Polarographic Diffusion Current Observed with Square Wave Voltage. I. Effect Produced by the Sudden Change of Electrode Potential

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In recent years several polarographic electrolyses with rectangular voltage have been reported, providing us many attractive findings. Therefore the present author intends to clear up at first the effects due to the sudden change of electrode potential and then the essential feature of electrolysis with square wave voltage theoretically and further elucidate some experimental results.

Note on the Boundary Condition

In order to discuss the diffusion current observed in the polarographic electrolysis, we must solve the system of differential equations for the diffusions of two materials, i.e. the oxydant (suffix O) and the reductant (suffix R), given by

$$\frac{\partial C_0}{\partial t}=D_0\frac{\partial^2 C_0}{\partial x^2}; \quad \frac{\partial C_R}{\partial t}=D_R\frac{\partial^2 C_R}{\partial x^2}. \tag{1}$$

Since before the electrolysis, the initial uniform concentrations $*C_0$ and $*C_R$ govern the system, the initial condition is shown by

$$t=0,\ 0\leqq x\leqq\infty,\ C_0=*C_0,\ C_R=*C_R. \tag{2}$$

The boundary condition, on the other hand, depends on the experimental condition. In the case that the electrolysis is carried out under the application of a constant voltage, it is imagined that each of the concentrations of oxidant and reductant at the electrode surface takes a constant value immediately after the beginning of electrolysis. Such a conception has been given by Cottrel[1] and Ilkovic.[2] We have treated this problem while taking the rates of forward and reverse reactions of the electrode process into consideration[3]; the analogous treatments are also given by Meiman,[4] Smutek[5] and Delahay.[6] In this article, however, let us suppose that the ratio of the concentrations of both forms at the electrode surface is given by the Nernst formula, i.e. the velocities of the electrode processes in two directions are so great that an equilibrium state is always attained thereat. Therefore it is seen that

$$x=0,\ t>0,\ C_R=K_1\cdot C_0, \tag{3}$$

where the equilibrium constant K_1 depends on the electrode potential E_1 and is given by

$$K_1=\exp\frac{-nF(E_1-E_0)}{RT}. \tag{4}$$

In this equation the symbols n, F, R, T and E_0 are used in their usual significances. On the other hand, as for the flows of the diffusing oxidant and reductant, it is obvious that the material flow must be continuous everywhere, provided that there is no accumulation or disappearance at the electrode surface. Accordingly it is found that

$$x=0,\ t>0,\ D_0\frac{\partial C_0}{\partial x}=-D_R\frac{\partial C_R}{\partial x} \tag{5}$$

This condition can be rigorously obtained, as shown by Sevcik,[7] when the amount of oxydant disappearing in unit time is considered to be equal to the amount of reductant produced newly by the electrode reaction in unit time.

As is well known, the general integrals of Eqs. (1) are given by

$$C_0=a_0+b_0\cdot\mathrm{erf}\frac{x}{2\sqrt{D_0t}};$$

$$C_R=a_R+b_R\cdot\mathrm{erf}\frac{x}{2\sqrt{D_Rt}}. \tag{6}$$

From the above cited conditions, it is seen that among four integral constants, a_0, b_0, a_R and b_R, the following relationships hold.

$$\left.\begin{aligned}&a_0+b_0=*C_0;\quad a_R+b_R=*C_R;\\&a_R=K_1a_0;\quad \sigma b_0=-b_R;\end{aligned}\right\}, \tag{7}$$

where

$$\sigma=\sqrt{D_0/D_R}\ .$$

Whence

$$\left.\begin{aligned}&a_0=\frac{\sigma*C_0+*C_R}{\sigma+K_1}={}^\circ_1C_0;\quad a_R=K_1\cdot a_0={}^\circ_1C_R;\\&b_0=*C_0-{}^\circ_1C_0;\quad b_R=*C_R-{}^\circ_1C_R;\end{aligned}\right\} \tag{9}$$

where ${}^\circ_1C_0$ and ${}^\circ_1C_R$ are the respective interfacial concentrations corresponding to the constant potential E_1. Therefore, it follows that

$$\left.\begin{aligned}&C_0={}^\circ_1C_0+(*C_0-{}^\circ_1C_0)\cdot\mathrm{erf}\frac{x}{2\sqrt{D_0t}};\\&C_R={}^\circ_1C_R+(*C_R-{}^\circ_1C_R)\cdot\mathrm{erf}\frac{x}{2\sqrt{D_Rt}}\end{aligned}\right\}. \tag{10}$$

Accordingly it is seen that in the integration of linear diffusion equation, upon supposing that the continuity of fluxes and an equilibrium state between the concentrations of two forms hold at the electrode surface, we have the result that

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[1] F. G. Cottrel, *Z. phys. Chem.*, **42**, 385 (1903).

[2] D. Ilkovic, *Collection Czech. Chem. Communs.*, **6**, 498 (1934); *J. chim. physique*, **35**, 129 (1938).

[3] T. Kambara and I. Tachi, This Bulletin, **25**, 135 (1952); T. Kambara, ibid., 281.

[4] N. Meiman, *J. Phys. Chem. USSR*, **22**, 1454 (1948).

[5] M. Smutek, *Chem. Listy*, **45**, 241 (1951); *Collection Czech. Chem. Communs.*, **18**, 171 (1953).

[6] P. Delahay, *J. Am. Chem. Soc.*, **75**, 1430 (1953).

[7] A. Sevcik, *Collection Czech. Chem. Communs.*, **13**, 349 (1948).

both interfacial concentrations have constant values.

This conclusion is identical with that given by Ilkovic,[2] by whose theory it is supposed that the boundary condition is given by

$$x=0,\ t>0,\ C_0={}_{1}^{\circ}C_0,\ C_R={}_{1}^{\circ}C_R. \qquad (11)$$

It must be mentioned here, however, that there is no rational reason for the constancies of ${}_{1}^{\circ}C_0$ and ${}_{1}^{\circ}C_R$, as pointed out by MacGillavry.[8] It is seen, for example, that even if ${}_{1}^{\circ}C_0$ and ${}_{1}^{\circ}C_R$ are both certain functions of time t, it is possible that the ratio ${}_{1}^{\circ}C_0/{}_{1}^{\circ}C_R$ might be independent of time. And it is obvious that merely from the condition of an equilibrium state at the surface, the conclusion that the concentrations ${}_{1}^{\circ}C_0$ and ${}_{1}^{\circ}C_R$ are constant, respectively, can not result, while their ratio is readily seen to be constant. Nevertheless it is clear that by employing Eq. (5) the identity of the conclusions derived from the above two theories is confirmed. Further it must be remembered that although the same conclusion is attained by employing the two different boundary conditions, such an accordance can not be derived when the solution does not stretch to infinity in one dimension, or the electrode shows not a flat surface but a spherical one.

Discontinuous Change of the Electrode Potential

Now, let us consider the case when the potential of the observation electrode is discontinuously and abruptly changed as shown in Fig. 1; i.e. from $t=0$ the electrolysis begins under the application of potential E_1 and at $t=T$ the potential jumps from E_1 to E_2 discontinuously.

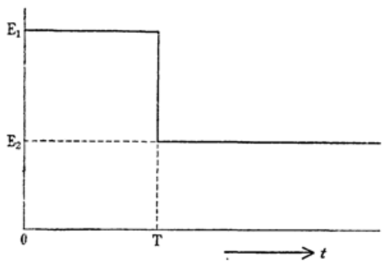

Fig. 1.

(1) Solution by Means of Laplace Transformation.—Let τ be the time elapsed after the potential was abruptly changed from E_1 to E_2; then it is clear that

$$\tau=t-T. \qquad (12)$$

Hence our problem comes to integrate the equations:

$$\frac{\partial C_0}{\partial\tau}=D_0\frac{\partial^2 C_0}{\partial x^2}\,;\quad \frac{\partial C_R}{\partial\tau}=D_R\frac{\partial^2 C_R}{\partial x^2} \qquad (13)$$

with the initial condition shown by

$$\left.\begin{aligned}&\tau=0,\ x>0,\\ &C_0=a_0+b_0\cdot\operatorname{erf}\frac{x}{2\sqrt{D_0T}}=C_0^{\pm}(x),\\ &C_R=a_R+b_R\cdot\operatorname{erf}\frac{x}{2\sqrt{D_RT}}=C_R^{\pm}(x).\end{aligned}\right\} \qquad (14)$$

This condition is required by the above discussions. The boundary condition is, on the other hand, demonstrated by

$$x=0,\ \tau>0,\ D_0\frac{\partial C_0}{\partial x}=-D_R\frac{\partial C_R}{\partial x},\ C_R=K_2\cdot C_0, \qquad (15)$$

where

$$K_2=\exp\frac{-nF(E_2-E_0)}{RT}. \qquad (16)$$

This condition results from the principle of continuity of fluxes and the assumption of a state of equilibrium between the concentrations of the two forms at the interface.

By means of the Laplace transformation defined by

$$\mathfrak{L}C(x,\tau)=p\int_0^{\infty}e^{-p\tau}\cdot C\cdot d\tau=u(x,p),$$

we can finally obtain the formulae for u_0 and u_R; i.e. they can be written in the form

$$\left.\begin{aligned}&u=A\cdot e^{nx}+B\cdot e^{-mx}\\ &+b\cdot\operatorname{erf}\frac{x}{2\sqrt{DT}}+2a\cdot\sinh\frac{mx}{2}\\ &-\frac{b}{2}\cdot e^{mx+pT}\left\{\operatorname{erf}\left(\frac{x}{2\sqrt{DT}}+\sqrt{pT}\right)-\operatorname{erf}\sqrt{pT}\right\}\\ &-\frac{b}{2}\cdot e^{-nx+pT}\left\{\operatorname{erf}\left(\frac{x}{2\sqrt{DT}}-\sqrt{pT}\ +\operatorname{erf}\sqrt{pT}\right\},\right.\end{aligned}\right\} \qquad (17)$$

where the subscripts O and R are omitted and the m's are shown by

$$m_0=\sqrt{p/D_0}\,;\ m_R=\sqrt{p/D_R}. \qquad (18)$$

Next the four integral constants A_0, B_0, A_R and B_R, can be determined by Eqs. (15) and (16). Then it can be readily seen that the transformations of the interfacial concentrations are given by

$$\left.\begin{aligned}&{}^{\circ}u_0=A_0+B_0=\frac{\sigma{}^*C_0+{}^*C_R}{K_2+\sigma}=\mathfrak{L}_2\overset{\circ}{C}_0\,;\\ &{}^{\circ}u_R=A_R+B_R=K_2(A_0+B_0)=\mathfrak{L}_2\overset{\circ}{C}_R.\end{aligned}\right\} \qquad (19)$$

There is no doubt that these equations imply that the interfacial concentrations are independent of time τ and that they are equal to the equilibrium interfacial concentrations which are to be observed when the constant potential E_2 is applied throughout from $t=0$ continuously [Cf. Eq. (9)].

Next we will evaluate the current intensity. From Eq. (17) it follows that

$$\left(\frac{\partial u_0}{\partial x}\right)_{x=0}=\sqrt{\frac{p}{D_0}}(A_0-B_0)=\frac{\sqrt{p}}{(K_2+\sigma)\sqrt{D_0}}\cdot$$
$$\{(K_2a_0-a_R)+(K_2b_0-b_R)\cdot e^{pT}\cdot\operatorname{erfc}\sqrt{pT}\}. \qquad (20)$$

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[8] D. MacGillavry, *Rec. trav. chim. Pays-Bas*, **57**, 33 (1938).

[9] Cf. Table of transformations given in R. V. Churchill: "Modern Operational Mathematics in Engineering." (1944).

Further it is found that

$$\frac{K_2a_0-a_R}{K_2+\sigma}={}^{\circ}_{1}C_0-{}^{\circ}_{2}C_0\,;\ \frac{K_2b_0-b_R}{K_2+\sigma}=b_0={}^{*}C_0-{}^{\circ}_{1}C_0. \tag{21}$$

Now, for the execution of inverse transformation, the following theorems are useful.

$$\mathfrak{L}^{-1}\sqrt{p}=\frac{1}{\sqrt{\pi\tau}}\,;$$

$$\mathfrak{L}^{-1}\sqrt{p}\cdot e^{pT}\cdot \operatorname{erfc}\sqrt{pT}=\frac{1}{\sqrt{\pi(T+\tau)}}. \tag{22}$$

Hence it is manifest that

$$\left(\frac{\partial C_0}{\partial x}\right)_{x=0}=\frac{{}^{*}C_0-{}^{\circ}_{1}C_0}{\sqrt{\pi D_0(T+\tau)}}+\frac{{}^{\circ}_{1}C_0-{}^{\circ}_{2}C_0}{\sqrt{\pi D_0\tau}}. \tag{23}$$

(2) Solution by Means of the Principle of Superposition.—It is obvious from the above deduction that when the voltage as shown in Fig. 1 is applied, it can be assumed that the interfacial concentrations in a state of equilibrium take constant values according to the electrode potential, provided that the rate of the electrode process is rapid enough. Accordingly our problem is now to solve the Eq. (1) with the initial condition given by Eq. (2) and with the boundary condition given by

$$x=0,\quad \left\{\begin{array}{ll} T>t>0, & C_0={}^{\circ}_{1}C_0\,; \\ t>T, & C_0={}^{\circ}_{2}C_0. \end{array}\right\} \tag{24}$$

Further it is clear that the applied voltage shown in Fig. 1 is equivalent to the superposition of the two constant voltages, as given by

$$\left.\begin{array}{ll} E=E_I+E_{II} & (t>0)\,; \\ E_I=E_1 & (t>0)\,; \\ E_{II}=\left\{\begin{array}{l} E_2-E_1 \\ 0 \end{array}\right. & \begin{array}{l}(t>T)\,; \\ (T>t>0).\end{array} \end{array}\right\} \tag{25}$$

This relation is illustrated in Fig. 2(a) and (b). It may be supposed analogously that as for the interfacial concentration the superposition of two concentrations as shown in Fig. 3(a) and (b) is also effective. Then we can divide the function $C_0(x,\,t)$ into two parts; namely

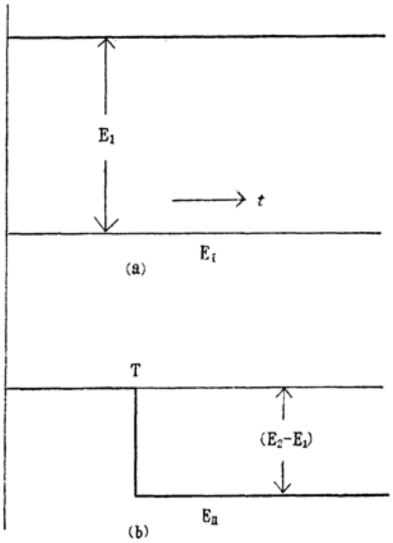

Fig. 2.

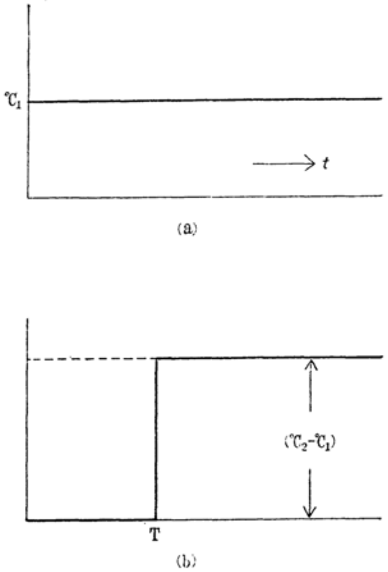

Fig. 3.

$$C_0=C_0(\mathrm{I})+C_0(\mathrm{II}), \tag{26}$$

and we have to integrate the following two equations.

$$\frac{\partial C_0(\mathrm{I})}{\partial t}=D_0\frac{\partial^2 C_0(\mathrm{I})}{\partial x^2}\,;\ \frac{\partial C_0(\mathrm{II})}{\partial t}=D_0\frac{\partial^2 C_0(\mathrm{II})}{\partial x^2}. \tag{27}$$

The conditions for $C_0(\mathrm{I})$ are shown by

$$\left.\begin{array}{lll} t=0, & 0\leq x\leq\infty, & C_0(\mathrm{I})={}^{*}C_0\,; \\ t>0, & x=0, & C_0(\mathrm{I})={}^{\circ}_{1}C_0, \end{array}\right\} \tag{28}$$

and as for the function $C_0(\mathrm{II})$, the following conditions are valid.

$$\left.\begin{array}{lll} t\leq T, & 0\leq x\leq\infty, & C_0(\mathrm{II})=0\,; \\ t>T, & x=0, & C_0(\mathrm{II})={}^{\circ}_{2}C_0-{}^{\circ}_{1}C_0. \end{array}\right\} \tag{29}$$

The solutions thereof are clearly given by

$$\left.\begin{array}{l} C_0(\mathrm{I})={}^{*}C_0-({}^{*}C_0-{}^{\circ}_{1}C_0)\cdot\operatorname{erfc}\dfrac{x}{2\sqrt{D_0t}}\,; \\ C_0(\mathrm{II})=\left\{\begin{array}{ll} 0: & (T\geq t) \\ ({}^{\circ}_{2}C_0-{}^{\circ}_{1}C_0)\cdot\operatorname{erfc}\dfrac{x}{2\sqrt{D_0(t-T)}}, & (t>T) \end{array}\right. \end{array}\right\} \tag{30}$$

and there is no doubt that by the sum of these two functions the desired solution is shown as given by Eq. (26). Thus the concentration gradient at the electrode surface is shown by

$$\left(\frac{\partial C_0}{\partial x}\right)_{x=0}=\frac{{}^{*}C_0-{}^{\circ}_{1}C_0}{\sqrt{\pi D_0t}}+\frac{{}^{\circ}_{1}C_0-{}^{\circ}_{2}C_0}{\sqrt{\pi D_0(t-T)}}, \tag{31}$$

where the second term in the right hand side of the equation should disappear for $t<T$. Eq. (31) is clearly identical with the conclusion of the preceding discussion shown by Eq. (23), since the relationship $\tau=t-T$ holds.

Indeed the solution given by Eqs. (26) and (30) is obtained only with the assumption that the interfacial concentration has a constant value according to the electrode potential. However, the fact that the solution satisfies the two conditions, i.e. the concentrations of both forms are in an equilibrium state at the electrode surface and also that the fluxes of both forms are continuous at the surface, can be easily verified. Further no discussion may be needed about the facts that for the reductant also a similar relation holds.

Discussion of the Result

In Fig. 4 is shown an example of the variation of concentration distribution near the electrode surface with time. The legitimacy of the above discussion can be rationally comprehensible from the consideration of special cases. Namely, when the discontinuous jump of the electrode potential at $t=T$ is zero, it follows that

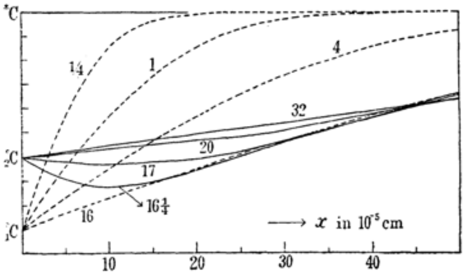

Fig. 4. Theoretical curves representing the variation of concentration distribution of depolarizer with time, drawn with the values: $\overset{\circ}{_1}C = \frac{1}{10}{}^*C$; $\overset{\circ}{_2}C = \frac{4}{10}{}^*C$; $D = 10^{-6}\,\mathrm{cm}^2.\,\mathrm{sec}^{-1}$. Figures show the times elapsed after the electrolysis in the unit of 1/100 sec., and the potential is converted from E_1 to E_2 at $T=16/100$ sec.

$$E_1=E_2\,;\ \overset{\circ}{_1}C_0=\overset{\circ}{_2}C_0\,;\ \left(\frac{\partial C_0}{\partial x}\right)_{x=0}=\frac{{}^*C_0-\overset{\circ}{_1}C_0}{\sqrt{\pi D_0 t}}. \quad (32)$$

This conclusion is, of course, quite in harmony with the Cottrel-Ilkovic theory for the current at a stationary plane electrode. Further, when the condition given by $t \gg T$ is satisfied, viz. when a considerable long time has elapsed after the change of voltage from E_1 to E_2, the hysterisis of the diffusion layer produced by the electrolysis with the application of voltage E_1 during the time interval from $t=0$ to $t=T$ should be ignored, compared with the long history of electrolysis performed after that. This can be well demonstrated by the following equation.

$$\left(\frac{\partial C_0}{\partial x}\right)_{x=0}\approx\frac{{}^*C_0-\overset{\circ}{_2}C_0}{\sqrt{\pi D_0(t-T)}}\approx\frac{{}^*C_0-\overset{\circ}{_2}C_0}{\sqrt{\pi D_0 t}}. \quad (33)$$

According to the above theoretical treatment, however, it is required that the current intensities at $t=0$ and $t=T$ become infinite. This is clearly irrational; but in order to surmount this difficulty, it is necessary to take the rates of the electrode processes into consideration. As reported in the above quoted papers[3,5]; the mathematical treatment thereof, however, seems to be much more complicated.

Summary

Change of the structure of diffusion layer with time and the course of diffusion current at a stationary and reversible electrode due to the sudden change of the applied voltage are discussed mathematically.

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