Activation Energy of Electrochemical Reaction at a Constant Value of Electrode Potential

F. I. Danilov[z] and V. S. Protsenko

Ukrainian State University of Chemical Technology, Dnepropetrovsk, Ukraine

Received August 11, 2008

Abstract—Equations were derived interrelating ideal activation energy W (determined at the constant Galvani potential value), real activation energy A (determined at a constant overpotential), and the so called formal activation energy Ω (calculated at a constant electrode potential vs. an arbitrarily chosen reference electrode). The obtained equations include only the parameters of the studied reaction and no characteristics of the reaction occurring on the reference electrode. The type of the Ω dependence on the electrode potential is established. Conditions are found, under which the real and formal activation energies of the electrochemical reactions can simultaneously remain constant in the given temperature range and it becomes possible to use them in the integral forms of the Arrhenius equation.

Key words: activation energy, electrochemical reaction, electrode potential, Arrhenius equation

INTRODUCTION

To describe the temperature dependence of the electrode reaction rate quantitatively, M.I. Temkin suggested [1] two quantities: ideal (W) and real (A) activation energies, accordingly, determined by the following relationships:

$$\left(\frac{\partial \ln i}{\partial T}\right)_{\varphi, c} = \frac{W}{RT^2}, \qquad (1)$$

$$\left(\frac{\partial \ln i}{\partial T}\right)_{\eta, c} = \frac{A}{RT^2}, \qquad (2)$$

where φ is the Galvani potential drop at the electrode/solution interface; η is the overpotential (deviation of the electrode potential from the equilibrium potential value); i is the current density; T is the absolute temperature; c is the molar concentration of the reagents; R is the universal gas constant.

As the value of the separate potential drop φ is inaccessible for measurement, only the real activation energy A can be determined on the basis of the experimental data. The relationship between the values of W and A is established in the following equation [1, 2]:

$$A = W - \alpha q, \qquad (3)$$

where α is the transfer coefficient of the electrode reaction; q is the hidden heat of the electrode process (inaccessible for experimental determination); the signs of quantities in this equation are given for the cathodic direction of the reaction studied.

[z] Corresponding author: fdanilov@optima.com.ua (F.I. Danilov).

However, in a number of cases (in the first instance, for strongly irreversible electrochemical systems), using (2) is practically impossible due to the fact that it is difficult to determine experimentally the equilibrium electrode potential and overpotential values and theoretical calculation is fraught with errors.

Meanwhile, there is a possibility in principle to determine the activation energy at a constant electrode potential E measured vs. an arbitrarily chosen reference electrode at the same temperature, as the studied electrode:

$$\left(\frac{\partial \ln i}{\partial T}\right)_{E, c} = \frac{\Omega}{RT^2}, \qquad (4)$$

where Ω is the value that will further be named the formal activation energy.

In the case of strongly irreversible electrochemical processes, the value of the formal activation energy Ω at a given electrode potential becomes practically the only accessible characteristics of the temperature dependence of the electrochemical process rate. Thus, the activation energy at a constant electrode potential vs. an arbitrarily chosen reference electrode was determined for the processes of molecular oxygen reduction [3, 4], hydrogen peroxide oxidation [5], electroreduction of hexavalent chromium oxo anions [6], electrooxidation of chloride ions [7], a number of organic electrosynthesis reactions [8–10].

It was pointed out [2] that the Ω value is generally devoid of physical sense due to the arbitrary character of choosing the reference electrode.

We could not find in the literature papers on the establishment of relationship between the Ω and A val-

ues. Therefore it is not quite clear if one can use the formal activation energy values alongside with the real activation energy values for discussing kinetic regularities and mechanism of electrode reactions.

The aim of the paper consists in elucidation of the relationship between the Ω, A, and W values and also finding the type of the Ω dependence on electrode potential E. Earlier, in [11], the relationship was found for the A value and the activation energy determined at a constant electrode potential measured vs. a standard electrode maintained at a constant temperature, which introduces ambiguity into the results of such measurements due to appearance of thermal electromotive force in the circuit. In this paper, relationship is found between Ω, A, and W under the conditions when the working electrode and reference electrode are at the same temperature.

DERIVATION OF EQUATIONS

Let us consider a single–electron process:

$$Me^+ + e \rightleftarrows Me. \qquad (5)$$

In this communication, let us restrict ourselves to analysis of the cases when the reagent concentrations on the surface and in the solution volume coincide.

The formal activation energies of the direct (cathodic) $\overrightarrow{\Omega}$ and reverse (anodic) $\overleftarrow{\Omega}$ reactions are determined by the following expressions:

$$\left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{E,c} = \frac{\overrightarrow{\Omega}}{RT^2}, \qquad (6)$$

$$\left(\frac{\partial \ln \overleftarrow{i}}{\partial T}\right)_{E,c} = \frac{\overleftarrow{\Omega}}{RT^2}, \qquad (7)$$

where $\overrightarrow{i}$, $\overleftarrow{i}$ are the current densities of the direct and reverse reactions, accordingly.

As $\ln \overrightarrow{i}$ can be considered, on the one hand, as a function of variables T and E, and on the other hand, as a function of variables T and φ, then the equality is valid:

$$\left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{E,c} = \left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{\varphi,c} + \left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{T,c}\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}. \qquad (8)$$

Using the classical linear relationship between the activation energy and potential drop $\overrightarrow{W} = \overrightarrow{W}_0 + \alpha\varphi F$ [1] and also Arrhenius equation in the form of (1), it is easy to show that

$$\left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{T,c} = -\frac{\alpha F}{RT}, \qquad (9)$$

where F is the Faraday constant.

Then, equation (8) with account for (9), takes the following form:

$$\left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{E,c} = \left(\frac{\partial \ln \overrightarrow{i}}{\partial T}\right)_{\varphi,c} - \frac{\alpha F}{RT}\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}. \qquad (10)$$

Similar discussions for the reverse (anodic) reaction lead to the following expression:

$$\left(\frac{\partial \ln \overleftarrow{i}}{\partial T}\right)_{E,c} = \left(\frac{\partial \ln \overleftarrow{i}}{\partial T}\right)_{\varphi,c} + \frac{(1-\alpha)F}{RT}\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}. \qquad (11)$$

(It is assumed here that the sum of the charge transfer coefficients for the direct and reverse reactions of electrochemical conversion is equal to unity).

It follows from (1), (6), (7), (10), (11) that

$$\overrightarrow{\Omega} = \overrightarrow{W} - \alpha FT\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}, \qquad (12)$$

$$\overleftarrow{\Omega} = \overleftarrow{W} + (1-\alpha)FT\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}, \qquad (13)$$

where $\overrightarrow{W}$, $\overleftarrow{W}$ are the ideal activation energies of the direct and reverse reactions, accordingly.

For the further transformations of (12), (13), it is necessary to express derivative $\left(\frac{\partial \varphi}{\partial T}\right)_{E,c}$ through the thermodynamic parameters of the reaction occurring in the considered electrochemical system.

Let an isothermal electrochemical circuit be used to measure the potential of the electrode, on which reaction (5) occurs:

$$Me_1|E_2\|E_1|Me_1, \qquad (14)$$

where $E_1|Me_1$ is the studied (working) polarizable electrode; $E_2|Me_1$ is the reference electrode.

The expression for the electrode potential of the working electrode in the case when the diffusion potential on the $E_2\|E_1$ electrolyte interface is eliminated takes the following form:

$$E = \varphi - \varphi_{R.E.}, \qquad (15)$$

where $\varphi_{R.E.}$ is the equilibrium Galvani potential of the reference electrode.

As follows from (15):

$$\left(\frac{\partial \varphi}{\partial T}\right)_{E,c} = \frac{\partial \varphi_{R.E.}}{\partial T}. \qquad (16)$$

In the case of the electrochemical process occurring on the reference electrode, the following relationship will be valid:

$$\varphi_{R.E.} = +\frac{\Delta G_{R.E.}}{F}, \qquad (17)$$

where $\Delta G_{R.E.}$ is the variation of the Gibbs thermodynamic potential on an equilibrium reference electrode.

The sign in this equation is presented for an arbitrarily chosen anodic direction of reaction flow. Besides, it is assumed for the sake of simplicity that the amount of electrons participating in the electrochemical process at the reference electrode is $z = 1$ (the choice of the reference electrode is in principle arbitrary).

Then, taking into account a simple thermodynamic relationship for entropy $\Delta S_{R.E.} = -\dfrac{\partial \Delta G_{R.E.}}{\partial T} = -F\dfrac{\partial \varphi_{R.E.}}{\partial T}$, with account also for (16), we have:

$$\left(\frac{\partial \varphi}{\partial T}\right)_{E,\,c} = -\frac{\Delta S_{R.E.}}{F}. \qquad (18)$$

Then, we substitute (18) into (12):

$$\overrightarrow{\Omega} = \overrightarrow{W} + \alpha T\Delta S_{R.E.} = \overrightarrow{W} + \alpha q_{R.E.}, \qquad (19)$$

where $q_{R.E.} = T\Delta S_{R.E.}$ is the hidden equilibrium heat of the reaction occurring on the reference electrode.

Similar calculations for the reverse stage of reaction (5) allow obtaining the following expression:

$$\overleftarrow{\Omega} = \overleftarrow{W} - (1-\alpha)T\Delta S_{R.E.} = \overleftarrow{W} - (1-\alpha)q_{R.E.}. \qquad (20)$$

Equations (19) and (20) establish the relationship between the values of the formal activation energies of the direct and reverse reaction of electrochemical process (5) that can be determined experimentally and the values of the ideal activation energy that cannot be directly measured.

In connection with the linear character of the relationship between the ideal activation energy and Galvani potential drop $\overrightarrow{W} = \overrightarrow{W}_0 + \alpha\varphi F$ and $\overleftarrow{W} = \overleftarrow{W}_0 - (1-\alpha)\varphi F$ [1, 2], dependences similar to $\Omega(E)$ follow from equations (15), (19), and (20):

$$\overrightarrow{\Omega} = \overrightarrow{\Omega}_0 + \alpha EF, \qquad (21)$$

where

$$\begin{aligned}\overrightarrow{\Omega}_0 &= \overrightarrow{W}_0 + \alpha(F\varphi_{R.E.} + q_{R.E.}) \\ &= \overrightarrow{W}_0 + \alpha(\Delta G_{R.E.} + T\Delta S_{R.E.}) = \overrightarrow{W}_0 + \alpha\Delta H_{R.E.},\end{aligned} \qquad (22)$$

and also:

$$\overleftarrow{\Omega} = \overleftarrow{\Omega}_0 - (1-\alpha)EF, \qquad (23)$$

where

$$\begin{aligned}\overleftarrow{\Omega}_0 &= \overleftarrow{W}_0 + (1-\alpha)(-F\varphi_{R.E.} - q_{R.E.}) \\ &= \overleftarrow{W}_0 - (1-\alpha)(\Delta G_{R.E.} + T\Delta S_{R.E.}) \\ &= \overleftarrow{W}_0 - (1-\alpha)\Delta H_{R.E.}.\end{aligned} \qquad (24)$$

In equations (21)–(24), values $\overrightarrow{\Omega}_0$ and $\overleftarrow{\Omega}_0$ represent the corresponding values of formal activation energies $\overrightarrow{\Omega}$, $\overleftarrow{\Omega}$ at $E = 0$, $\overrightarrow{W}_0$, $\overleftarrow{W}_0$ are the corresponding ideal activation energies at $\varphi = 0$ and $\Delta H_{R.E.}$ is the vari-

ation of enthalpy in the course of an electrochemical reaction occurring on the reference electrode (in the arbitrarily chosen anodic direction).

The obtained equations show that there is a certain relationship between the experimentally measured formal activation energies $\overrightarrow{\Omega}$, $\overleftarrow{\Omega}$ and theoretically faultless though experimentally undeterminable ideal activation energy values. However, these equations, alongside with the characteristics of the studied process, also include the reaction parameter of the reference electrode ($\Delta H_{R.E.}$). The choice of such an electrode is generally arbitrary, which would supply ambiguousness into analysis of the corresponding kinetic data. To overcome this problem, one can in principle arrange for using all the electrochemical processes of any single reference electrode to determine the formal activation energy.

Let us show now that after the mathematic relationship between the formal and real activation energies is established, one can wholly eliminate the parameters of the reaction occurring on the reference electrode from the equations.

For this, let us take into account the known equations [1, 2]:

$$A_0 = \overrightarrow{W}_0 - \alpha\Delta H = \overleftarrow{W}_0 + (1-\alpha)\Delta H, \qquad (25)$$

where A_0 is the real activation energy of the reaction at the equilibrium potential ($\eta = 0$); ΔH is the variation of the enthalpy of the studied electrochemical reaction at the equilibrium potential (for the arbitrarily chosen cathodic direction of the reaction).

After simple algebraic transformations of (22), (24), (25), one can obtain two important equations:

$$A_0 = (1-\alpha)\overrightarrow{\Omega}_0 + \alpha\overleftarrow{\Omega}_0, \qquad (26)$$

$$\overrightarrow{\Omega}_0 - \overleftarrow{\Omega}_0 = \Delta H_{R.E.} + \Delta H = \Delta H_{\text{circuit}}. \qquad (27)$$

Equation (26) establishes the relationship between the real and formal activation energies that can be determined experimentally in principle. It is essential that this expression interrelates only the parameters of the studied reaction (and excludes no characteristics of the reaction occurring at the reference electrode).

It is of interest that in the specific case of $\alpha = 0.5$, equation (26) is transformed into $A_0 = \dfrac{1}{2}(\overrightarrow{\Omega}_0 + \overleftarrow{\Omega}_0)$, i.e., the real activation energy is the arithmetic mean of the formal activation energies of the direct and reverse stages at $E = 0$.

Equation (27) shows that the difference between the formal activation energies of the direct and reverse stages of the electrochemical reaction at $E = 0$ is equal to variation of the enthalpy ($\Delta H_{\text{circuit}} = \Delta H_{R.E.} + \Delta H$) of the overall reaction occurring in electrochemical circuit (14) composed of the electrode, on which the studied reaction occurs (cathode) and the arbitrarily chosen reference electrode (anode). The $\Delta H_{\text{circuit}}$, as opposed to its

separate components of $\Delta H_{R.E.}$ and ΔH, can be directly measured and calculated.

With account for equation (26) for strongly irreversible electrode processes, the real activation energy A_0 can be calculated as follows:

—on the basis of the experimental data and $\overrightarrow{i} = f(T)$, the $\overrightarrow{\Omega}$ values were calculated according to equation (6) at several fixed values of E (in practice, it is more convenient to find these values from the slope of the Arrhenius linear dependence in $\ln \overrightarrow{i}$, $1/T$-coordinates obtained for $E = $ const); $\overrightarrow{\Omega}_0$ is found by extrapolation of the linear $\overrightarrow{\Omega}$, E-dependence to the value of $E = 0$ on the basis of (21);

—as one cannot usually perform polarization measurements for strongly irreversible electrode processes in a wide range of potentials encompassing both the cathodic and anodic directions of the reaction, the $\overleftarrow{\Omega}_0$ value is found from (27) (the $\Delta H_{\text{circuit}}$ value is determined on the basis of the independent thermodynamic data).

In conclusion, we must turn our attention to the fact that the above equations interrelating Ω, A, and W are based on using the Arrhenius equation in the differential form (1), (2), (4), (6), (7); herewith, it is not required in principle to observe the constancy the values of these activation energies under the temperature variation. Meanwhile, introduction of the concept of the activation energy gains practical importance in the case when the activation energy is constant in at least a given temperature range and it becomes possible to use the integral Arrhenius equation. It is therefore expedient to find, in which cases it is possible to fulfill simultaneously the following conditions:

$$\frac{\partial A_0}{\partial T} = 0, \quad \frac{\partial \overrightarrow{\Omega}_0}{\partial T} = 0, \quad \frac{\partial \overleftarrow{\Omega}_0}{\partial T} = 0. \quad (28)$$

By differentiating expressions (26) by temperature, it is easy to find that the following is the necessary condition for fulfillment of equations (28):

$$\overrightarrow{\Omega}_0 \frac{\partial \alpha}{\partial T} = \overleftarrow{\Omega}_0 \frac{\partial \alpha}{\partial T}. \quad (29)$$

Thus, the real A_0 and formal activation energies of the direct and reverse stages of the electrochemical reaction $\overrightarrow{\Omega}_0$ and $\overleftarrow{\Omega}_0$ simultaneously retain constant values in a certain temperature range under the condition of the constancy of the transfer coefficient $\left(\frac{\partial \alpha}{\partial T} = 0\right)$ and (or) at

the equality of the formal activation energies of the direct and reverse reactions $\overrightarrow{\Omega}_0 = \overleftarrow{\Omega}_0$. The method of calculation of $\overrightarrow{\Omega}_0$ and $\overleftarrow{\Omega}_0$ at the given $\Delta H_{\text{circuit}}$ value is described above. The values of transfer coefficient α are determined from the slope of the corresponding Tafel curves.

CONCLUSION

Thus, alongside with the ideal activation energy W (being a parameter of the electrochemical reaction inaccessible for experimental determination) and real activation energy A (determined at the constant overpotential), it is suggested to use the formal activation energy Ω found at a constant potential measured vs. an arbitrarily chosen reference electrode at the same temperature, as the working electrode, to establish the temperature dependence of the electrode reaction rate. Equations are obtained that interrelate the quantities of Ω, A, and W. The obtained equations include only the parameters of the studied reaction and no characteristics of the reaction occurring on the reference electrode. An algorithm is suggested for calculating the real activation energy on the basis of the experimentally determined value of the formal activation energy.

REFERENCES

1. Temkin, M.I., *Zh. Fiz. Khim.*, 1948, vol. 22, p. 1081.
2. Krishtalik, L.I. and Erenburg, R.G., *Kinetika slozhnykh elektrokhimicheskikh reaktsii* (The Kinetics of Complex Electrochemical Reactions), Moscow: Nauka, 1981.
3. Sepa, D.B., Vojnovic, M.V., Vracar, Lj.M., and Damjanovic, A., *Electrochim. Acta*, 1986, vol. 31, p. 1105.
4. Damjanovic, A. and Sepa, D.B., *Electrochim. Acta,* 1990, vol. 35, p. 1157.
5. Hall, S.B., Khudaish, E.A., and Hart, A.L., *Electrochim. Acta*, 1999, vol. 44, p. 2455.
6. Balanchivadze, D.I. and Chelidze, T.R., *Elektrokhimiya*, 1989, vol. 25, p. 1390.
7. Chertykovtseva, T.A., Shub, D.M., and Veselovskii, V.I., *Elektrokhimiya*, 1978, vol. 14, p. 275.
8. Meretskii, A.M., Kudryashov, I.V., Vasil'ev, Yu.B., and Belik, V.V., *Elektrokhimiya*, 1979, vol. 15, p. 541.
9. Grinberg, V.A., Kanevskii, L.S., and Vasil'ev, Yu.B., *Elektrokhimiya*, 1979, vol. 15, p. 857.
10. Lushnikov, V.I., Kanevskii, L.S., and Vasil'ev, Yu.B., *Elektrokhimiya*, 1979, vol. 15, p. 1438.
11. Agar, J.N., *Disc. Faradey Soc., I. Electrode Processes,* 1947, p. 81.