted relationships.

3. The Brønsted relationships only involve the heat of the elementary step being considered, rather than the heat of the entire, complex electrode process.

These three conditions have been utilized in numerous papers on the kinetics of electrode processes. It is important, however, to note that in deriving the explicit potential dependence one has always made the additional assumption that the number of electrons effectively transferred during an individual, elementary step is integral. Because of changes in electric double-layer structure, this additional assumption may prove to be violated for adsorption steps. Such a possibility had first been taken into account in work on the theory of the impedance of electrochemical reactions [2].

We shall analyze the kinetic equations of slow-discharge theory while taking into consideration that a fractional number of electrons can effectively be transferred in individual adsorption steps of complex electrode processes.

As an example we shall discuss a two-step electrochemical reaction of the type

$$\mathrm{Ox} = ne = \mathrm{Rd}.$$

proceeding according to the scheme of Fig. 1. When the activational nature of the adsorption processes is taken into account, the kinetic equations of slow-discharge theory can be represented in the form

$$\left.\begin{aligned} V_1 &= k_{1f}\Phi_{1f}(A)\exp[-W_{1f}(\varphi,\ A)/RT] - k_{1b}c_1\Phi_{1b}(A)\exp[-W_{1b}(\varphi,\ A)/RT],\\ V_2 &= k_{2f}\Phi_{2f}(A)\exp[-W_{2f}(\varphi,\ A)/RT] - k_{2b}c_2\Phi_{2b}(A)\exp[-W_{2b}(\varphi,\ A)/RT],\end{aligned}\right\} \quad (1)$$

where V_1 and V_2 are the flows of reacting species of steps 1 and 2, respectively (the direction from the electrode into the solution is taken as the positive direction); the functions Φ only depend on the quantity of species A being in the adsorbed state a (Fig. 1); the k are rate constants, R is the gas constant, T is the absolute temperature, c_1 and c_2 are the concentrations of species of the oxidized and reduced forms near the electrode surface (the solution will be regarded as dilute with respect to the reacting species); f is the index of the forward process, and b is that of the reverse process of an individual, elementary step.

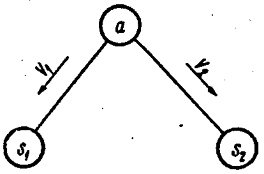

Fig. 1. The scheme of a complex electrochemical reaction with two adsorption steps: s_1 and s_2 arbitrarily designate the states of reacting species of the oxidized and reduced form near the electrode surface, and a is the arbitrary designation for the adsorbed state.

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It has been taken into account in Eqs. (1) that in the general case. the energies of activation W can be functions of electrode potential φ and of the adsorbed quantity A. The question of selecting the electrical variable becomes unimportant in such a formulation.

We shall assume that linear Brønsted relationships exist:

$$\left.\begin{aligned} dW_{1f}=-\beta_1 dW_1, \quad dW_{1b}=\alpha_1 dW_1,\\ dW_{2f}=\alpha_2 dW_2, \quad dW_{2b}=-\beta_2 dW_2,\end{aligned}\right\} \tag{2}$$

where dW_1 and dW_2 are the heat changes of processes 1 and 2, respectively; $\alpha_1+\beta_1=1$, $\alpha_2+\beta_2=1$, α_1, β_1, α_2, and β_2 are constants.

It follows from (2) that

$$\alpha_1 dW_{1f}+\beta_1 dW_{1b}=0, \quad \beta_2 dW_{2f}+\alpha_2 dW_{2b}=0.$$

For A =const we obtain from this,

$$\alpha_1\left(\frac{\partial W_{1f}}{\partial\varphi}\right)_A+\beta_1\left(\frac{\partial W_{1b}}{\partial\varphi}\right)_A=0, \quad \beta_2\left(\frac{\partial W_{2f}}{\partial\varphi}\right)_A+\alpha_2\left(\frac{\partial W_{2b}}{\partial\varphi}\right)_A=0. \tag{3}$$

On the basis of the Gibbs adsorption equation for the reversible electrode [3] or of the Onsager reciprocal relations [4] one can write down

$$\left(\frac{\partial\mu_1}{\partial\varphi}\right)_A=n_1F, \quad \left(\frac{\partial\mu_2}{\partial\varphi}\right)_A=-n_2F, \tag{4}$$

where μ_1 and μ_2 are the chemical potentials of substances 1 and 2, which are regarded as functions of potential and adsorbed quantity, n_1 and n_2 are the numbers of electrons effectively transferred during the elementary act of steps 1 and 2, respectively [4].

Using the ideality of the solution with respect to particles 1 and 2 we shall rewrite (4) as

$$RT\left(\frac{\partial\ln c_1}{\partial\varphi}\right)_A=n_1F, \quad RT\left(\frac{\partial\ln c_2}{\partial\varphi}\right)_A=-n_2F. \tag{5}$$

Under equilibrium conditions, the adsorption isotherms follow from the kinetic equations (1).

$$\left.\begin{aligned} k_{1f}\Phi_{1f}(A)\exp[-W_{1f}(\varphi, A)/RT]=k_{1b}\Phi_{1b}(A)c_1\cdot\exp[-W_{1b}(\varphi, A)/RT],\\ k_{2f}\Phi_{2f}(A)\exp[-W_{2f}(\varphi, A)/RT]=k_{2b}\Phi_{2b}(A)c_2\exp[-W_{2b}(\varphi, A)/RT].\end{aligned}\right\} \tag{6}$$

From (6) we find, after taking logarithms and differentiating with respect to potential while keeping the adsorbed quantity constant,

$$\left.\begin{aligned} -\left(\frac{\partial W_{1f}}{\partial\varphi}\right)_A=RT\left(\frac{\partial\ln c_1}{\partial\varphi}\right)_A-\left(\frac{\partial W_{1b}}{\partial\varphi}\right)_A,\\ -\left(\frac{\partial W_{2f}}{\partial\varphi}\right)_A=RT\left(\frac{\partial\ln c_2}{\partial\varphi}\right)_A-\left(\frac{\partial W_{2b}}{\partial\varphi}\right)_A.\end{aligned}\right\} \tag{7}$$

Let us compare relations (3), (5), and (7). As a result we find that the activation energies of adsorption steps in electrochemical reactions and the numbers of electrons effectively transferred during these steps are connected by the relationships

$$\left.\begin{aligned} \left(\frac{\partial W_{1f}}{\partial\varphi}\right)_A=-\beta_1 n_1F, \quad \left(\frac{\partial W_{1b}}{\partial\varphi}\right)_A=\alpha_1 n_1F,\\ \left(\frac{\partial W_{2f}}{\partial\varphi}\right)_A=\alpha_2 n_2F, \quad \left(\frac{\partial W_{2b}}{\partial\varphi}\right)_A=-\beta_2 n_2F.\end{aligned}\right\} \tag{8}$$

Let us apply relations (8) to the widely known case of electroreduction of organic substances with preceding equilibrium adsorption step [5]. We shall assume for the sake of simplicity that the adsorption isotherm is a Henry isotherm with quadratic dependence of the work of adsorption on electrode potential:

$$B_0\exp[-a(\varphi-\varphi_M)^2]c_1=A, \tag{9}$$

where B_0 and a are constants, and φ_M is the potential of maximum adsorption. After taking logarithms we obtain from (9)

$$\ln c_1=\ln A+a(\varphi-\varphi_M)^2-\ln B_0. \tag{10}$$

Inserting (10) into the first equation of (5) leads to a linear connection between the effective number of electrons and the electrode potential:

$$n_1F = RT\left(\frac{\partial \ln c_1}{\partial \varphi}\right)_A = 2RTa(\varphi - \varphi_{\text{м}}). \tag{11}$$

Hence for the activation energies of the slow second adsorption step one can write, according to (8) and (11),

$$\left.\begin{aligned} \left(\frac{\partial W_{2f}}{\partial \varphi}\right)_A &= \alpha_2F(n-n_1) = \alpha_2F[n - 2RTa(\varphi-\varphi_{\text{м}})/F], \\ \left(\frac{\partial W_{2b}}{\partial m}\right) &= -\beta_2F(n-n_1) = -\beta_2F[n - 2RTa(\varphi-\varphi_{\text{м}})/F]. \end{aligned}\right\} \tag{12}$$

From this it follows directly that the equation of slow discharge for the second adsorption process is of the form

$$\begin{aligned} V_2 = {} & k_{2f}A\exp[-\alpha_2Fn(\varphi-\varphi_{\text{м}})/RT + \alpha_2a(\varphi-\varphi_{\text{м}})^2] - \\ & -k_{2b}c_2\exp[\beta_2Fn(\varphi-\varphi_{\text{м}})/RT - \beta_2a(\varphi-\varphi_{\text{м}})^2], \end{aligned} \tag{13}$$

providing that the adsorption flow of this process is proportional to the bulk concentration of the reduced form, c_2, while the desorption flow is proportional to the concentration A of adsorbed species.

Eliminating the surface concentration of adsorbed species, A, by using the isotherm (9) we arrive at the final expression for the kinetic equation of the electrode process considered:

$$\begin{aligned} V_2 = {} & k_{2f}'c_1\exp[-\alpha_2Fn(\varphi-\varphi_{\text{м}})/RT]\exp[-\beta_2a(\varphi-\varphi_{\text{м}})^2] - \\ & -k_{2b}c_2\exp[\beta_2Fn(\varphi-\varphi_{\text{м}})/RT]\exp[-\beta_2a(\varphi-\varphi_{\text{м}})^2], \end{aligned} \tag{14}$$

where $k_{2f}' = k_{2f}B_0$.

In the case of strong irreversibility we obtain the equation

$$V_2 = k_{2f}'c_1\exp[-\alpha_2Fn(\varphi-\varphi_{\text{м}})/RT]\exp[-\beta_2a(\varphi-\varphi_{\text{м}})^2], \tag{15}$$

which differs from the kinetic equation of [5] by the fact that instead of the factor $\exp[-a(\varphi-\varphi_M)^2]$ it involves a factor $\exp[-\beta_2a(\varphi-\varphi_M)^2]$. These factors can substantially differ in magnitude as one gets away from the potential of maximum adsorption.

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