Theoretical Analysis of Polarographic Waves. I. Reduction of Simple Metal Ions

By Hiroaki MATSUDA and Yuzo AYABE

(Received December 24, 1954)

Introduction

Theoretical analysis of the polarographic current-voltage curves was first attempted by J. Heyrovsky and D. Ilkovic¹⁾, who assumed that the potential of the dropping mercury electrode was given by Nernst's equation. Although their treatment was successful in analysing the various types of reversible waves, it was soon shown that the numerous waves corresponding to the so-called irreversible electrode processes could not be analysed on the basis of Heyrovsky-Ilkovic's theory. Being promted by this inadequency, the theoretical treatments of the irreversible waves have been developed by various authors²⁾, who applied the absolute reaction rate theory to the polarographic problems. However, these authors assumed that the diffusion current was proportional to the difference between the concentration of the depolarizer in the bulk of the solution and that at the electrode surface, by using the concept of Nernst's diffusion layer. This assumption is valid only in the case in which the concentration of depolarizer at the electrode surface is independent of time, and consequently it cannot be adapted to the present problem.

Recently, T. Kambara and I. Tachi³⁾ and P. Delahay⁴⁾ have independently derived the equation of the instantaneous diffusion current during the drop age for any point along the wave, by solving the corresponding diffusion problem for the case of first-order electrode reaction. However, their results cannot be quantitatively applied to the dropping mercury electrode, since they assume that the diffusion process proceeds in a stationary medium.

In this paper, we shall derive a general equation of the instantaneous diffusion current, taking into account the movement of the solution caused by the expansion of the mercury drop with the same accuracy as Ilkovic's equation for the limiting diffusion current. Then, the general expression for the current-voltage curve will be given and its characteristics discussed upon being divided into three cases, i. e. reversible, "quasi"-reversible and irreversible.

Theoretical Derivation of the Equation for the Instantaneous Diffusion Current

Consider the reduction to the metallic state (amalgam) of a simple ion of a metal that is soluble in mercury.

According to MacGillavry and Rideal⁵⁾, the concentration distributions of the simple metal ion (denoted by suffix *ox*) and of the amalgamated metal (denoted by suffix *red*) can be determined by solving the following system of differential equations.

$$\frac{\partial C_{ox}}{\partial t}=D_{ox}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{ox}}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_{ox}}{\partial r}\,(r\geqq r_0) \tag{1}$$

$$\frac{\partial C_{red}}{\partial t}=D_{red}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{red}}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_{red}}{\partial r}\,(r\leqq r_0) \tag{2}$$

In these equations, D is the diffusion coefficient; C is the concentration; r is the distance from the center of mercury drop; t is the time elapsed after the growth of the drop has begun; r_0 is the radius of the mercury drop, which is given by

$$r_0=(3m/4\pi d)^{1/3}\,t^{1/3}=at^{1/3} \tag{3}$$

where m is the constant rate of flow of mercury out of the capillary and d is the density of mercury.

The initial condition is given by

$$\left.\begin{array}{l} t=0,\ r>r_0\ :\ C_{ox}={}^*C_{ox} \\ t=0,\ r<r_0\ :\ C_{red}=0 \end{array}\right\} \tag{4}$$

where ${}^*C_{ox}$ is the concentration of the metal ion in the bulk of the solution. The bound-

---

1) J. Heyrovský and D. Ilkovič, *Collection Czechoslov. Chem. Communs.*, **7**, 198 (1935).

2) N. Tanaka and R. Tamamushi, This Bulletin, **22**, 187, 227 (1949) ; *Sbornik*, **1**, 486 (1951) ; H. Eyring, L. Marker and T.C. Kwoh, *J. Phys. Colloid. Chem.*, **53**, 1453 (1949); R. Goto and I. Tachi, *J. Electrochem. Soc. Japan*, **18**, 207 (1950); *Sbornik*, **1**, 69 (1951); M. Kalousek and A. Tockstein, *Sbornik*, **1**, 563 (1951).

3) T. Kambara and I. Tachi, This Bulletin, **25**, 135 (1952).

4) P. Delahay, *J. Am. Chem. Soc.*, **75**, 1430 (1953).

5) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

ary condition is controlled by the current $i(t)$ flowing through the surface of the dropping mercury electrode and is manifested by

$$t>0,\ r=r_0\ :\ D_{ox}\frac{\partial C_{ox}}{\partial r}=D_{red}\frac{\partial C_{red}}{\partial r}=i(t)/nF\cdot q\,, \tag{5}$$

where n is the number of faradays of electricity required per mole of electrode reaction, F is the faraday and q is the surface area of the dropping mercury electrode, which is given by $4\pi r_0^2$.

In order to integrate the system of the differential equations, it is convenient to perform a substitution of the variables to simplify the calculation. Let

$$x=r^3-r_0^3=r^3-a^3t \tag{6}$$

$$y=t^{7/3} \tag{7}$$

Then

$$\frac{\partial}{\partial t}=-\frac{7}{3}t^{4/3}\frac{\partial}{\partial y}-a^3\frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial r}=3r^2\frac{\partial}{\partial x}=3(x+a^3t)^{2/3}\frac{\partial}{\partial x}\,. \tag{8}$$

Owing to the very small values of the diffusion coefficients of metal ion and amalgamated metal, the inhomogeneities of concentration distributions occur only in the regions which are very close to the surface of the dropping mercury electrode, and since in these regions r differs only slightly from r_0, it follows that $|x|$ is very much smaller than a^3t. When $|x|\ll a^3t$, we have

$$\frac{\partial}{\partial r}\simeq 3a^2t^{2/3}\frac{\partial}{\partial x}=3a^2y^{2/7}\frac{\partial}{\partial x} \tag{9}$$

Substituting the relations expressed by Eqs. (6), (7), (8) and (9) into Eqs. (1), (2), (4) and (5) leads to

$$\frac{\partial C_{ox}}{\partial y}=\frac{27}{7}a^4D_{ox}\frac{\partial^2 C_{ox}}{\partial x^2}\ \ (x\geqq 0) \tag{1'}$$

$$\frac{\partial C_{red}}{\partial y}=\frac{27}{7}a^4D_{red}\frac{\partial^2 C_{red}}{\partial x^2}\ \ (x\leqq 0) \tag{2'}$$

with the following initial and boundary conditions

$$\left.\begin{array}{l} y=0,\ x>0\ :\ C_{ox}={}^*C_{ox} \\ y=0,\ x<0\ :\ C_{red}=0 \end{array}\right\} \tag{4'}$$

$$y>0,\ x=0: 3a^2y^{2/7}D_{ox}\frac{\partial C_{ox}}{\partial x}$$

$$=3a^2y^{2/7}D_{red}\frac{\partial C_{red}}{\partial x}=i(y)/nF\cdot q \tag{5'}$$

The above derived differential equations (1)′ and (2)′ can be easily solved by using the method of the Laplace transformation. The solutions of Eqs. (1)′ and (2)′, which fulfil the initial and boundary conditons (4)′ and (5)′, are shown to be

$$C_{ox}={}^*C_{ox}-\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D_{ox}}}\int_0^y e^{-\frac{x^2}{4(27/7)a^4D_{ox}(y-s)}}\cdot$$

$$\times\frac{s^{-2/7}[i/nF\cdot q]}{\sqrt{y-s}}\,ds\ (x\geqq 0)$$

$$C_{red}=\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D_{red}}}\int^y e^{-\frac{x^2}{4(27/7)a^4D_{red}(y-s)}}\cdot$$

$$\times\frac{s^{-2/7}[i/nF\cdot q]}{\sqrt{y-s}}\,ds\ (x\leqq 0)$$

Therefore, the concentration of the amalgam formed on the surface of the mercury drop, designated by $^\circ C_{red}$, and the concentration of the reducible metal ion in the layer of solution at the surface of the drop, designated by $^\circ C_{ox}$, can be expressed as

$$^\circ C_{ox}={}^*C_{ox}-\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D_{ox}}}\int_{,}^{y}\frac{s^{-2/7}[i/nF\cdot q]}{\sqrt{y-s}}\,ds \tag{10}$$

$$^\circ C_{red}=\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D_{red}}}\int^y\frac{s^{-2/7}[i/nF\cdot q]}{\sqrt{y-s}}\,ds\,, \tag{11}$$

respectively.

The current flowing through the electrode surface depends on the electrode potential and the concentrations of the metal ion and of the amalgam at the electrode surface. According to the reaction rate theory[3], the current flowing can be expressed as

$$[i/nF\cdot q]=k_f^0(f_{ox}{}^\circ C_{ox})e^{-\frac{\alpha nF}{RT}E}$$

$$-k_b^0(f_{red}{}^\circ C_{red})e^{\frac{(1-\alpha)nF}{RT}E}\,, \tag{12}$$

where f is the activity coefficient; E is the electrode potential, measured with respect to the normal hydrogen electrode; α is the transfer coefficient; k_f^0 and k_b^0 are the rate constants of the reduction process and of the oxydation process at the potential of the normal hydrogen electrode, respectively.

Eliminating $^\circ C_{ox}$ and $^\circ C_{red}$ from Eqs. (10), (11) and (12) leads to Volterra's integral equation of the second kind with respect to the unknown function $[i/nF\cdot q]$,

$$[i/nF\cdot q]=k_f^0f_{ox}{}^*C_{ox}e^{-\frac{\alpha nF}{RT}E}$$

$$-\sqrt{\frac{3}{7\pi}}\lambda\int_0^y\frac{s^{-2/7}[i/nF\cdot q]}{\sqrt{y-s}}\,ds\,,$$

where

---

[6] S. Glasstone, K. J. Laidler and H. Eyring: The Theory of Rate Processes, p. 575 (1941).

$$\lambda=\frac{k_f{}^0 f_{ox}}{\sqrt{D_{ox}}}e^{-\frac{\alpha nF}{RT}E}+\frac{k_b{}^0 f_{red}}{\sqrt{D_{red}}}e^{\frac{(1-\alpha)nF}{RT}E}. \qquad (13)$$

In order to obtain a description of our problem formulated by means of dimensionless parameters, we perform the following substitution

$$[i/nF\cdot q]=k_f{}^0 f_{ox}{}^*C_{ox}e^{-\frac{\alpha nF}{RT}E}\cdot\psi \qquad (14)$$

$$\xi=\lambda y^{3/14}=\lambda t^{1/2} \qquad (15)$$
$$\eta=\lambda s^{3/14}.$$

Then we obtain

$$\psi(\xi)=1-2\sqrt{\frac{7}{3\pi}}\int_0^{\xi}\frac{\eta^{7/3}\phi(\eta)}{\sqrt{\xi^{14/3}-\eta^{14/3}}}d\eta \qquad (16)$$

By the method of successive substitution, the solution of the integral equation (16) can be expressed by the equation in form of power series,

$$\psi(\xi)=1+\sum_{p=1}^{\infty}(-1)^p\left\{\prod_{l=1}^{p}\frac{\Gamma\left(\frac{3l+7}{14}\right)}{\Gamma\left(\frac{3l+14}{14}\right)}\right\}\left(\sqrt{\frac{3}{7}}\xi\right)^p, \qquad (17a)$$

where Γ represents Euler's Gamma function. This power series is convergent for any value of ξ, but it shows a very slow convergence for the value of ξ larger than about $\sqrt{7/3}$. For the large values of ξ, as shown in the Appendix, the following asymptotic expansion is applicable,

$$\psi(\xi)\sim\frac{1}{\sqrt{\pi}}\left(\sqrt{\frac{3}{7}}\xi\right)^{-1}\left\{1+\sum_{p=1}(-1)^p\left[\prod_{l=1}^{p}\left(\frac{7-3l}{14}\right)\frac{\Gamma\left(\frac{14-3l}{14}\right)}{\Gamma\left(\frac{21-3l}{14}\right)}\right]\left(\sqrt{\frac{3}{7}}\xi\right)^{-p}\right\} \qquad (17b)$$

Therefore, considering the relations expressed by Eqs. (13), (14) and (15), we obtain the general expression showing the instantaneous diffusion current for any point along the wave,

$$\begin{aligned} i&=4\pi\left(\frac{3m}{4\pi d}\right)^{2/3}\cdot nF.\\ &\times(f_{ox}\cdot{}^*C_{ox})k_f{}^0e^{-\frac{\alpha nF}{RT}E}t^{2/3}\psi(\lambda\sqrt{t})\\ &=i_d\left[1+\frac{k_b{}^0 f_{red}/\sqrt{D_{red}}}{k_f{}^0 f_{ox}/\sqrt{D_{ox}}}e^{\frac{nF}{RT}E}\right]^{-1}\\ &\times\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\psi(\lambda\sqrt{t}), \end{aligned} \qquad (18)$$

where the surface area of the dropping mercury electrode q is replaced by $4\pi r_0{}^2=4\pi\left(\frac{3m}{4\pi d}\right)^{2/3}t^{2/3}$, and i_d represents Ilkovic's equation for the instantaneous limiting difusion current, which can be written as

$$i_d=4\sqrt{\frac{7\pi}{3}}\left(\frac{3}{4\pi d}\right)^{2/3}nF\cdot D_x^{1/2}\cdot m^{2/3}{}^*C_{ox}t^{1/6}.$$

In Table I, the values of function $\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\psi(\lambda\sqrt{t})$ evaluated by means of Eqs. (17a) and (17b) are given for various values of $\lambda\sqrt{t}$.

TABLE I

VALUES OF THE FUNCTION $\sqrt{\frac{3\pi}{7}}\cdot(\lambda\sqrt{t})\cdot\psi(\lambda\sqrt{t})$ FOR VARIOUS VALUES OF $\lambda\sqrt{t}$.

$\lambda\sqrt{t}$	$\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\psi(\lambda\sqrt{t})$	$\lambda\sqrt{t}$	$\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\psi(\lambda\sqrt{t})$
0.0	0.000	4.0	0.865
0.05	0.0555	4.5	0.879
0.1	0.106	5.0	0.890
0.2	0.195	5.5	0.900
0.3	0.271	6.0	0.907
0.4	0.336	7.0	0.920
0.5	0.391	8.0	0.930
0.6	0.439	9.0	0.937
0.7	0.481	10	0.943
0.8	0.518	12	0.953
0.9	0.551	14	0.959
1.0	0.579	16	0.964
1.2	0.628	18	0.968
1.4	0.668	20	0.971
1.6	0.700	25	0.977
1.8	0.728	30	0.981
2.0	0.750	40	0.986
2.2	0.770	50	0.988
2.4	0.786	60	0.990
2.6	0.801	80	0.993
2.8	0.813	100	0.994
3.0	0.824		
3.5	0.847	∞	1.000

Theoretical Derivation of the Equation for the Current-Voltage Curve

Upon integrating Eq. (18) with respect to t from zero to the drop time τ and dividing by τ, the mean diffusion current is given by

$$\bar{i}=4\pi\left(\frac{3m}{4\pi d}\right)^{2/3}nF\cdot(f_{ox}\cdot{}^*C_{ox})$$
$$\times k_f{}^0e^{-\frac{\alpha nF}{RT}E}\frac{1}{\tau}\int_0^{\tau}t^{2/3}\psi(\lambda\sqrt{t})\ dt$$

Then, after writing $\xi=\lambda\sqrt{t}$ and rearranging, we obtain

$$\bar{i}=\bar{i}_d\left[1+\frac{k_b{}^0 f_{red}/\sqrt{D_{red}}}{k_f{}^0 f_{ox}/\sqrt{D_{ox}}}e^{\frac{nF}{RT}E}\right]^{-1}$$

$$\times\sqrt{\frac{7\pi}{3}}(\lambda\sqrt{\tau})^{-7/3}\int^{\lambda\sqrt{\tau}}\psi(\xi)\xi^{7/3}d\xi,$$

where $\bar{i}_d$ represents Ilkovic's equation for the average value of the limiting diffusion current and can be written as

$$\bar{i}_d=\frac{24}{7}\sqrt{\frac{7\pi}{3}}\left(\frac{3}{4\pi d}\right)^{2/3}\cdot nF\cdot{}^*C_{ox}\cdot m^{2/3}\cdot D_x^{1/2}\cdot\tau^{1/6}. \tag{19}$$

If we use the following expression for the half-wave potential in the case in which the electrode reaction takes place reversibly,

$$E_{1/2}^r=(RT/nF)$$

$$\times\ln(k_f{}^0\cdot f_{ox}\cdot\sqrt{D_{red}}/k_b{}^0\cdot f_{red}\cdot\sqrt{D_{ox}}), \tag{20}$$

$\frac{k_b{}^0 f_{red}/\sqrt{D_{red}}}{k_f{}^0 f_{ox}/\sqrt{D_{ox}}}e^{\frac{nF}{RT}E}$ and $\lambda\sqrt{\tau}$ can be written as follows, respectively,

$$\frac{k_b{}^0 f_{red}/\sqrt{D_{red}}}{k_f{}^0 f_{ox}/\sqrt{D_{ox}}}e^{\frac{nF}{RT}E}=e^{\zeta}-$$

$$\lambda\sqrt{\tau}=\Lambda(e^{-\alpha\zeta}+e^{(1-\alpha)\zeta}),$$

where

$$\zeta=(nF/RT)(E-E_{1/2}^r), \tag{21}$$

and

$$\Lambda=(k_f{}^0 f_{ox}/\sqrt{D_{ox}})^{1-\alpha}(k_b{}^0 f_{red}/\sqrt{D_{red}})^{\alpha}\sqrt{\tau}, \tag{22}$$

or by using the rate constant k_s at the standard potential of the electrode reaction,

$$\Lambda=k_s(f_{ox}/\sqrt{D_{ox}})^{1-\alpha}(f_{red}/\sqrt{D_{red}})^{\alpha}\sqrt{\tau}. \tag{22$'$}$$

Accordingly, it is shown that the above derived equation for $\bar{i}$ can be transformed into the form,

$$\bar{i}=\frac{\bar{i}_d}{1+e^{\zeta}}\varphi(\Lambda e^{-\alpha\zeta}[1+e^{\zeta}]).$$

In this equation, the function φ is defined as

$$\varphi(z)=\sqrt{\frac{7\pi}{3}}z^{-7/3}\int_0^z\psi(\xi)\xi^{7/3}d\xi,$$

TABLE II

COMPARISON OF THE VALUES OF FUNCTION $\varphi(z)$ WITH THE VALUES OF FUNCTION $\frac{z^{1.04}}{1.13+z^{1.04}}$ FOR VARIOUS VALUES OF z.

z	$\varphi(z)$	$\frac{z^{1.04}}{1.13+z^{1.04}}$	z	$\varphi(z)$	$\frac{z^{1.04}}{1.13+z^{1.04}}$
0.0	0.000	0.000	4.0	0.791	0.789
0.1	0.0759	0.0747	4.5	0.811	0.809
0.2	0.142	0.142	5.0	0.827	0.825
0.3	0.201	0.202	5.5	0.840	0.839
0.4	0.252	0.254	6.0	0.852	0.851
0.5	0.298	0.301	7.0	0.871	0.870
0.6	0.339	0.342	8.0	0.885	0.885
0.7	0.376	0.379	9.0	0.897	0.897
0.8	0.410	0.412	10	0.907	0.907
0.9	0.440	0.442	12	0.921	0.921
1.0	0.467	0.470	14	0.932	0.932
1.2	0.515	0.517	16	0.940	0.941
1.4	0.556	0.557	18	0.946	0.947
1.6	0.590	0.591	20	0.951	0.952
1.8	0.620	0.620	25	0.961	0.962
2.0	0.646	0.645	30	0.967	0.968
2.2	0.669	0.668	35	0.972	0.973
2.4	0.689	0.688	40	0.975	0.976
2.6	0.707	0.705	50	0.980	0.981
2.8	0.723	0.721	60	0.983	0.984
3.0	0.737	0.735	80	0.987	0.988
3.5	0.767	0.765	100	0.990	0.991
			∞	1.000	1.000

with $z=\Lambda e^{-\alpha\zeta}(1+e^{\zeta})$. The values of $\varphi(z)$ calculated by performing numerically the indicated integration with the aid of Eqs. (17a) and (17b) are given in Table II. By comparing the values of $\varphi(z)$ with the values of function $z^{1.04}/(1.13+z^{1.04})$, which are also given in Table II, it is seen that the function $\varphi(z)$ can be, with sufficient accuracy, written as

$$\varphi(z)\cong\frac{z^{1.04}}{1.13+z^{1.04}}. \tag{24}$$

Therefore Eq. (23) becomes

$$\bar{i}=\frac{\bar{i}_d}{1+e^{\zeta}}\frac{\{\Lambda e^{-\alpha\zeta}(1+e^{\zeta})\}^{1.04}}{1.13+\{\Lambda e^{-\alpha\zeta}(1+e^{\zeta})\}^{1.04}}. \tag{25}$$

This is the general equation of the current-voltage curve for the reduction of the simple metal ion. It is easily shown from Eq. (25) that $\bar{i}$ approaches to the limiting diffusion current $\bar{i}_d$ as the electrode potential becomes sufficiently negative.

In the following, we discuss the characteristics of the polarographic waves, upon dividing into three cases, viz., reversible, irreversible and "quasi"-reversible, corresponding to the magnitude of the parameter Λ (or k_s).

Reversible Waves

Consider the case in which the value of Λ is larger than $50\times\alpha^{\alpha}(1-\alpha)^{1-\alpha}$. Then, since it can be easily shown that

$$\exp(-\alpha\zeta)+\exp(1-\alpha)\zeta\geqq\alpha^{-\alpha}(1-\alpha)^{-(1-\alpha)}$$

for any value of ζ, Eq. (25) can be transformed into the following form,

$$\bar{i}=\bar{i}_d/(1+e^{\zeta})$$

or

$$E=E^r_{1/2}-\frac{RT}{nF}\ln\frac{\bar{i}}{\bar{i}_d-\bar{i}}. \tag{26}$$

This is the well-known equation for the reversible waves. Consequently, the condition under which the reversible waves are observed, can be written as

$$\Lambda>50\times\alpha^{\alpha}(1-\alpha)^{1-\alpha}.$$

Assuming that $f_{ox}=f_{red}=1$, $D_{ox}=D_{red}=10^{-5}$ cm²/sec., $\tau=3$ sec. and $\alpha\approx0.5$, the above condition becomes

$$k_s>2\times10^{-1}\ (\text{cm./sec.}). \tag{27}$$

Irreversible Waves

In case of $\Lambda<2\times10^{-2(1-\alpha)}$, $\bar{i}$ is smaller than about 2 per cent of the limiting diffusion current $\bar{i}_d$ in the range of

$$\zeta>-4.6,$$

and the appreciable values of $\bar{i}$ are observed only for the values of ζ for which the condition

$$\zeta<-4.6$$

is satisfied. Then, since it is found that

$$\exp\zeta<10^{-2}\ \text{for}\ \zeta<-4.6,$$

Eq. (25) becomes

$$\bar{i}=\bar{i}_d(\Lambda e^{-\alpha\zeta})^{1.04}/[1.13+(\Lambda e^{-\alpha\zeta})^{1.04}]$$

$$=\bar{i}_d\frac{\left\{\frac{k_f^0 f_{ox}}{D_{ox}}\sqrt{\tau}\exp\left(-\frac{\alpha nF}{RT}E\right)\right\}^{1.04}}{1.13+\left\{\frac{k_f^0 f_{ox}}{\sqrt{D_{ox}}}\sqrt{\tau}\exp\left(-\frac{\alpha nF}{RT}E\right)\right\}^{1.04}}. \tag{28}$$

By solving the equation derived above with respect to E, it will be found that

$$E=\frac{RT}{\alpha nF}\left\{2.3\log\frac{k_f^0 f_{ox}}{\sqrt{D_{ox}}}\sqrt{\tau}-0.12\right.$$

$$\left.-2.2\log\frac{\bar{i}}{\bar{i}_d-\bar{i}}\right\} \tag{28$'$}$$

Since Eq. (28) or (28)′ can be obtained by ignoring the effect of the reverse process (oxydation process), the waves for such cases may be called as irreversible. Thus the condition under which the irreversible waves appear, can be written as

$$\Lambda<2\times10^{-2(1+\alpha)},$$

or

$$k_s<4\times10^{-6}\ (\text{cm./sec.}) \tag{29}$$

assuming that $f_{ox}=f_{red}=1$, $D_{ox}=D_{red}=10^{-5}$ cm²/sec., $\tau=3$ sec. and $\alpha\approx0.5$.

Eq. (28)′ is the equation of the current-voltage curves for the irreversible waves. As it comes from Eq. (28)′, the plot of $-E$ versus $\log(\bar{i}/\bar{i}_d-\bar{i})$ must be linear, and the inclination of this line is found to be 2.2 $RT/\alpha nF$ ($=57/\alpha n$ mV. at 25°C). Consequently, if this plot is carried out and the tangent of this line is determined, the value of αn can be calculated.

From Eq. (28)′ the half-wave potential $E_{1/2}$ can be obtained as

$$E_{1/2}=\frac{RT}{\alpha nF}\left\{2.3\log\frac{k_f^0 f_{ox}}{\sqrt{D_{ox}}}+\frac{2.3}{2}\log\tau-0.12\right\}. \tag{30}$$

Therefore, by introducing the values of D_{ox}, f_{ox}, τ and αn into Eq. (30), the rate constant k_f^0 can be calculated from the observed value of $E_{1/2}$. Eq. (30) shows that the half-wave potential of the irreversible wave varies with the drop time as follows:

$$\Delta E_{1/2}/\Delta\log\tau=29.6/\alpha n\,(mV) \tag{31}$$

at 25°C. But this shift in $E_{1/2}$ is appreciably small, i.e. $14.1/\alpha n$ mV. at 25°C, as the drop time varies from 2 sec. to 6 sec.

In the following, we will determine the inflection point E_p of the current-voltage curve (i.e. the potential corresponding to the maximum value of the corresponding derivative curve). By deriving the second derivative of Eq. (28) with respect to E and by putting this derivative equal to zero, E_p can be calculated as

$$E_p=E_{1/2} \tag{32}$$

i.e., the inflection point is identical with the half-wave potential. Furthermore, the maximum value of the derivative curve can be shown as

$$[d\bar{i}/d(-E)]_{E=E_p}=0.26\,\bar{i}_d(\alpha nF/RT) \tag{33}$$

by calculating the first derivative of Eq. (28) with respect to E at $E=E_p$.

"Quasi"-Reversible Waves

According to Delahay[4], the polarographic waves for the case of $50\times\alpha^{\alpha}(1-\alpha)^{1-\alpha}>\Lambda>2\times10^{-2(1+\alpha)}$ (or 2×10^{-1} cm./sec.$>k_s>4\times10^{-6}$ cm./sec.) may be called "quasi"-reversible in order to distinguish them from reversible and irreversible waves. In such cases, the equation for the current-voltage curve can not be reduced to a simple form as well as in the reversible and irreversible cases. In order to analyse the characteristics of the "quasi"-reversible wave, we must therefore use Eq. (25) which is a complicated function containing the unknown parameters Λ and α. For the several assumed values of Λ and

α, the current-voltage curves have been numerically calculated by the aid of Eq. (25). The results are shown in Fig. 1. As illustrated in Fig. 1, the wave shifts towards more negative potentials with regard to the corresponding reversible wave, as Λ decreases. Furthermore it is found that the value of α has a remarkable effect on the wave form.

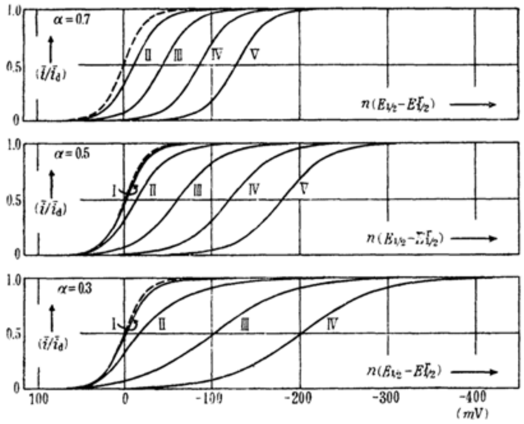

Fig. 1. Current-voltage curves for various values of Λ and α. Currents are in per cent of the limiting diffusion current $\bar{i}_d$.
I: $\Lambda=10$, II: $\Lambda=1$, III: $\Lambda=10^{-1}$, IV: $\Lambda=10^{-2}$, V: $\Lambda=10^{-3}$, Dotted curve: $\Lambda=\infty$ (reversible).

From Eq. (25) it is easily shown that the half-wave potentials of the "quasi"-reversible waves can be numerically calculated by the following equation,

$$\alpha\zeta_{1/2}-2.2\log(1-e^{\zeta_{1/2}})-0.09\log(1+e^{\zeta_{1/2}})$$
$$=2.3\log\Lambda-0.12$$

where $\zeta_{1/2}=(nF/RT)(E_{1/2}-E^r_{1/2})$.

$n(E_{1/2}-E^r_{1/2})$ versus $\log\Lambda$ diagram is illustrated in Fig. 2.

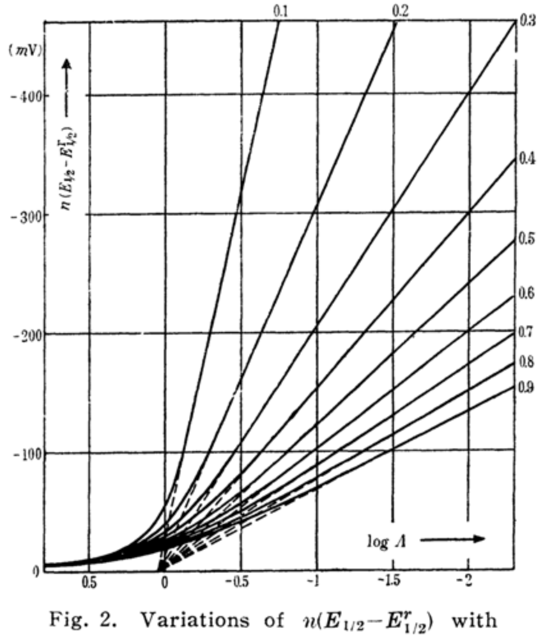

Fig. 2. Variations of $n(E_{1/2}-E^r_{1/2})$ with the values of $\log\Lambda$. Number on each curve is the value of α. Dotted lines are the ones given by Eq. (30).

Polarographic Waves of Organic Substances

Consider the waves due to the reductions of organic substances and suppose that the reactions which take place at the electrode surface, are shown by

$$R+ne \underset{k_b{}^0}{\overset{k_f{}^0}{\rightleftarrows}} R^{n-} \tag{34}$$

$$R^{n-}+nH^{+} \underset{\text{rapid process}}{\rightleftarrows} RH_n\,.$$

Then, the equations derived above are all applicable to this case, by using the following expressions for Λ and $E^r_{1/2}$ in place of the above defined ones,

$$\Lambda=(k_f{}^0\cdot f_R/\sqrt{D_R})^{1-\alpha}$$
$$\times(k_b{}^0K\cdot f_{RH}/\sqrt{D_{RH}})^{\alpha}(C_H)^{-\alpha n}\sqrt{\tau}$$

$$E^r_{1/2}=2.3(RT/nF)$$
$$\times\log\{(k_f{}^0/k_b{}^0\cdot K)(f_R/f_{RH})\sqrt{D_{RH}/D_R}\}$$
$$-2.3(RT/F)\mathrm{pH}\,,$$

where K is the equilibrium constant of the reaction (35); C_H is the concentration of the hydrogen ion in the solution, which is assumed to be well buffered.

In the present case, it must be noticed that the classification into three cases, viz., reversible, irreversible and "quasi"-reversible, depends on pH of the solution, since the value of Λ varies with pH. It must be also kept in mind that the half-wave potential varies linearly with pH in the reversible case but is independent of pH in the irreversible case.

Summary

In the present paper, the general equation of the instantaneous diffusion current has been derived, by taking into account the expansion of the mercury drop with the same accuracy as Ilkovic's equation. Then, the general expression of the current-voltage curve for the reduction of simple metal ion has been given and its characteristics discussed upon being divided into three cases,

i.e. reversible, irreversible and "quasi"-reversible. Reversible waves are given by electrode processes for which the value of k_s is larger than 2×10^{-1} cm./sec., and on the other hand, irreversible waves are observed when the value of k_s is smaller than 4×10^{-6} cm./sec. In the irreversible case, it has been shown that the rate constant $k_f{}^0$ and the transfer coefficient α can be calculated from the observed values of the half-wave potential and the tangent of log-plot, respectively.

At last, the equation of the current-voltage curve due to the reduction of organic substance has been derived.

Addendum.—Recently J. Koutecky[7] reported a theoretical treatment of the instantaneous and mean diffusion current for any point along the wave, in which the present diffusion problem was solved by an other method. The present work has been independently carried out.

Appendix

If we write u in place of ξ in Eq. (16), then multiply both sides of Eq. (16) by $\frac{14}{3}u^{11/3}/\sqrt{\xi^{14/3}-u^{14/3}}$ and integrate from zero to ξ with respect to u, we obtain,

$$\frac{14}{3}\int_0^{\xi}\frac{u^{11/3}\phi(u)}{\sqrt{\xi^{14/3}-u^{14/3}}}\,du$$
$$=2\xi^{7/3}-2\sqrt{\frac{7\pi}{3}}\int_0^{\xi}\phi(\eta)\eta^{7/3}d\eta\,.$$

By differentiating both sides of the above derived equation with respect to ξ, we have after rearranging,

$$\phi(\xi)=\sqrt{\frac{7}{3\pi}}\xi^{-1}-\sqrt{\frac{7}{3\pi}}\xi^{-7/3}\frac{d}{d\xi}\int_0^{\xi}\frac{u^{11/3}\phi(u)}{\sqrt{\xi^{14/3}-u^{14/3}}}du\,.$$

By the method of successive substitution, it is found that the solution of the above derived integro-differential equation can be expressed by the following asymptotic expansion,

$$\phi(\xi)\sim\frac{1}{\sqrt{\pi}}\left(\sqrt{\frac{3}{7}}\xi\right)^{-1}$$
$$\times\left\{1+\sum_{p=1}(-1)^p\left[\prod_{l=1}^{p}\left(\frac{7-3l}{14}\right)\frac{\Gamma\left(\frac{14-3l}{14}\right)}{\Gamma\left(\frac{21-3l}{14}\right)}\right]\left(\sqrt{\frac{3}{7}}\xi\right)^{-p}\right\}$$

The present authors wish to express their thanks to Dr. T. Kambara who has kindly read the manuscript of this paper and given them helpful advise. The authors' thanks are also due to Dr. Y. Kotera for his interest in this research.

Government Chemical Industrial Research Institute, Tokyo

---

[7] J. Koutecky: Chem. Listry. 47, 323 (1953); Collection Czechoslov. Chem. Communs., 18, 597 (1953). These papers of J. Koutecky have been here cited at the suggestion of the editor.