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Abstract

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ON A RIGOROUS METHOD FOR CALCULATING THE ACTIVATION ENERGY OF ELECTROCHEMICAL REACTIONS

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The principal parameters determining the character of the kinetic dependences potential—current density are the exchange current i_0 and the activation energy (a.e.). Although by the present time a considerable amount of experimental material has been accumulated on the influence of temperature on the rate of electrochemical processes, the actual values of the a.e. for most of them are unknown.

The temperature-kinetic method for calculating the a.e. is based on the approximate empirical dependence

$$(\lg i)_{\Delta\varphi} = \text{const} - E/2.303RT, \tag{1}$$

where i is the total current in the electrochemical cell, and E is the so-called effective a.e.

The method of determining E from equation (1), most widely used in the works of S. V. Gorbachev and co-workers ([1,2]) and employed in a number of other investigations, suffers from substantial shortcomings. The Arrhenius equation, in the sense of its derivation, is applicable to irreversible reactions. If the process is kinetically reversible, i.e., proceeds in the forward and reverse directions, then the Arrhenius equation should be applied separately to each of them.

Electrochemical reactions are usually reversible in the indicated sense. The total current i is the difference between the rates of the forward and reverse reactions

$$i = k_1 \exp(-E_1/RT) -$$

$$-k_2 \exp(-E_2/RT). \tag{2}$$

Fig. 1. Theoretical dependences $\Delta\varphi$—i and $\lg i$—$1/T$.
1—$\Delta\varphi = 0.05$ V; 2—0.10 V; 3—0.15 V; 4—0.20 V

Since in the general case $E_1 \neq E_2$, at low $\Delta\varphi$* analysis of experimental data by equation (1) can give** only a certain fictitious constant E, whose meaning is unclear.

Formally, by means of (1) one may find an "effective"a.e. also in the region of the limiting current. The value obtained, however, indicates only the temperature dependence of the diffusion coefficient and cannot properly be a characteristic of the electrode process itself.

According to the currently generally accepted theory of electrochemical kinetics, the total current i in stirred solutions containing excess inert electrolyte, is determined by the equation:

$$i = i_0 \left[\left(1 - \frac{i}{i^{\mathrm{k}}_{\mathrm{lim}}}\right) e^{-\alpha n F \Delta\varphi / RT} - \left(1 + \frac{i}{i^{\mathrm{a}}_{\mathrm{lim}}}\right) e^{(1-\alpha) n F \Delta\varphi / RT} \right], \qquad (3)$$

where $i^{\mathrm{k}}_{\mathrm{lim}}$ and $i^{\mathrm{a}}_{\mathrm{lim}}$ are, respectively, the cathodic and anodic limiting currents.

In logarithmic form, equation (3) is transformed into

$$\Delta\varphi = b_{\mathrm{k}} \lg i_0 - b_{\mathrm{k}} f(i, \Delta\varphi), \qquad (4)$$

where $b_{\mathrm{k}} = 2.303\, RT/\alpha n F$ and

$$f(i, \Delta\varphi) = \lg i - \lg \left[(1 - i/i^{\mathrm{k}}_{\mathrm{lim}}) - (1 + i/i^{\mathrm{a}}_{\mathrm{lim}})\, e^{nF\Delta\varphi/RT} \right].$$

Equation (4) is the most convenient for comparison with experimental data. Representing the latter in the coordinates $\Delta\varphi$–$f(i, \Delta\varphi)$, it is easy to find the values of i_0 and α.

The nature of equations (3), (4) gives no grounds for regarding $\lg i$ as a linear function of $1/T$ (at $\Delta\varphi = \mathrm{const}$). A clear confirmation of this is provided by Fig. 1, which gives calculated curves i–$\Delta\varphi$ in the interval $t = 0$-$100°$ and their analysis in the coordinates $\lg i$–$1/T$. The calculation was made from equation (3). The following initial data were taken: $i_0 = 10^{-4}$ A/cm^2 ($t = 0°$), $i^{\mathrm{k}}_{\mathrm{lim}} = i^{\mathrm{a}}_{\mathrm{lim}} = 10^{-2}$ A/cm^2, $\alpha = 0.5$, activation energy of viscous flow 3 kcal/mol, activation energy of the forward and reverse reactions at the equilibrium potential 15 kcal/mol.

As is seen from Fig. 1, the dependences $\lg i$–$1/T$ are in general of a complex nature. They may be useful, for example, for estimating the relative influence of

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* For example, in works (3,4) the calculation of the "effective" activation energy is given beginning from $\Delta\varphi = 5$—10 mV.

** Even when there is a linear relation between $\lg i$ and $1/T$.

kinetic and diffusion factors on the rate of the overall process, if the true values of the activation energy are known for the cathodic and anodic reactions. It is obvious that calculating E directly from such curves cannot give any reliable values.

From the considerations presented it follows that the “effective”activation energy is unsuitable as a reliable kinetic parameter of electrochemical reactions. In our opinion, the real activation energy (^{5}) of the electrochemical act itself should be adopted as such a parameter; the concept of it is introduced in the theory of delayed discharge. According to the initial premises of this theory, the real activation energy of the forward and reverse reactions is a linear function of $\Delta\varphi$:

$$A = A_0 + \alpha nF\Delta\varphi, \tag{5}$$

$$A' = A_0 - (1-\alpha)nF\Delta\varphi, \tag{6}$$

where A_0 is the real activation energy of the exchange current.

Table 1

Kinetic parameters of the electrochemical redox reactions

$Q + 2H^+ + 2e \rightleftarrows H_2Q$ (I) and $Fe^{3+} + e \rightleftarrows Fe^{2+}$ (II)

t, °C	I i_0, A/cm^2	I α	I β	II i_0, A/cm^2	II α	II β
5	$1.35 \cdot 10^{-5}$	0.36	0.64	$6.02 \cdot 10^{-3}$	0.62	0.32
15	$2.40 \cdot 10^{-5}$	0.36	0.63	$9.54 \cdot 10^{-3}$	0.61	0.31
25	$4.07 \cdot 10^{-5}$	0.36	0.64	$1.45 \cdot 10^{-2}$	0.62	0.30
35	$6.92 \cdot 10^{-5}$	0.35	0.63	$2.04 \cdot 10^{-2}$	0.63	0.30
45	$1.10 \cdot 10^{-4}$	0.34	0.63	$3.02 \cdot 10^{-2}$	0.63	0.29

A and A' characterize the kinetics of the partial reactions at the electrode, with reference not to the overall cathodic or anodic process, but only to the electrochemical stage proper of discharge or ionization. According to (5), (6), the exponential terms in the equations for the rate of the partial reactions at any values of $\Delta\varphi$ ultimately depend on the value of A_0. The latter, together with i_0 and α, also determines the nature of the overall kinetic dependences of current density—potential.

Figure 2

Figure 1: Figure 2

Thus, the proposed method for determining the activation energy of electrochemical reactions reduces to finding, by one method or another—for example, by means of equation (4)—i_0 at various temperatures. Theoretically, a linear relation should be observed between $\lg i_0$ and $1/T$ according to the equation

$$(\lg i_0)_{\Delta\varphi=0} = B_0 - A_0/2.303\,RT. \tag{7}$$

For $\Delta\varphi \gg RT/F$ and $i \ll i_{\text{lim}}$, the total polarization curves in the first approximation coincide with the partial ones. For this case the quantity A_0 can be found by determining, in the usual way, A, A' at arbitrary values of $\Delta\varphi$ in the indicated range of $\Delta\varphi$ and i, and extrapolating the data obtained to $\Delta\varphi = 0$. Determination of the angular coefficient of the experimental dependences $A - \Delta\varphi_{\text{k}}$, $A' - \Delta\varphi_{\text{a}}$ makes it possible to calculate, with the aid of (5), (6), the values of α and β.

Fig. 2. Dependence of the "effective" (1) and real (2) activation energy on the electrode polarization $\Delta\varphi$

As an example, below are given the results of determinations of the true values of the activation energy of the electrochemical redox reactions

$$\text{benzoquinone} \xrightleftharpoons{2\text{H}^+2e} \text{hydroquinone}; \tag{I}$$

$$\text{Fe}^{2+} \overset{e}{\rightleftharpoons} \text{Fe}^{3+} \tag{II}$$

Measurements of the polarization dependences for system (II) were performed on a rotating Pt electrode ($S = 0.5$ cm^2, 980 rpm). In other respects the measurement procedure did not differ from that described previously (^{6}).

The analysis of the polythermal curves was carried out according to equation (4). Examples of such analysis were given earlier (^{6}). The experimental data, in agreement with the kinetic equations (3), (4), lay on straight lines in coordinates $\Delta\varphi - f(i, \Delta\varphi)$. The values of i_0, α, β found graphically are given in Table 1, according to which $\lg i_0$ is a linear function of $1/T$. The values of A_0 for systems (I), (II) are respectively 9150 and 6860 cal/mol.

In Fig. 2, for comparison, the real and the effective activation energies as a function of potential are given for the system $Q - \text{H}_2Q$. It is evident that the deviation, usually observed experimentally, of the dependence $E - \Delta\varphi$ from linearity is by no means proof of the incorrectness of relations (5), (6), as it

Figure 3

Figure 2: Figure 3

is sometimes assumed (^{1}), but merely indicates the fundamental difference between the fictitious constant E and the real activation energy of electrochemical reactions. For example, calculation of E by the "temperature-kinetic" method for the $Fe^{2+}-Fe^{3+}$ system gives a value close to 3 kcal/mol* and independent of the electrode potential. The actual value of the activation energy, according to the data presented, is at least twice as large (in the region of working potentials for reduction of Fe^{3+} and oxidation of Fe^{2+}) and is a linear function of $\Delta\varphi$.

Fig. 3. Comparative values of E and A for electrochemical reactions with different exchange currents.
1—A, $\Delta\varphi$; 2—E, $\Delta\varphi$ ($i_0 = 10^{-7}$ A/cm^2); 3—E, $\Delta\varphi$ ($i_0 = 10^{-5}$ A/cm^2 at $t = 0°$)

It was noted above that direct analysis of polythermal curves $\lg i - \Delta\varphi$ makes it possible to find the activation energy of electrochemical processes only in those cases when the reverse reaction can be neglected and diffusion limitations are small. These conditions are partly fulfilled in a narrow interval of $\Delta\varphi$ in the electroreduction of benzoquinone (Fig. 2), where the values of E are close to the real activation energy. If the electrochemical reaction is characterized by a lower i_0, then on the polarization curves one can de— distinguish a region strictly satisfying the requirements $\Delta\varphi \gg RT/F$ and $i \ll i_{\text{lim}}$, for which the numerical values of E and A are practically identical.

As an example, Fig. 3 gives comparative values of the effective and real activation energies for two electrochemical reactions having, at $t = 0°$, exchange currents of 10^{-5} and 10^{-7} A/cm^2, respectively, and $i^k_{\text{lim}} = i^a_{\text{lim}} = 10^{-2}$ A/cm^2. The values of E were found by analysis of polythermal curves calculated from equation (4). The initial data for the calculation are indicated above. It follows from the figure that reliable determination of the activation energy from equation (1) is possible at $i_0/i_{\text{lim}} \ll 10^{-4}$—$10^{-5}$ A/cm^2 ($t = 0°$) in a limited region of $\Delta\varphi$. Such values of the ratio i_0/i_{lim} are characteristic, for example, of electrodeposition of metals of the iron group [7], hydrogen evolution on cathodes of the mercury type, and also electrocrystallization of a number of metals from solutions with additions of surface-active substances. For the overwhelming majority of other electrochemical reactions, in particular oxidation-reduction reactions, determination of E from equation (1) and conclusions based on it are devoid of rigorous meaning.

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* An analogous value of E was obtained by V. A. Milchev (^{3,4}).

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Note: Figure translations are in progress. See original paper for figures.