KINETIC EQUATION OF IRREVERSIBLE REACTIONS IN OSCILLOGRAPHIC POLAROGRAPHY

The equation for the maximum current of an irreversible polarographic wave,

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Abstract

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A. Ya. Gokhshtein and Ya. P. Gokhshtein

KINETIC EQUATION OF IRREVERSIBLE REACTIONS IN OSCILLOGRAPHIC POLAROGRAPHY

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The equation for the maximum current of an irreversible polarographic wave,

$$I_p = 3.01 \cdot 10^5 n(\alpha n)^{1/2} S D^{1/2} C_0 v^{1/2},$$

derived by Delahay $^{(1)}$, reflects the diffusion nature of the current. It relates the current to the diffusion coefficient D and to the rate of change of the potential v. Here and below the following notation is adopted: C_0 is the concentration of the initial substance in the bulk of the solution (mole/ml); $C(0,t)$ is the concentration near the electrode at time t after the beginning of electrolysis; E is the electrode potential relative to the normal hydrogen electrode (V); E_p is the peak potential; I is the current of the electrochemical reaction (A); I_p is the peak current; k_0 is the rate constant referred to the potential of the normal hydrogen electrode (cm/sec); m, μ, ψ are auxiliary variables; n is the number of electrons in the reaction; $q = vnF/RT$; S is the electrode area (cm^2); x is the distance from the electrode (cm); F is the faraday; R is the gas constant; T is the temperature (°K); α is the barrier coefficient; αn corresponds to the rate-determining stage; δ is a conditional unit for measuring the quantity m; $\varphi(t) = \partial C(0,t)/\partial x$.

Below a simple equation will be derived which expresses the maximum current through the rate constant and the peak potential, which are always known from the oscillogram. At the same time, it will not contain the rate of change of the potential or the diffusion coefficient, which is often unknown. The derivation is based on the assertion that the ratio of the concentration of the reacting substance in the near-electrode layer to its concentration in the bulk of the solution for the peak point is always constant and equal to 0.230. It does not depend on D, v, or other quantities. To show this, it is expedient to bring the integral relation between the concentration and its gradient at the electrode boundary $^{(2)}$

$$C(0,t) = C_0 - \sqrt{\frac{D}{\pi}} \int_0^t \frac{\varphi(\tau)\, d\tau}{\sqrt{t-\tau}} \qquad (1)$$

to dimensionless form. Substitution

$$\varphi = C_0\sqrt{\pi q/D}\,\psi, \qquad t = \delta m/q, \qquad \tau = \delta\mu/q \tag{2}$$

and subsequent division by C_0 give

$$\frac{C(0,t)}{C_0} = 1 - \sqrt{\delta}\int_0^m \frac{\psi(\delta\mu)\,d\mu}{\sqrt{m-\mu}}. \tag{3}$$

If the substance is supplied to the electrode only by diffusion, then for an irreversible reaction

$$\frac{I}{nFS} = D\varphi(t) = C(0,t)k_0\exp\left[-\alpha\frac{nF}{RT}E\right]. \tag{4}$$

Expressing from this $C(0,t)$ and substituting its value into (1), we obtain an equation for $\varphi(t)$

$$D\varphi(t) = k_0\exp\left(-\alpha\frac{nF}{RT}E\right)\left[C_0 - \sqrt{\frac{D}{\pi}}\int_0^t \frac{\varphi(\tau)\,d\tau}{\sqrt{t-\tau}}\right]. \tag{5}$$

The same substitution (2) transforms it into an equation for $\psi(\delta m)$

$$\psi(\delta m) = \frac{k_0}{\sqrt{D\pi q}}\exp\left(-\alpha\frac{nF}{RT}E\right)\left[1 - \sqrt{\delta}\int_0^m \frac{\psi(\delta\mu)\,d\mu}{\sqrt{m-\mu}}\right]. \tag{6}$$

For a potential varying linearly with time, $E = \bar{E} - vt$, the factor before the square brackets in (6) is transformed to the form $\exp(\delta m - \sigma)$, where

$$\sigma = \alpha nF\bar{E}/RT + {}^1\!/_2\ln D\pi q - \ln k_0. \tag{7}$$

In this notation

$$\psi(\delta m) = \exp(\delta m - \sigma)\left[1 - \sqrt{\delta}\int_0^m \frac{\psi(\delta\mu)\,d\mu}{\sqrt{m-\mu}}\right]. \tag{8}$$

At the beginning $(t = 0,\ m = 0)$ the current and the quantity ψ proportional to it are practically equal to zero. From (8) it follows that

$$\psi(+0) = e^{-\sigma} - o(e^{-\sigma}), \tag{9}$$

i.e., $\psi(+0)$ differs from $e^{-\sigma}$ by a small quantity of higher order than $e^{-\sigma}$, and therefore for small $e^{-\sigma}$ they may be regarded as equal. The possibility of choosing σ according to (9) eliminates the need to calculate it by formula (7). In calculations, σ may be chosen so that $\psi(+0)$ is equal to some specified small value, for example 10^{-3}. The latter is chosen commensurate with the permissible error. Within the indicated limits, an arbitrary choice of σ does not substantially change the function $\psi(\delta m)$, but only changes the distance between the origin of the argument and that value at which it reaches its maximum.

Thus, $\psi(\delta m)$ and, consequently, the integral

$$\tilde{I} = \sqrt{\delta} \int_0^m \frac{\psi(\delta\mu)\, d\mu}{\sqrt{m-\mu}} \tag{10}$$

do not depend on the parameters of the experiment and of the substance. But then the ratio of concentrations determined by expression (3) must not depend on them either. Since the current of the electrochemical reaction and the function $\psi(\delta m)$ pass through a maximum simultaneously, the maximum value of the current always corresponds to one and the same ratio of concentrations.

To determine it, the integral (10) was represented by the formulas described earlier (3). Then, from (8), (10), and (3), the values of $\psi(\delta m)$, $\tilde{I}(m)$, and $C(0,m)/C_0$ were successively determined for $m = 1, 2, \ldots, 35$. It was assumed that $\sigma = \ln 10^{3.2}$, $\delta = 0.23026$. The results are given in Table 1.

Table* 1

m	$\frac{C(0,t)}{C_0}$	$\tilde{I}$	ψ	m	$\frac{C(0,t)}{C_0}$	$\tilde{I}$	ψ
0	1.0000	0.0000	0.0000	18	0.9329	0.0671	0.0371
1	0.9995	0.0005	0.0008	19	0.9165	0.0835	0.0459
2	0.9989	0.0011	0.0010	20	0.8977	0.1023	0.0566
3	0.9984	0.0016	0.0013	21	0.8720	0.1280	0.0693
4	0.9978	0.0022	0.0016	22	0.8427	0.1573	0.0843
5	0.9970	0.0030	0.0020	23	0.8078	0.1922	0.1017
6	0.9960	0.0040	0.0025	24	0.7667	0.2333	0.1215
7	0.9949	0.0051	0.0031	25	0.7192	0.2808	0.1435
8	0.9934	0.0066	0.0040	26	0.6654	0.3346	0.1671
9	0.9916	0.0084	0.0050	27	0.6057	0.3943	0.1915
10	0.9893	0.0107	0.0062	28	0.5412	0.4588	0.2155
11	0.9864	0.0136	0.0078	29	0.4738	0.5262	0.2375
12	0.9828	0.0172	0.0098	30	0.4057	0.5943	0.2560
13	0.9783	0.0217	0.0123	31	0.3394	0.6606	0.2697
14	0.9727	0.0273	0.0154	32	0.2777	0.7223	0.2777
15	0.9657	0.0343	0.0192	33	0.2223	0.7777	0.2800
16	0.9570	0.0430	0.0240	34	0.1747	0.8253	0.2771

m	$\dfrac{C(0,t)}{C_0}$	$\tilde{I}$	ψ	m	$\dfrac{C(0,t)}{C_0}$	$\tilde{I}$	ψ
17	0.9462	0.0538	0.0299	35	0.1364	0.8636	0.2723

* The conventional unit of the argument is
$\Delta E = 0.2303\,\dfrac{RT}{nF}\,\dfrac{1}{\alpha}$ V. At 25° $\Delta E = 0.00591/\alpha n$.

By interpolation with polynomials of the 7th degree, the value m_p was found at which ψ is maximal, and the ratio $C(0,t)/C_0$ at this point:

$$m_p = 32.86; \qquad C(0,t_p)/C_0 = C\left(0, \frac{\delta m_p}{q}\right)/C_0 = 0.2297. \tag{11}$$

Relations (11) and (4) finally lead to the formula for the maximum current of an irreversible reaction

$$I_p = 0.230\, nFSC_0 k_0 \exp\left[-\alpha\,\frac{nF}{RT} E_p\right]. \tag{12}$$

One application of this formula is the determination of the rate constant k_0 from the known current and potential at the maximum point

$$k_0 = 4.35\,\frac{I_p}{nFSC_0}\exp\left[\alpha\,\frac{nF}{RT}E_p\right]. \tag{13}$$

At 25°

$$I_p = 2.22 \cdot 10^4 nSC_0 k_0\, 10^{-16.91\alpha n E_p}; \tag{12*}$$

$$k_0 = 0.450 \cdot 10^{-4}\,\frac{I_p}{nSC_0}\,10^{16.91\alpha n E_p}. \tag{13*}$$

Since here the peak potential enters the exponent with a large coefficient, it must be measured with the greatest possible accuracy. When E_p changes by 1 mV, k_0 acquires a factor of 1.04. A method for the exact determination of the peak potential was developed by Favero and Vianello (4). Taking into account the current produced by the background also makes it possible to reduce significantly the error in determining the peak potential (5). A large excess of supporting electrolyte, by reducing the potential drop in the diffusion layer, also contributes to increased accuracy (6).

As an example, k_0 was calculated for the reduction of Nb^{5+} in a 0.1 M solution of Trilon B at 25°. For the first, irreversible wave $n = 1$, $E_p = -0.616$ relative to the normal hydrogen electrode, $I_p = 14.28 \cdot 10^{-6}$ A, $C_0 = 2.152 \cdot 10^{-6}$ mol/ml, $S = 1.529 \cdot 10^{-2}$ cm^2, $v = 2.45$ V/sec (v is not involved in the calculations), $\alpha n = 0.34$. Then from (13*) $k_0 = 0.56 \cdot 10^{-5}$ cm/sec.

The quantity αn enters formulas (12) and (13). Its value can be obtained by comparing the current at the maximum with the current of the descending branch of the polarographic oscillogram. From the equation of the descending branch (7) it follows, for example, that $I_p/I_{0.3} = 3.18\sqrt{\alpha n}$, where $I_{0.3}$ is the value of the current at a potential 0.3 V more negative than the peak potential.

Institute of Electrochemistry
Academy of Sciences of the USSR

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

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