PROBLEM OF THE STOICHIOMETRIC NUMBER OF AN ELECTRODE REACTION

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The stoichiometric reaction number as determined either from the true or the extrapolated exchange current is not a function of the α-transfer coefficient of the discharge or electrochemical desorption stages. The stoichiometric number ν' determined from the extrapolated exchange current (extrapolation of the semilogarithmic line closest to the equilibrial potential) is equal in all the selected cases to the number of repetitions of the slowest stage required for the reaction to occur as a whole along the given lines. Given comparable rates of the two stages, ν' loses a clear-cut physical sense. For a number of different mechanisms the polarization curves can be described by a general expression.

A few years ago, Frumkin [1] showed that contrary to the widely held opinion the experimentally determined stoichiometric number ν' (see below) may differ considerably from the true stoichiometric number ν; ν' is equal to unity both for slow electrochemical desorption as well as slow discharge with subsequent rapid electrochemical desorption. It is only at comparable rates of both processes that $\nu' > 1$. Similar conclusions were also reached by Lukovtsev [2], Vetter [3], and Makrides [4, 5], although in a less complete form.*

In most of the papers mentioned, it is assumed for convenience in calculation that the transfer coefficients for the discharge and electrochemical desorption reactions α_1 and α_2 are equal. In our work [6, 7], we showed the possibility in principle of processes with α ranging from 0 to 1, and that in a number of cases considerably different values of α_1 and α_2 were probable. The aim of the present communication is to supplement the results in [1] by considering the case $\alpha_1 \neq \alpha_2$ and certain other mechanisms. In our discussion we will follow Frumkin's argument [1].

The initial equations in [1] are

$$\vec{i}/\overleftarrow{i} = f(\eta) \tag{1†}$$

$$\nu = 2i_0(\partial\eta / \partial i)_{\eta=0} = 2 / f'(0);\ \nu' = 2(i_0)_e(\partial\eta / \partial i)_{\eta=0} \tag{2}$$

$$i = v_1 - v_2 + v_3 - v_4 = 2(v_1 - v_2) = 2(v_3 - v_4) \tag{3}$$

$$\begin{gathered} v_1 = k_1(1-\theta) = k_1^0 e^{\alpha_1\eta}(1-\theta);\ v_2 = k_2\theta = k_2^0 e^{-\beta_1\eta}\theta \\ v_3 = k_3\theta = k_3^0 e^{\alpha_2\eta};\ v_4 = k_4(1-\theta) = k_4^0 e^{-\beta_2\eta}(1-\theta). \end{gathered} \tag{4}$$

Here, $\vec{i}$ and $\overleftarrow{i}$ are the exchange rates (in electrical units) between the solution and gas and in the reverse direction; i is the total current; v is the rate of separate processes, η is the excess voltage (in RT/F units), i_0 is the true and $(i_0)_e$ the extrapolated exchange currents, the subscripts 1 and 3 relate to discharge and electrochemical desorption, 2 and 4 to the corresponding reverse reactions, and θ is the degree of filling.

The equilibrium conditions and stationary conditions give us

$$k_1^0 k_3^0 = k_2^0 k_4^0;\ \theta = (k_1 + k_4) / (k_1 + k_2 + k_3 + k_4). \tag{5}$$

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* Paper [5] repeats the arguments in [1] regarding electrochemical desorption.

† This general equation was first derived by Horiuti and Ikusima [8].

From (4)-(5) we get the exchange currents for the discharge i_{0I} and desorption i_{0II} stages

$$i_{0I} = k_1^0 k_2^0 / (k_1^0 + k_2^0); \quad i_{0II} = k_1^0 k_3^0 / (k_1^0 + k_2^0). \tag{6}$$

Their ratio $\gamma = i_{0I} / i_{0II} = k_2^0 / k_3^0$ describes the mechanism of the process. For exchange rates Frumkin found the following expressions [1, 9]

$$\vec{i} = v_1 v_3 / (v_2 + v_3) + v_3; \quad \overleftarrow{i} = v_2 v_4 / (v_2 + v_3) + v_4. \tag{7}$$

Applying (4-7), we can get

$$f(\eta) = (2\gamma e^{(\alpha_1+\beta_2)\eta} + 1) / (2\gamma e^{-(\alpha_2+\beta_1)\eta} + 1). \tag{8}$$

Equation (8) differs somewhat from the corresponding equation in [1], changing into it at $\alpha_1 = \alpha_2$. But $f'(0)$, as is easy to see, does not depend on our assumption of the quality of α_1 and α_2; it is equal to

$$f'(0) = 4\gamma / (2\gamma + 1). \tag{9}$$

Substituting (9) into (2) for ν, we get

$$\nu = 1 + 1 / 2\gamma = 1 + i_{0II} / 2i_{0I}, \tag{10}$$

which coincides with Eq. (11) in [1].*

Further transition from the above derived stoichiometric number ν to the experimentally determined one ν' is made by the same method as in [1].† Neither i_0 nor $f'(0)$ depends on the numerical values of α_1 or α_2; the same applies to $(\partial\eta / \partial i)_{\eta=0}$.

$$i_0 = i_{0I}(1 + 2\gamma) / \gamma(1 + \gamma); \quad (\partial\eta / \partial i)_{\eta=0} = {}^1\!/\!_4 (1 / i_{0I} + 1 / i_{0II}). \tag{11}$$

Nor is the extrapolated exchange current associated with any assumptions regarding the ratio between α_1 and α_2, as is easy to see from the equations (19) and (21) given later in this paper. Hence the results in [1] are still valid whether or not we assume the quality of α_1 and α_2

$$\begin{gathered} \nu' = 1 \text{ at } \gamma \gg 1; \quad \nu' = 1 \text{ at } \gamma \ll 1; \\ \nu' = \frac{1+\gamma}{\gamma} \cdot \frac{k_1^0 + k_2^0}{k_1^0 + k_3^0} \text{ at } \gamma \simeq 1. \end{gathered} \tag{12}$$

For the latter case ($\gamma \sim 1$), for small equilibrial degrees of filling, we get $k_2^0 \gg k_1^0$ and $\nu' \simeq 1 + \gamma$.

Makrides [5] obtained the following expression for the stoichiometric number during recombination removal of adsorbed hydrogen (or other intermediate product)

$$\nu = (\gamma + 2) / (\gamma + 1), \tag{13}$$

where $\gamma = i_{0I}/i_{0III}$ and i_{0III} are the recombination change current equal to $2k_5^0[k_1^0/(k_1^0 + k_2^0)]^2$. At $\gamma \gg 1$ (slow recombination) $\nu = 1$, at $\gamma \ll 1$ (slow discharge) $\nu = 2$. During slow recombination the polarization curve is expressed by the equation

$$i = i_{0III}(e^{2\eta} - 1), \tag{14}$$

and during slow discharge

$$i = i_{0I}(e^{\alpha_1\eta} - e^{-\beta_1\eta}). \tag{15}$$

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* In [1] there is a misprint: the subscripts in the numerator and denominator alongside i_0 are the wrong way round and the results are discussed in relation to a wrong form of Eq. (11). This has already been pointed out in [5].

† Condition $\eta \ll \ln\gamma$ at $\gamma \gg 1$ is replaced by $\eta \ll (\alpha_2 + \beta_1)^{-1} \ln\gamma$; correspondingly, at $\gamma \ll 1$ it is assumed that $\eta \ll (\alpha_1 + \beta_2)^{-1} \ln\gamma^{-1}$.

On the basis of (14) and (15) we can demonstrate that for the two given limiting cases the extrapolated exchange current coincides with the true current and, consequently, $\nu' = \nu$. The same result is obtained in the case in which the rate of removal of the intermediate product is determined by a first-order reaction, for example, decomposition of a surface complex $v_7 = k_7\theta$. In this case, too, for slow discharge $\nu = \nu' = 2$; for slow removal $\nu = \nu' = 2$. If $\gamma = k_2{}^0 / k_7{}^0 \simeq 1$, $\nu' = 2(1 + \gamma)/\gamma \cdot (k_1^0 + k_2^0)/(k_1^0 + k_7^0)$; at $\gamma = 1$ we get $\nu' = 4$.

Let us find the stoichiometric number of one more mechanism – the adsorption-electrochemical mechanism – which consists in electrochemical desorption of adsorbed atoms occurring not through discharge (the discharge rate is negligibly small), but through adsorption from the gas phase (or a solution), for example

$$H_2 \rightarrow 2H_{ads}; \quad H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O.$$

The possibility in principle of this mechanism was demonstrated in [6, 10]. In this case, $\nu_5 \simeq \nu_6 >> \nu_3 \geq \nu_4 >> \nu_1 \geq \nu_2$; $\theta = \theta_0 = k_4^0/(k_3^0 + k_4^0)$;

$$\vec{i} = v_3; \quad \overleftarrow{i} = v_4; \quad f(\eta) = e^\eta; \quad f'(0) = 1; \quad \nu = 2 \tag{16}$$

$$i_0 = i_{0II} = k_3{}^0 k_4{}^0 / (k_3{}^0 + k_4{}^0); \quad (\partial\eta / \partial i)_{\eta=0} = 1 / i_{0II} \tag{17}$$

$$i = i_{0II}(e^{\alpha_2\eta} - e^{-\beta_2\eta}); \quad (i_0)_e = i_{0II} = i_0; \quad \nu' = \nu = 2 \tag{18}$$

Although the formation of the end product – X_2 molecules – does occur through electrochemical desorption, $\nu = \nu' = 2$, just as during delayed discharge with nonelectrochemical removal.[*] There is no contradiction here, incidentally, for two acts of electrochemical desorption (with intermediate chemical adsorption) are required for the formation of X_2 molecules from two $X^\pm$ ions contained in the solution.

Although in certain cases ν may be arbitrarily large (see Eq. (10)), the value ν' in no case exceeds a few units.[†] Here, in all cases in which the rate of the process is determined by the rate of only one stage, ν' proves equal to the number of repetitions of the slowest stage required for the process to occur as a whole. But if the rates of the two stages are comparable, ν' may assume values different from those characteristic of each stage separately.[‡]

It is interesting to note that in many cases the dependence of the current on the excess voltage may be represented in the fairly simple and general form given below. For a delayed discharge during electrochemical removal [1][**]

$$i = 2k_1{}^0 k_2{}^0 (e^{(1+\alpha_1)\eta} - e^{-\beta_1\eta}) / (k_1{}^0 + k_2{}^0 e^\eta). \tag{19}$$

Delayed discharge usually occurs for electrodes poorly adsorbing the intermediate product X, i.e., $\theta_0 << 1$. Then $k_2^0 e^\eta \geq k_2^0 >> k_1^0$ and instead of (19) we get

$$i = 2k_1{}^0 (e^{\alpha_1\eta} - e^{-(1+\beta_1)\eta}). \tag{20}$$

For slow electrochemical desorption we get [1]

$$i = 2k_1{}^0 k_3{}^0 (e^{(1+\alpha_2)\eta} - e^{-\beta_2\eta}) / (k_1{}^0 e^\eta + k_2{}^0). \tag{21}$$

In this case it is more difficult to assess the ratio between the two items in the denominator. If, as above, $\theta_0 << 1$, then when η is not too large $k_1^0 e^\eta < k_2^0$ and instead of (21) we get

$$i = 2k_1{}^0 \gamma^{-1} (e^{(1+\alpha_2)\eta} + e^{-\beta_2\eta}). \tag{22}$$

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[*] The analogy in this respect between the adsorption-electrochemical mechanism and delayed discharge was pointed out by us before on the basis of qualitative considerations [6].

[†] Makrides [5] points out that for slow electrochemical desorption we may get $\nu' = 1 + \gamma$ with extrapolation of the semilogarithmic line from the region of very high excess voltages ($\eta >> \ln \gamma$). But it is obvious that it would be more correct to use for extrapolation the section of the polarization curve closer to the region $\eta \simeq 0$ in which $(\partial\eta / \partial i)_{\eta=0}$ is determined. In this case, τ' need not be big.

[‡] However, in such conditions it is hardly possible to formulate the problem of the number of times ony one slow stage is repeated.

[**] It may be demonstrated that Eqs. (19) and (21) are valid whether or not we assume α_1 and α_2 to be equal.

But if the electrode material adsorbs X properly, which is more probable for slow electrochemical desorption (see [6, 10], for example), i.e., $\theta_0 \geq 1/2$, then $k_1^0 e^{\eta} > k_2^0$. In this case,

$$i = 2k_3{}^0 (e^{\alpha_3\eta} - e^{(1+\beta_3)\eta}). \tag{23}$$

It is easy to see that for all the selected mechanisms at which the reaction rate is determined by one of the stages, the kinetic equations of the Tafel type (Eqs. (14), (15), (18), (20), (22), and (23)) may be described by one general expression

$$i = (i_0)_e (e^{\alpha'\eta} - e^{-(\lambda'-\alpha')\eta}). \tag{24}$$

Here, α' is the formal value of the transfer coefficient obtained from the slope of the semilogarithmic line, $\lambda' = 2/\nu'$. The relationship (24) was used by us earlier when considering the mechanism of the anodic generation of chlorine [11].

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