# *Studies on A.C. Polarography. V. Theory of Reversible Wave**

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## Introduction

Recently Breyer and Hacobian¹⁾ have developed an equation of the reversible polarographic wave. Their treatment, however, referred to the stationary state of the electrode process when a small sinusoidal alternating potential is superimposed upon the constant potential applied to the electrode. Grahame²⁾ has also shown the change of faradaic admittance against the applied constant potential, in which, however, Nernst's diffusion layer was assumed for the diffusion process of reactants.

In the first paper of this series³⁾ a general equation for the electrolytic current in a.c. electrolysis has been mathematically deduced. In the present paper an approximate solution of the general equation will be given for the case of the reversible redox-system, in which the electrode process at the transitionary state is also taken into account, and not only Breyer's polarogram but also Fournier's polarogram will be theoretically derived.

## Reversibility in A.C. Polarography

When an alternating voltage, $\Delta E p(wt+\theta)$, is superimposed upon the constant voltage, $E$, applied to the steady plane electrode, the resulting current, $i$, is, after proper rearrangements, given as follows³⁾;

$$\begin{aligned}\frac{i}{nFq}&=\phi(t)=\varphi_0(\xi)\\&=\varphi_1(\xi)+\varphi_2(\xi)\frac{1}{\sqrt{\omega}}\int_0^{\xi}\frac{\varphi_0(\xi)}{\sqrt{\pi(\xi-\eta)}}d\eta,\end{aligned}\tag{1}$$

where the functions $\varphi_1(\xi)$ and $\varphi_2(\xi)$ are shown by

$$\begin{aligned}\varphi_1(\xi)=k_s\Big[&f_O{}^*C_O\exp\Big\{-\frac{\alpha nF}{RT}(-E_0+E\\&+\Delta Ep(\xi+\theta))\Big\}-f_R{}^*C_R\exp\Big\{\frac{(1-\alpha)nF}{RT}\\&\times(-E_0+E+\Delta Ep(\xi+\theta))\Big\}\Big],\\ \varphi_2(\xi)=k_s\Big(&\frac{f_0}{\sqrt{D_0}}\Big)^{1-\alpha}\Big(\frac{f_R}{\sqrt{D_R}}\Big)^{\alpha}\Big[\exp\Big\{\frac{-\alpha nF}{RT}\\&\times(-E_{1/2}+E+\Delta Ep(\xi+\theta))\Big\}\\&+\exp\Big\{\frac{(1-\alpha)nF}{RT}(-E_{1/2}+E\\&\qquad+\Delta Ep(\xi+\theta)\Big\}\Big],\end{aligned}$$

and $wt$ is transformed to $\xi$ by the equation,

$$wt=\xi.\tag{2}$$

In these equations $\Delta E$ is the amplitude of alternating voltage and $p(wt+\theta)$ is an arbituary periodic function, in which $w$ is the angular velocity, $t$ the time and $\theta$ the phase angle; $^*C$ is the concentration of reactant in the bulk solution, $f$ the activity coefficient, $D$ the diffusion coefficent, $n$ the number of

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1) B. Breyer and S. Hacobian, *Australian J. Chem.*, **7**, 225 (1954).

2) D. C. Grahame, *J. electrochem. Soc.*, **99**, 370C (1952).

3) I. Tachi and T. Kambara, This Bulletin, **28**, 25 (1955).

faradays of electricity required per mole of the electron exchange reaction, $k_s$ the rate constant at the standard potential, $\alpha$ the transfer coefficient of forward reaction, and the suffixed $O$ and $R$ are referred to oxidized and reduced form, respectively. $F$, $R$, and $T$ are employed in the usual sense. $q$ is the surface area of electrode. $E_{1/2}$ is the half-wave potential of the reversible polarographic wave and is related to the standard potential, $E_o$, by the equation;

$$E_{1/2}=E_o+\frac{RT}{nF}\ln\frac{f_O\sqrt{D_R}}{f_R\sqrt{D_O}}$$

In deriving the above theoretical equation it was assumed that the electrolysis is carried out in the presence of excess amounts of supporting electrolytes, so that the depolarisers move exclusively by diffusion and the potential drop (ohmic and diffusion) in the solution is negligibly small. This condition also allows us to assume that the activity coefficient remains practically unchanged in the solution and that practically all of the potential drop between electrode and solution is limited to the Helmholz double layer, because the diffused electrical double layer is compressed.

For the greater value of $k_s$ eq. (1) can be transformed to a more convenient form[4];

$$\varphi_0(\xi)=g_0(\xi)-\lambda\frac{d}{d\xi}\int_0^{\xi}\frac{\varphi_0(\eta)}{\sqrt{\pi(\xi-\eta)}}\,\frac{1}{e^{\alpha\varepsilon}+e^{-(1-\alpha)\varepsilon}}d\eta, \tag{4}$$

where

$$\lambda=\sqrt{w}/k_s\left(\frac{f_O}{\sqrt{D_O}}\right)^{1-\alpha}\left(\frac{f_R}{\sqrt{D_R}}\right)^{\alpha}, \tag{5}$$

$$\varepsilon=\frac{nF}{RT}(E_{1/2}-E-\Delta E\,p(\eta+\theta)),$$

and the function $g_0(\xi)$ is given by

$$g_0(\xi)=\sqrt{w}\frac{d}{d\xi}\int_0^{\xi}\frac{1}{\sqrt{\pi(\xi-\eta)}}[i_c(\eta+\theta)-i_a(\eta+\theta)]d\eta, \tag{6}$$

$$i_c(\eta+\theta)=\frac{1}{2}\sqrt{D_O}\,{}^*C_O(1+\tanh\frac{1}{2}\epsilon),$$

$$i_a(\eta+\theta)=\frac{1}{2}\sqrt{D_R}\,{}^*C_R(1-\tanh\frac{1}{2}\epsilon).$$

The integral equation (4) can be solved by the method of successive substitution and it is seen that

$$\varphi_0(\xi)=g_0(\xi)+\sum_{j=1}^{\infty}(-1)^j\lambda^j g_j(\xi), \tag{7}$$

where

$$g_j(\xi)=\frac{d}{d\xi}\int_0^{\xi}\frac{1}{\sqrt{\pi(\xi-\eta)}}\,\frac{g_{j-1}(\eta)}{e^{\alpha\varepsilon}+e^{-(1-\alpha)\varepsilon}}d\eta.$$

When $\lambda\ll 1$, (8)

the solution (7) is approximately reduced to

$$\varphi_0(\xi)\simeq g_0(\xi), \tag{9}$$

which is also derived when Peters' formula is assumed to be held at the interface of electrode[3] and should be called an equation for the reversible a.c. polarographic current. Thus it is seen that the parameter $\lambda$ defined by eq. (5) governs the a.c. polarographic behaviour of the redox-system and determines its characteristics whether it is reversible or not under the above stated conditions.

### Reversible Wave

For the sake of simplicity it is assumed that ${}^*C_R=0$, e.g., $i_a(\eta+\theta)=0$, in the following deduction. Thus from eqs. (6) and (9) the equation for the reversible a.c. polarographic current is rewritten as follows;

$$\begin{aligned}[\varphi_0(\xi)]_{rev.}&=\sqrt{w}\frac{d}{d\xi}\int_0^{\xi}\frac{1}{\sqrt{\pi(\xi-\eta)}}i_c(\eta+\theta)d\eta\\ &=\frac{\sqrt{w}}{\sqrt{\pi\xi}}i_c(\theta)-\int_{\xi}^{\infty}\frac{1}{\sqrt{\pi(\xi-\eta)}}\frac{d}{d\eta}i_c(\eta+\theta)d\eta\\ &\quad+\int_0^{\infty}\frac{1}{\sqrt{\pi(\xi-\eta)}}\frac{d}{d\eta}i_c(\eta+\theta)d\eta.\end{aligned} \tag{10}$$

The third term in the right hand of this equation corresponds to the electrode process after a sufficiently long time has elapsed and should be called the stationary term. On the other hand the first term and the second should be called the transitionary term. The function $i_c(\eta+\theta)$ defined in the preceding section can always be developed in the Fourier series;

$$\begin{aligned}i_c(\eta+\theta)=\frac{a_0}{2}&+\sum_{n=1}^{\infty}(a_n\cos[n(\eta+\theta)]\\ &+b_n\sin[n(\eta+\theta)]),\end{aligned} \tag{11}$$

where

$$\frac{a_0}{2}=\frac{1}{2\pi}\int_0^{2\pi}i_c(\eta+\theta)d\eta,$$

$$a_n=\frac{1}{\pi}\int_0^{2\pi}i_c(\eta)\cos n\eta\,d\eta,$$

$$b_n=\frac{1}{\pi}\int_0^{2\pi}i_c(\eta)\sin n\eta\,d\eta.$$

Inserting this series into the above equation, (10), and using the well known formula;

$$\int_0^{\infty}\frac{1}{\sqrt{\pi(\xi-\eta)}}\begin{bmatrix}\sin\\ \cos\end{bmatrix}n\eta\,d\eta=\frac{1}{\sqrt{n}}\begin{bmatrix}\sin\\ \cos\end{bmatrix}\left(n\xi-\frac{\pi}{4}\right),$$

we obtain the stationary term, $\varphi_s(\xi)$, which corresponds to the a.c. component defined in Part I of this series[3], e.g.

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[4] H. Matsuda, *Z. Elektrochem.*, in press.

$$\varphi_s(\xi)=\sqrt{w}\sum_{n=1}^{\infty}\Big(\sqrt{n}\,a_n\cos\Big[n(\xi+\theta)+\frac{\pi}{4}\Big]$$
$$+\sqrt{n}\,b_n\sin\Big[n(\xi+\theta)+\frac{\pi}{4}\Big]\Big). \qquad (12)$$

Upon employing the following approximate formula;

$$\int_{\xi}^{\infty}\frac{1}{\sqrt{\pi n}}\begin{bmatrix}\sin\\ \cos\end{bmatrix}n\eta\,d\eta\simeq\frac{1}{n\sqrt{\pi\xi}}\begin{bmatrix}\cos\\ -\sin\end{bmatrix}n\xi, \qquad (13)$$

the transitionary term, $\varphi_t(\xi)$, which corresponds to the d.c. component defined in the first paper of this series[3], is given by

$$\varphi_t(\xi)\simeq\frac{\sqrt{w}}{\sqrt{\pi\xi}}\frac{a_0}{2}. \qquad (14)$$

It is easily shown that the approximate formula (13) is held in the errors less than 1%, when $\xi$ is greater than $4\pi$ or

$$t>\frac{2\pi}{w}=\frac{2}{\nu}, \quad (\nu:\ cycle/sec). \qquad (15)$$

Thus the electrolytic current is given by the sum of a.c. and d.c. components. In practice, however, owing to the electric double layer present at the electrode interface, an alternating current will flow, which should be called capacity or base current. The double layer can be regarded as a constant capacitor when the amplitude of applied alternating potential does not exceed 30 mV.[5]. Thus by retransforming $\xi$ to $wt$ by Eq. (2) the total current is given by

$$[i]_{rev.}=nFq[\phi(t)]_{rev.}\simeq i_{a\cdot c}+i_{d\cdot c\cdot}+i_B,$$

where

$$i_{a\cdot c\cdot}=nFq\varphi_s(wt),$$
$$i_{d\cdot c\cdot}=nFq\varphi_t(wt),$$
$$i_B=wC_Dq\Delta Ep\Big(wt+\theta+\frac{\pi}{2}\Big).$$

The functions $\varphi_s(wt)$ and $\varphi_t(wt)$ are defined by eqs. (12) and (14). $i_B$ is the base current, where $C_D$ is the differential capacity of the double layer.

## Fournier's and Breyer's Polarograms

The above theoretical conclusion is derived with the assumption that the electrode is plane and the medium through which the depolarisers move, stays still. However, these results may be applied to the theoretical analysis of the electrode process at the dropping mercury electrode as a first approximation. At the dropping mercury electrode the surface area of the electrode, $q$, is given by[6]

$$q=4\pi\Big(\frac{3m}{4\pi d}\Big)^{2/3}t^{2/3},$$

where $m$ is the weight of mercury flowing out of the capillary per unit time, and $d$ the density of mercury. Accordingly Eq. (14) is a good approximation for the theoretical analysis of the electrode process at the dropping electrode, because the surface area of the mercury drop is very small at the beginning of the electrolysis and the mean value of the electrolytic current during each drop is observed. Usually it is also safe to assume that $q$ remains almost constant during each cycle of the alternating current. Accordingly the d.c. component, $i_{d\cdot c\cdot}$, in Eq. (16) corresponds to Fournier's current, e.g., the mean value of the total electrolytic current. Furthermore it is possible by use of the so called Stackelberg's integral equation[7] to take into consideration the effect of expansion of the mercury drop. Thus the equation of reversible Fournier's polarogram[8] is given by

$$I_F=\frac{1}{\tau}\int_0^{\tau}\sqrt{\frac{7}{3}}\,i_{d\cdot c\cdot}dt, \qquad (18)$$

where $\tau$ is the drop time. From Eqs. (6), (11), (14), (16) and (17) it is seen that

$$I_F=\bar{i}_d\,\frac{1}{2\pi}\int_0^{2\pi}\frac{1}{2}[1+\tanh\frac{nF}{2RT}(E_{1/2}-E$$
$$-\Delta Ep(\eta+\theta))]d\eta, \qquad (19)$$

in which $\bar{i}_d$ is the polarographic limiting diffusion current originally derived by Ilkovic[9] and is given by

$$\bar{i}_d=\frac{24}{7}\Big(\frac{7}{3\pi}\Big)^{1/2}nFD_O{}^{1/2}{}^*C_O\Big(\frac{3m}{4\pi d}\Big)^{2/3}\tau^{1/6}.$$

Since the condition that $\frac{1}{\tau}\ll\nu$ is satisfied in the usual experiments, it is easy to separate the a.c. component from the d.c. component by use of a current detector with proper frequency response. Thus is obtained Breyer's polarogram[10], which shows the change of the magnitude of a.c. component against the applied constant potential. From Eqs. (12), (16) and (17) the mean value of effective value of $i_{a\cdot c\cdot}$ during each drop is given by

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[5] D.C. Grahame, *J. Amer. Chem. Soc.*, **68**, 301 (1946).

[6] I. Tachi, "Polarography", Iwanami Book Co., Tokyo (1954), p. 76.

[7] M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

[8] M. Fournier, *Compt Rend.* **232**, 1673 (1951).

[9] D. Ilkovic, *Coll. Czech. Chem. Communs.*, **8**, 13 (1936).

[10] B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research* **A3** 558, 567, 595 (1951); B. Breyer and S. Hacobian, ibid. 604, 610 (1951).

$$[I_{A\cdot C\cdot}]_{eff}=nF\frac{12}{5}\pi\left(\frac{3m}{4\pi d}\right)^{2/3}\tau^{2/3}$$

$$\sqrt{\frac{w}{2}\sum_{n=1}^{\infty}(na_n^2+nb_n^2)}\ , \tag{20}$$

where $a_n$ and $b_n$ are defined in Eq. (11).

## A.C. Polarography with Sinusoidal Alternating Potential

When the applied voltage is given by

$$V=E+\Delta E\sin(wt+\theta),$$

the function $i_c(\eta+\theta)$ is demonstrated by

$$i_c(\eta+\theta)=\frac{1}{2}\sqrt{D_O}^*C_O[1+\tanh\frac{nF}{2RT}(E_{1/2}$$
$$-E-\Delta E\sin(\eta+\theta))] \tag{21}$$

It is difficult to develop this function in the Fourier series. When the amplitude is so small that $-\beta=\frac{nF}{2RT}\Delta E$ is less than unity, however, this function is approximately expressed by the following series;

$$i_c(\eta+\theta)\simeq j_c(\eta+\theta)=\frac{A_0}{2}+B_1\sin[\eta+\theta]$$
$$+A_2\cos[2(\eta+\theta)]+B_3\sin[3(n+\theta)]$$
$$+A_4\cos[4(\eta+\theta)]+\cdots\cdots, \tag{22}$$

where

$$\frac{A_0}{2}=j_0+\frac{1}{4}\beta^2j_2+\frac{3}{8}\frac{1}{4!}\beta^4j_4+\cdots\cdots,$$

$$B_1=\beta j_1+\frac{3}{4}\frac{1}{3!}\beta^3j_3+\cdots\cdots,$$

$$A_2=-\frac{1}{4}\beta^2j_2-\frac{1}{2}\frac{1}{4!}\beta^4j_4\cdots\cdots,$$

$$B_3=-\frac{1}{4}\frac{1}{3!}\beta^3j_3\cdots\cdots,$$

$$A_4=\frac{1}{8}\frac{1}{4!}\beta^4j_4+\cdots\cdots,$$

and

$$j_0=\left[\frac{1}{2}\sqrt{D_O}^*C_0(1+\tanh(-x))\right]_{x=-nF(E_{1/2}-E)/2RT}$$

$$j_1=\left[\frac{dj_0}{dx}\right]_{x=-nF(E_{1/2}+E)/2RT}$$

$$j_2=\left[\frac{d^2j_0}{dx}\right]_{x=-nF(E_{1/2}-E)/2RT},\cdots\cdots$$

It must be noted here that if we write $\bar{i}_d$ in place of $\sqrt{D_0}^*C_0$ in the above equation, the function $j_0$ coincides with the equation of reversible wave in classic polarography and $j_1$, $j_2$,……correspond to the first, second,…… derivative curve of it, respectively. From these equations being combined with Eqs. (12), (14) and (16) the electrolytic current is given by

$$j_{a\cdot c\cdot}=nFq\sqrt{w}\Big\{B_1\sin\left[wt+\theta+\frac{\pi}{4}\right]$$
$$+\sqrt{2}A_2\left[2(wt+\theta)+\frac{\pi}{4}\right]\Big\}$$
$$+\sqrt{3}B_3\left[3(wt+\theta)+\frac{\pi}{4}\right]+\cdots\cdots \tag{23}$$

and

$$j_{a\cdot c\cdot}=nFq\frac{1}{\sqrt{\pi t}}\frac{A_0}{2} \tag{24}$$

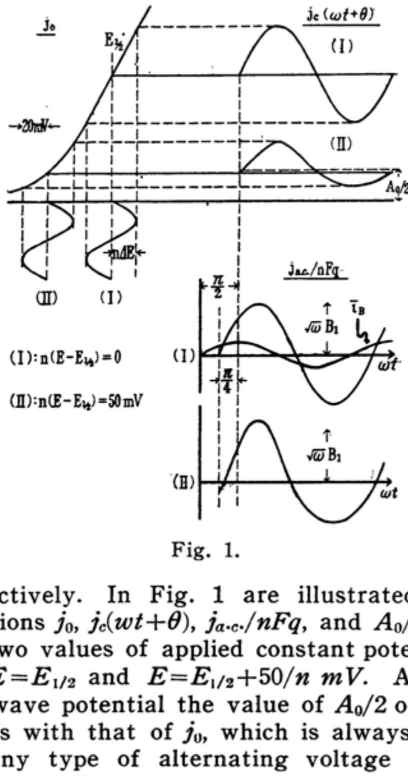

Fig. 1.

respectively. In Fig. 1 are illustrated the functions $j_0$, $j_c(wt+\theta)$, $j_{a\cdot c\cdot}/nFq$, and $A_0/2$ for the two values of applied constant potential, e.g. $E=E_{1/2}$ and $E=E_{1/2}+50/n\ mV$. At the half-wave potential the value of $A_0/2$ or $a_0/2$ agrees with that of $j_0$, which is always true for any type of alternating voltage being employed. When the amplitude is so small that $-\beta\ll1$, the a.c. component is approximately expressed by

$$j_{a\cdot c\cdot}\simeq nFq\sqrt{w}\frac{nF}{4RT}\Delta E\left(\sqrt{D_O}^*C_O+\sqrt{D_R}^*C_R\right)$$
$$\times\cosh^{-2}\left[\frac{nF}{2RT}(E_{1/2}-E)\right]\sin\left(wt+\theta+\frac{\pi}{4}\right), \tag{25}$$

in which the presence of reduced form is also taken into account. A similar result was reported by Breyer and Hacobian[1]. The value of Eq. (25) at the half-wave potential was also mathematically derived by Delahay and Adams[11]. Thus Breyer's polarogram coincides with the derivative curve of classical polarogram with respect to the applied constant potential when the amplitude is sufficiently small, but it begins to deviate from the derivative curve with increasing value of the amplitude as is expected from Eq. (23). Eq. (25) shows that the electrode interface is electrically equivalent to the series combination of Resistor, $R$, and capacitor $C$, which are given by

$$R=\frac{1}{wC}=\frac{1}{q}\,\frac{2\sqrt{2}}{(\sqrt{D_O^*}C_O+\sqrt{D_R^*}C_R)}\,\frac{RT}{n^2F^2}\,\frac{1}{\sqrt{w}}\left[\cosh^2\left[\frac{nF}{2RT}(E_{1/2}-E)\right]\right]$$

This is a more generalized expression for the faradaic impedance of reversible electrode interface[2] at the equilibrium d.c. potential originally derived by Randles[12], Ershler[13] and Gerisher[14].

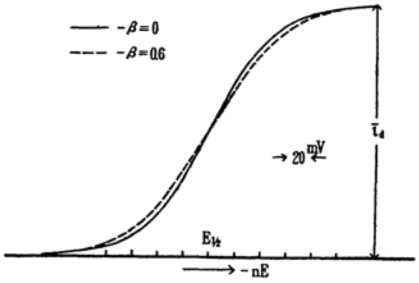

Fig. 2.

In Fig. 2 are shown the classical polarogram and Fournier's polarogram, which were calculated by substituting Eq. (24) in Eq. (18), when the amplitude is 30 $n$ $mV$.

The theoretical conclusion described in this paper shows a good agreement with the experimental results given in the previous papers of this series[15] and of other investigators[10,16,17]. More detailed comparison with them will be given in the succeeding papers.

## Summary

The electrolytic current due to the superposition of an alternating potential upon a constant potential applied to the electrode is approximately derived for the case of reversible reaction. The parameter which determines the reversibility of the a.c. electrolysis is also given. Using the above derived results, the instateneous electrolytic current as well as current-voltage curves of reversible Breyer's and Fournier's polarogram are shown.

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[11] P. Delahay and T. J. Adams, *J. Amer. Chem. Soc.*, **74**, 5740 (1952).

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[16] E. Niki, *Study of Polarography*, **1**, No. 4 p. 27 (1954).

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