

Electrode reactions which proceed at appreciable overvoltage are characterized by [1]: an overall electrode polarization

$$-\pi = \frac{RT}{anF} \ln \frac{i}{nFk_s A_0 (B_\infty / A_\infty)^a}, \quad (1)$$

an electrode overvoltage (activation polarization) given by

$$-\eta = \frac{RT}{anF} \ln \frac{i}{nFk_s A_\infty^{(1-a)} B_\infty^a}, \quad (2)$$

at fixed concentration, and a concentration polarization

$$-\varepsilon = \frac{RT}{nF} \ln \frac{A_\infty B_0}{A_0 B_\infty}. \quad (3)$$

Here k_s is the standard rate constant for the elementary electrochemical reaction, A is the concentration (activity) of the reactant and B the concentration of the product; the subscript 0 is used to designate concentrations at the electrode surface and the subscript ∞ , concentration in the body of the electrolyte. The remaining symbols have their usual significance.

Direct experimental study of the electrochemical system through development of the volt-ampere characteristics leads only to the $\pi = \pi(i)$ relation. The $\eta = \eta(i)$ relation can be obtained experimentally only when $\varepsilon = 0$, i.e., when $\pi = \eta$. It is, on the other hand, exactly this relation which is of greatest significance for the theory of electrode reactions and the study of irreversible electrochemical processes.

The purely electrochemical studies of electrode reactions have recently been supplemented by drawing on the concepts of irreversible thermodynamics. The basic concept involved here is that of the entropy production in reaction, $\sigma_\pi = \partial S / \partial t$, t being the time and S the entropy. The entropy production is determined by the thermal energy, Q , liberated on the electrode, and is given, according to the Joule-Lentz law, by

$$\sigma_\pi = \frac{\partial S}{\partial t} = \frac{\partial Q}{\partial t} \frac{1}{T} = \frac{-\pi i}{T} \quad (4)$$

T being the temperature.

When $\pi = \eta$, the entropy production is equal to

$$\sigma_\eta = -\eta i / T. \quad (5)$$

The value of σ_η measures the irreversibility of the electrochemical step, regardless of the concentration changes occurring on the electrode. It is convenient to designate this as the entropy production in reaction, thus distinguishing it from σ_π which depends on the path traced out by the reaction (mixing, convection, etc.).

The relations $\eta = \eta(i)$ and $\sigma_\eta = \sigma_\eta(i)$ cannot, in general, be developed by direct measurement, and one must, therefore, obtain information concerning the $\pi = \pi(i)$ function from $\eta = \eta(i)$ curves. Information of this kind is found in the ordinary polarization curves for the irreversible reaction.

For the steady-state electrode reaction, one has

$$A_0 = (\kappa_A A_\infty - i) / \kappa_A = (i_A - i) / \kappa_A \quad (6)$$

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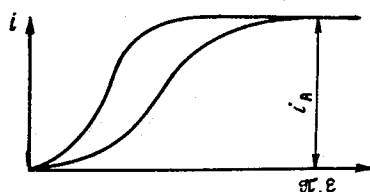


Fig. 1. Comparison of reversible and irreversible polarograms plotted in current vs. polarization coordinates.

$$B_0 = i / \kappa_B \quad (7)$$

κ_A and κ_B being the rate constants for mass transfer of A and B, and i_A the maximum rate of transfer of A. From this relation one readily obtains the equation for the irreversible polarogram first proposed by V. S. Bagotskii [2]

$$\begin{aligned} -\pi &= \frac{RT}{\alpha nF} \ln \frac{i \kappa_A}{n F k_s (B_\infty / A_\infty)^\alpha (i_A - i)} \\ &= \text{const} + \frac{RT}{\alpha nF} \ln \frac{i}{i_A - i} \end{aligned} \quad (8)$$

and the equation proposed by Heyrovsky and Ilkovic [3] for the reversible polarogram

$$-\varepsilon = \frac{RT}{nF} \ln \frac{A_\infty \kappa_A i}{B_\infty \kappa_B (i_A - i)} = \text{const} + \frac{RT}{nF} \ln \frac{i}{i_A - i} \quad (9)$$

Analysis of the experimentally developed polarogram usually involves construction of a plot in the coordinates π (or ε) vs $\ln[i / (i_A - i)]$; from this one can determine the value of the pre-exponential coefficient, RT/nF or $RT/\alpha nF$, together with the constant so-called half-wave potential of Eq. (8) or (9). Such information is obviously inadequate and cannot be used to develop the $\eta = \eta(i)$ function.

In calculating the overvoltage from the irreversible polarogram, one must rely entirely on the theory of Eyring, Marker, and Ting Chang, Kwoh [4] which is based on rather vague concepts. This theory assumes that the polarograms for reversible and irreversible reaction at fixed i_A will coincide at low and high polarizations (Fig. 1). The origin for the irreversible polarogram should then coincide with that for the hypothetical reversible process (concentration polarization curve). Having selected the origin in this way, one then chooses one or several points, determines the current and potential at each, and then calculates the half-wave potential for the hypothetical reversible polarogram from (9) and the relation

$$-\text{const} = \varepsilon + \frac{RT}{nF} \ln \frac{i}{i_A - i} \quad (10)$$

The value of the constant obtained in this way is then used to develop the entire curve for the reversible process from (9). The difference between this and the experimentally developed irreversible polarogram is taken to represent the function $\eta = \eta(i)$.

This procedure is open to two objections.

First. If the currents marked out on the two curves asymptotically approach i_A in the region of high polarizations (Fig. 1), their only common value in the region of low polarizations would be $i = 0$. If it could be assumed that the two curves would, within the limits of experimental error, merge before reaching a common asymptotic value, this conclusion would no longer apply in the low polarization region.

Second. Even if the hypothetical reversible polarogram, $\varepsilon = \varepsilon(i)$, has been correctly constructed, it does not follow that the difference, $\pi - \varepsilon$, between it and the experimentally developed irreversible polarogram is the function $\eta = \eta(i)$. In fact Eqs. (8) and (9) show that the difference $\pi - \varepsilon$ is equal to

$$-(\pi) - (-\varepsilon) = \frac{RT}{\alpha nF} \ln \frac{\kappa_A^{(1-\alpha)} \kappa_B^\alpha}{n F k_s} + \frac{RT}{nF} \frac{1-\alpha}{\alpha} \ln \frac{i}{i_A - i}, \quad (11)$$

which is certainly not the same as the expression for $\eta = \eta(i)$ given by (2).

We propose a direct and trustworthy method for developing the $\eta = \eta(i)$ curve from a rather simple treatment of the experimental polarogram for the irreversible reaction. The point is that there is no necessity for developing the $\varepsilon = \varepsilon(i)$ function. According to Eqs. (2) and (8), the activation polarization, η , can be obtained from the over-all polarization, π , through the equation

$$-\eta = -\pi - \frac{RT}{\alpha nF} \ln \frac{i_A}{i_A - i} \quad (12)$$

The following is involved in the treatment of the experimental polarogram. Working in semilogarithmic coordinates, one determines the pre-logarithmic coefficient $RT/\alpha nF$. Then a calculation of $(RT/\alpha nF) \ln[i_A / (i_A - i)]$ from the $\pi = \pi(i)$ curve gives the $\eta = \eta(i)$ relation.

One can also obtain one other significant piece of information concerning the electrode reaction. The Eqs. (1), (2), and (8), (9) contain the initial concentrations, A_∞ , B_∞ . These values affect the form of the $\pi = \pi(i)$ and $\eta = \eta(i)$ curves. A more nearly independent characterization of the reaction could be obtained by working from some sort of standard conditions, e.g., from a standard concentration, C_∞ , instead of A_∞ and B_∞ .

This procedure would lead to standard values of the volt-ampere parameters

$$-\pi_s = \frac{RT}{\alpha nF} \ln \frac{i}{nFk_s C_0} = \frac{RT}{\alpha nF} \ln \frac{i\kappa_A}{nFk_s (C_\infty \kappa_A - i)}, \quad (13)$$

$$-\eta_s = \frac{RT}{\alpha nF} \ln \frac{i}{nFk_s C_\infty}. \quad (14)$$

One would, at the same time, have one standard value for the entropy production in the process

$$\sigma_{\pi_s} = -\pi_s i / T \quad (15)$$

and another for the entropy production in the reaction

$$\sigma_{\eta_s} = -\eta_s i / T. \quad (16)$$

The values $\pi_s = \pi_s(i)$ and $\eta_s = \eta_s(i)$ and the relations $\sigma_{\pi_s} = \sigma_{\pi_s}(i)$ and $\sigma_{\eta_s} = \sigma_{\eta_s}(i)$ can be obtained from the experimentally developed polarogram, $\pi = \pi(i)$. Combination of Eqs. (8) and (13) gives

$$-\pi_s = -\pi - \frac{RT}{\alpha nF} \ln \frac{(C_\infty \kappa_A - i)}{(B_\infty / A_\infty)^\alpha (i_A - i)} = -\pi - \frac{RT}{\alpha nF} \ln \frac{\frac{C_\infty}{A_\infty} i_A - i}{i_A - i} + \frac{RT}{nF} \ln \frac{A_\infty}{B_\infty}, \quad (17)$$

while combination of (8) and (14) gives

$$-\eta_s = -\pi - \frac{RT}{\alpha nF} \ln \frac{\kappa_A C_\infty}{(B_\infty / A_\infty)^\alpha (i_A - i)} = -\pi - \frac{RT}{\alpha nF} \ln \left(\frac{C_\infty}{A_\infty} \frac{i_A}{i_A - i} \right) + \frac{RT}{nF} \ln \frac{A_\infty}{B_\infty}. \quad (18)$$

Under the conditions of (6) and (7), the substance B was not initially present in the system but appeared as a product of the exchange reaction. Thus the B_∞ of Eqs. (17) and (18) is not defined. It can be eliminated through the basic Nernst equation

$$\varphi_{in} = \varphi_0 + \frac{RT}{nF} \ln \frac{A_\infty}{B_\infty} \quad (19)$$

in which φ_{in} is the initial value of the equilibrium electrode potential, and φ_0 the standard potential. One finally has:

$$-\pi_s = -\pi - \frac{RT}{\alpha nF} \ln \frac{\frac{C_\infty}{A_\infty} i_A - i}{i_A - i} + \varphi_{in} - \varphi_0, \quad (20)$$

$$-\eta_s = -\pi - \frac{RT}{\alpha nF} \ln \left(\frac{C_\infty}{A_\infty} \frac{i_A}{i_A - i} \right) + \varphi_{in} - \varphi_0. \quad (21)$$

All of the quantities in these equations are either known (A_∞ , C_∞ , φ_0) or are open to experimental determination (π , $RT/\alpha nF$, i_A , φ_{in} , i). The same standard concentrations are selected for the volt-ampere determination of the standard potential, φ_0 , and for the standard rate constant, k_s .

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