# Concentration Polarization and the Polarographic Current-Time Curve. II. The Spherical Diffusion Current

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## Mathematical Part

It is reported in our preceding paper(1) that the problem of linear diffusion current can be treated reasonably when the boundary condition demonstrates the equality of the three quantities, i. e., the rate of diffusion of the depolarizer, the rate of the electrode reaction, and the rate of diffusion of the reaction product. In this article, the mathematical treatment for the spherical electrode will be given. Suppose that a spherical electrode is immersed in an infinite solution of depolarizer and the suitable supporting electrolyte and that the electrode reaction product is water soluble. Two movements of the depolarizer and the reaction product are shown by the following system of equations:

$$\left.\begin{aligned} \frac{1}{D_1}\frac{\partial C_1}{\partial t} &= \frac{\partial^2 C_1}{\partial r^2}+\frac{2}{r}\frac{\partial C_1}{\partial r}\,; \\ \frac{1}{D_2}\frac{\partial C_2}{\partial t} &= \frac{\partial^2 C_2}{\partial r^2}+\frac{2}{r}\frac{\partial C_2}{\partial r} \end{aligned}\right\} \qquad (1)$$

where $r$ is the distance from the center of the spherical electrode, $t$ is the time, and $C$ and $D$ are the concentrations and the diffusion coefficients, respectively. The suffices 1 and 2 indicate the quantities concerning the depolarizer and the product, respectively. The initial condition is shown by

$$t=0, \quad r\geqq r_e, \quad C_1={}^*C_1, \quad C_2={}^*C_2, \qquad (2)$$

where $^*C$'s represent the initial uniform concentrations and $r_e$ is the radius of the electrode.

Employing the Laplace transformation defined by

$$\mathfrak{L}C_i=p\int_0^\infty e^{-pt}\cdot C_i(x,\ t)dt=u_i(x,\ p) \text{ for } i=1,\ 2, \qquad (3)$$

it is found that Eqs. (1) are converted into the system of the ordinary differential equations. Further, the proper boundary condition is given by

$$t>0,\ r=r_e,\ D_1\frac{\partial C_1}{\partial r}=k_1C_1-k_2C_2=-D_2\frac{\partial C_2}{\partial r}, \qquad (4)$$

where $k_1$ and $k_2$ are the rate constants of the forward and reverse reactions. Thus we obtain finally the expressions:

$$\left.\begin{aligned} u_1&={}^*C_1-K_r\cdot\sqrt{D_2}\left(\frac{\xi_1}{\sqrt{p}+m}+\frac{\eta_1}{\sqrt{p}+n}\right) \\ &\qquad\cdot\exp\left(-z_1\sqrt{p}\right); \\ u_2&={}^*C_2+K_r\cdot\sqrt{D_1}\left(\frac{\xi_2}{\sqrt{p}+m}+\frac{\eta_2}{\sqrt{p}+n}\right) \\ &\qquad\cdot\exp\left(-z_2\sqrt{p}\right). \end{aligned}\right\} \qquad (5)$$

In these equations:

$$\left.\begin{aligned} &z_1=\frac{r-r_e}{\sqrt{D_1}}\,;\ z_2=\frac{r-r_e}{\sqrt{D_2}}\,; \\ &K_r=\frac{r_e(k_1{}^*C_1-k_2{}^*C_2)}{r\sqrt{D_1D_2}}\,;\ \xi_1=\frac{m-d_1}{m-n}\,; \\ &\xi_2=\frac{m-d_2}{m-n}\,;\ \eta_1=\frac{d_1-n}{m-n}\,;\ \eta_2=\frac{d_2-n}{m-n}\,; \\ &m=\frac{b+\sqrt{b^2-4ac}}{2a}\,;\ n=\frac{b-\sqrt{b^2-4ac}}{2a}\,; \\ &a=\sqrt{D_1D_2}\,;\ b=k_1\sqrt{D_2}+k_2\sqrt{D_1} \\ &\qquad+\frac{\sqrt{D_1D_2}}{r_e}(\sqrt{D_1}+\sqrt{D_2}); \\ &c=\frac{1}{r_e}\left(k_1D_2+k_2D_1+\frac{D_1D_2}{r_e}\right); \\ &d_1=\frac{\sqrt{D_2}}{r_e}\,;\ d_2=\frac{\sqrt{D_1}}{r_e}. \end{aligned}\right\} \qquad (6)$$

And it it is seen that between these quantities the following relationships hold:

$$\left.\begin{aligned} &m+n=\frac{b}{a}\,;\ m-n=\frac{\sqrt{b^2-4ac}}{a}\,;\ mn=\frac{c}{a}\,; \\ &\xi_1+\eta_1=1; \quad \xi_2+\eta_2=1. \end{aligned}\right\} \qquad (7)$$

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

Now let us perform the inverse transformation. For this purpose, the following rule is favorable.

$$\left.\begin{aligned}\mathfrak{L}^{-1}\frac{\lambda}{\lambda+\sqrt{p}}\cdot\exp(-z\sqrt{p})&=G(z,\ \lambda,\ t)\\ &=1-\operatorname{erf}\frac{z}{2\sqrt{t}}-\Psi(z,\ \lambda,\ t);\\ \Psi(z,\ \lambda,\ t)&=\exp(z\lambda+\lambda^2t)\\ &\quad\times\left\{1-\operatorname{erf}\left(\frac{z}{2\sqrt{t}}+\lambda\sqrt{t}\right)\right\}.\end{aligned}\right\}\quad(8)$$

Hence it is found that the appropriate integrals are shown by

$$\left.\begin{aligned}C_1&={}^*C_1-K_r\sqrt{D_2}\left\{\frac{\xi_1}{m}G(z_1,\ m,\ t)\right.\\ &\qquad\left.+\frac{\eta_1}{n}G(z_1,\ n,\ t)\right\};\\ C_2&={}^*C_2+K_r\sqrt{D_1}\left\{\frac{\xi_2}{m}G(z_2,\ m,\ t)\right.\\ &\qquad\left.+\frac{\eta_2}{n}G(z_2,\ n,\ t)\right\}.\end{aligned}\right\}\quad(9)$$

## Verification of the Above Developed Theory

**(1) Linear Diffusion Current at the Plane Electrode.**—The above stated theory must become identical with that reported in the Part 1 of this study, when the conditions given by

$$r_e\to\infty;\quad r-r_e\equiv x;\quad r/r_e=1\qquad(10)$$

are fulfilled. Then it is found that

$$\begin{aligned}c=n=d_1=d_2=\eta_1=\eta_2=0;\ \ \xi_1=\xi_2=1;\\ z_1=x/\sqrt{D_1};\ \ z_2=x/\sqrt{D_2},\end{aligned}\qquad(11)$$

where $x$ is the distance from the electrode surface. It is also found that the quantities $\eta_1/n$ and $\eta_2/n$ are finite and that

$$\left.\begin{aligned}&\lim_{r_e\to\infty}m=\frac{b}{a}=\frac{k_1}{\sqrt{D_1}}+\frac{k_2}{\sqrt{D_2}}=s;\\ &\lim_{n\to0}G(z,\ n,\ \mathrm{t})=0;\end{aligned}\right\}\quad(12)$$

$$\left.\begin{aligned}\lim_{r_e\to\infty}C_1&={}^*C_1-\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_1}}\cdot G\left(\frac{x}{\sqrt{D_1}},\ s,\ t\right);\\ \lim_{r_e\to\infty}C_2&={}^*C_2+\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_2}}\cdot G\left(\frac{x}{\sqrt{D_2}},\ s,\ t\right):\end{aligned}\right\}\quad(13)$$

Thus the conclusions obtained with the plane electrode can be derived as the limiting case of the present treatment.

**(2) Final Concentrations at the Electrode Surface.**—Concentrations at the electrode surface can be obtained by putting $r=r_e$ Writing

$$\left.\begin{aligned}K&=\frac{k_1{}^*C_1-k_2{}^*C_2}{\sqrt{D_1D_2}};\\ F(y)&=\exp y\cdot(1-\operatorname{erf}\sqrt{y});\end{aligned}\right\}\quad(14)$$

it is found that the interfacial concentrations ${}^\circ C_1$ and ${}^\circ C_2$ are shown by

$$\left.\begin{aligned}{}^\circ C_1&={}^*C_1-K\sqrt{D_2}\left[\frac{\xi_1}{m}\{1-F(m^2t)\}\right.\\ &\qquad\left.+\frac{\eta_1}{n}\{1-F(n^2t)\}\right];\\ {}^\circ C_2&={}^*C_2+K\sqrt{D_1}\left[\frac{\xi_2}{m}\{1-F(m^2t)\}\right.\\ &\qquad\left.+\frac{\eta_2}{n}\{1-F(n^2t)\}\right].\end{aligned}\right\}\quad(15)$$

Putting $t\to\infty$ gives the final concentrations at the interface, *i.e.*

$$\left.\begin{aligned}{}^\circ C_1(\text{fin.})&=\frac{k_2({}^*C_1D_1+{}^*C_2D_2)+({}^*C_1D_1D_2/r_e)}{k_1D_2+k_2D_1+(D_1D_2/r_e)};\\ {}^\circ C_2(\text{fin.})&=\frac{k_1({}^*C_1D_1+{}^*C_2D_2)+({}^*C_2D_1D_2/r_e)}{k_1D_2+k_2D_1+(D_1D_2/r_e)}.\end{aligned}\right\}\quad(16)$$

**(3) Diffusion-Controlled Current Intensity.**—If the electrode reaction of one mol of the depolarizer requires the electricity of $n$ Faraday, it is seen that the current intensity $i$ is shown by

$$\left.\begin{aligned}i/nFq&=i'=k_1{}^\circ C_1-k_2{}^\circ C_2=i_1'+i_2';\\ i_1'&=(k_1{}^*C_1-k_2{}^*C_2)\\ &\quad-K\times\left\{k_1\sqrt{D_2}\left(\frac{\xi_1}{m}+\frac{\eta_1}{n}\right)\right.\\ &\qquad\left.+k_2\sqrt{D_1}\left(\frac{\xi_2}{m}+\frac{\eta_2}{n}\right)\right\};\\ i_2'&=K\left\{\left(k_1\sqrt{D_2}\frac{\xi_1}{m}+k_2\sqrt{D_1}\frac{\xi_2}{m}\right)\right.\\ &\qquad\times F(m^2t)+\left(k_1\sqrt{D_2}\frac{\eta_1}{n}\right.\\ &\qquad\left.\left.+k_2\sqrt{D_1}\frac{\eta_2}{n}\right)\cdot F(n^2t)\right\},\end{aligned}\right\}\quad(17)$$

where $q=4\pi r_e^2$ is the surface area of the spherical electrode. From Eqs. (6) it is seen that

$$\left.\begin{aligned}
&\frac{\xi_1}{m}+\frac{\eta_1}{n}=\frac{d_1}{mn}=\frac{a\sqrt{D_2}}{r_e c};\\
&\frac{\xi_2}{m}+\frac{\eta_2}{n}=\frac{d_2}{mn}=\frac{a\sqrt{D_1}}{r_e c};\\
&i_1'=(k_1{}^*C_1-k_2{}^*C_2)\frac{D_1D_2}{r_e{}^2c}\\
&\quad=\frac{(k_1{}^*C_1-k_2{}^*C_2)D_1D_2}{\left(k_1D_2+k_2D_1+\dfrac{D_1D_2}{r_e}\right)r_e}.
\end{aligned}\right\}\quad(18)$$

If the overall reaction rate is governed by the diffusion process, it can be shown asymptotically that

$$\begin{aligned}
i_2'\sim&\frac{K}{\sqrt{\pi t}}\cdot\frac{1}{m^2n^2}\{n^2(k_1\sqrt{D_2}\xi_1+k_2\sqrt{D_1}\xi_2\\
&+m^2(k_1\sqrt{D_2}\eta_1+k_2\sqrt{D_1}\eta_2)\}\\
&=\frac{K}{\sqrt{\pi t}}\cdot\frac{a^2}{c^2}\Big[[k_1\sqrt{D_2}\{-mn+d_1(m+n)\}\\
&+k_2\sqrt{D_1}\{-mn+d_2(m+n)\}]\Big]\\
&=\frac{Ka}{\sqrt{\pi t}}\Big\{-\frac{k_1\sqrt{D_2}+k_2\sqrt{D_1}}{c}\\
&+\frac{b}{r_e c^2}(k_1D_2+k_2D_1)\Big\}\\
&=\frac{(k_1{}^*C_1-k_2{}^*C_2)(k_1D_2{}^2\sqrt{D_1}+k_2D_1{}^2\sqrt{D_2})}{\sqrt{\pi t}\left(k_1D_2+k_2D_1+\dfrac{D_1D_2}{r_e}\right)^2}.
\end{aligned}\qquad(19)$$

Since $k_1$ is much larger than $k_2$, $D_1$ and $D_2$, it can be written approximately that

$$i_2'\simeq\frac{D_1(k_1{}^*C_1-k_2{}^*C_2)}{\sqrt{\pi D_1 t}}\,\frac{D_2}{\left(k_1D_2+k_2D_1+\dfrac{D_1D_2}{r_e}\right)}.\qquad(20)$$

Thus it follows that

$$\begin{aligned}
i'=i_1'+i_2'\simeq&\left(\frac{1}{r_e}+\frac{1}{\sqrt{\pi D_1 t}}\right)\\
&\cdot\frac{D_1D_2(k_1{}^*C_1-k_2{}^*C_2)}{k_1D_2+k_2D_1+(D_1D_2/r_e)}.
\end{aligned}\qquad(21)$$

On the other hand, it follows from the Eqs. (16) that

$${}^*C_1-{}^\circ C_1(\text{fin.})=\frac{D_2(k_1{}^*C_1-k_2{}^*C_2)}{k_1D_2+k_2D_1+(D_1D_2/r_e)}.\qquad(22)$$

It can be, therefore, manifested that

$$i=nFq\cdot D_1\{{}^*C_1-{}^\circ C_1(\text{fin.})\}\cdot\left(\frac{1}{r_e}+\frac{1}{\sqrt{\pi D_1 t}}\right).\qquad(23)$$

Analogously it can be concluded that

$$i=nFq\cdot D_2\{{}^\circ C_2(\text{fin.})-{}^*C_2\}\cdot\left(\frac{1}{r_e}+\frac{1}{\sqrt{\pi D_2 t}}\right).\qquad(23\text{a})$$

This result derived asymptotically can be readily obtained when we solve the system of Eqs. (1) with the boundary conditions given by

$$t>0,\ r=r_e,\ C_1={}^\circ C_1(\text{fin.}),\ C_2={}^\circ C_2(\text{fin.}),\qquad(24)$$

i. e. when we assume that the interfacial concentrations take their final value immediately after the beginning of the electrolysis.

**(4) The Current Intensity Controlled by the Electrode Process.**—In this case the rate constants $k_1$ and $k_2$ being much smaller than the diffusion coefficients, it can be shown approximately that

$$\left.\begin{aligned}
&b=\frac{\sqrt{D_1D_2}}{r_e}(\sqrt{D_1}+\sqrt{D_2});\quad c=\frac{D_1D_2}{r_e{}^2};\\
&b^2-4ac=\frac{D_1D_2}{r_e{}^2}(\sqrt{D_1}-\sqrt{D_2})^2;\\
&m=d_2=\sqrt{D_1}/r_e;\quad n=d_1=\sqrt{D_2}/r_e;\\
&\frac{\xi_1}{m}=\frac{r_e}{\sqrt{D_1}};\quad\frac{\eta_2}{n}=\frac{r_e}{\sqrt{D_2}};\quad\frac{\xi_2}{m}=\frac{\eta_1}{n}=0.
\end{aligned}\right\}\qquad(25)$$

Hence it follows that

$$\begin{aligned}
i'=(k_1{}^*C_1-k_2{}^*C_2)\Big[&1-\frac{k_1r_e}{D_1}\{1-F(m^2t)\}\\
&-\frac{k_2r_e}{D_2}\{1-F(n^2t)\}\Big].
\end{aligned}\qquad(26)$$

$k_1$ and $k_2$ being very small, and upon neglecting the higher powers of $k$'s it is found that

$$i=nFq(k_1{}^*C_1-k_2{}^*C_2),\qquad(27)$$

which is a satisfactory result.

**(5) Establishment of the Concentration Equilibrium at the Spherical Electrode Surface.**—It follows from the Eqs. (16) that

$${}^\circ C_1(\text{fin.})/{}^\circ C_2(\text{fin.})\neq k_2/k_1,\qquad(28)$$

indicating that even after the elapse of the infinite time the concentrations at the interface do not reach strictly to their equilibrium values. This may appear irrational at the first sight, but the same conclusion can be derived very simply as follows. Upon integrating the Eqs. (1) with the boundary condition given by Eq. (24), it can be readily seen that

$$\begin{aligned} i' &= k_1 \cdot {}^\circ C_1(\text{fin.}) - k_2 \cdot {}^\circ C_2(\text{fin.}) \\ &= D_1\{{}^*C_1 - {}^\circ C_1(\text{fin.})\} \cdot \left(\frac{1}{\sqrt{\pi D_1 t}} + \frac{1}{r_e}\right) \\ &= D_2\{{}^\circ C_2(\text{fin.}) - {}^*C_2\} \cdot \left(\frac{1}{\sqrt{\pi D_2 t}} + \frac{1}{r_e}\right). \quad (29) \end{aligned}$$

This relation holds at any time, and it can be immediately found that putting $t = \infty$ gives the Eqs. (16). Owing to the term $1/r_e$, it is seen that the electrolytic current continues to flow *for ever*; this means that the concentrations at the electrode surface are *always* deviated from their equilibrium state. Therefore, it may be said that the curvature of electrode is the essential factor affecting the electrode processes. It is manifested by Kaishev[2] that the equilibrium potential of a reversible metal electrode differs from the value predicted by the Nernst formula when the curvature radius is finite. This opinion is in harmony with the present considerations.

**(6) Polarographic Current-Time Curves.** —The above treatment for the spherical electrode is much more complicated than that for the plane electrode; but the course of polarographic current-time curve as discussed in our preceding paper[1] is seen to be explained reasonably by the theoretical treatment given here. The oscillographic findings are comprehensible from the present theory; the procedure therefore can be carried out quite analogously to that given in our preceding paper.

## Summary

Provided that the depolarizer and the electrode reaction product are water soluble, the spherical diffusion equations are integrated. The boundary condition is so chosen that the three elementary processes, i. e., the diffusion of depolarizer, the electrode reaction, and the diffusion of the product, proceed in an equal velocity at the electrode surface. The result thus obtained can explain the essential rôle of the curvature of the electrode in some problems concerning the electrode reaction.

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(2) R. Kaishev, *Annuaire Univ. Sofia, Faculté phys.-m-at.*, **43**, *Livre* 2, 53—62 (1941~1947); *C. A.* **44**, 3818 (1950).