Concentration Polarization and the Polarographic Current-Time Curve. I. Rate of the Consecutive Reaction Consisting of the Linear Diffusion Process and the Electrode Reaction

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Introductory Remarks on the Consecutive Reaction

As the simplest consecutive reaction, let us suppose the reaction:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \qquad \text{(i)}$$

where k_1 and k_2 are the rate constants. Let C_A, C_B and C_C represent the respective concentrations, and if the initial condition is given by

$$C_A = a, \quad C_B = C_C = 0 \text{ when } t = 0, \qquad \text{(ii)}$$

it can be demonstrated that,⁽¹⁾,⁽²⁾

$$C_C = a\left\{1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t)\right\}, \qquad \text{(iii)}$$

where it is assumed that $k_1 \neq k_2$. It is clear that the condition

$$k_1 \gg k_2 \qquad \text{(a)}$$

reduces the Eq. (iii) to the form:

$$C_C = a\{1 - \exp(-k_2 t)\}. \qquad \text{(iii-a)}$$

And it is seen that this is equivalent to the supposition that the overall reaction is controlled by the process

$$A \xrightarrow{k_2} C. \qquad \text{(i-a)}$$

Similarly the condition

$$k_2 \gg k_1 \qquad \text{(b)}$$

reduces Eq. (iii) to the form:

$$C_C = a\{1 - \exp(-k_1 t)\}. \qquad \text{(iii-b)}$$

This result can be readily obtained, if we assume that the whole reaction is equivalent to the process

$$A \xrightarrow{k_1} C. \qquad \text{(i-b)}$$

From the above-stated deductions, it can be readily seen that the velocity of the overall reaction is approximately equal to the velocity of the slowest process, *i.e.* of the rate-determining step; but comparison of Eq. (iii) with Eqs. (iii-a) and (iii-b) clearly shows that this simplification is not always legitimate.

We have been hitherto accustomed to the conception that the velocity of the heterogeneous reaction in liquid phase, *e.g.* the electrode reaction, is governed by the rate of the slower one of the two processes, *i.e.* the rate of diffusion of the depolarizer transported from the bulk of the solution to the electrode surface and the rate of the electrode reaction of depolarizer at the surface. In this article, the author will discuss a rigorous mathematical treatment for the rate of heterogeneous reaction, in which neither of the rates of these two elementary processes can be neglected.

Basic Theory for the Overall Velocity of the Electrode Reaction Including the Diffusion Process

Electrolysis by means of the polarographic method gives one of the most convenient methods for the theoretical consideration; *viz.* the applied E. M. F. shows the potential of the dropping electrode relative to the constant potential of the impolarizable bottom electrode, and the depolarizer is obliged to reach to the dropping electrode surface only by diffusion. In this way the depolarizer diffuses towards the electrode surface and then the electrode reaction takes place; the reaction product thus produced also moves by thermal agitation. (When the product is soluble in the electrolytic solution, it diffuses away into the solution,

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(1) S. Glasstone, "Textbook of Phys. Chemistry" (1940) p. 1055.

(2) E.A. Moelwyn-Hughes, "Phys. Chemistry" (1940) p. 526, 639.

and when the product forms an amalgam with the electrode mercury, it diffuses into the electrode.) In general we must consider the movements of two matters, *i. e.*, the depolarizer (denoted by the suffix 1) and the product (denoted by the suffix 2); and neglecting the curvature of the electrode surface, the following two equations hold:

$$\frac{\partial C_1}{\partial t}=D_1\frac{\partial^2 C_1}{\partial x^2} \quad \text{and} \quad \frac{\partial C_2}{\partial t}=D_2\frac{\partial^2 C_2}{\partial x^2}\ . \tag{1}$$

In these equations D_1 and D_2 are the diffusion coefficients and x_1 is the distance from the interface to the solution, and x_2 is also the distance from the interface, the sign of which depends on the nature of the reaction product. In our case we will suppose that

$$x=x_1=-x_2. \tag{2}$$

This simplification does not lose the generality of the mathematical procedure given below (This corresponds to the case that the cadmium ion in solution deposits on the mercury cathode).

The initial condition is given by

$$C_1={}^*C_1,\ C_2={}^*C_2 \text{ when } t=0,\ x>0, \tag{3}$$

where ${}^*C_1$ and ${}^*C_2$ are the concentrations in the body of solution. The boundary condition is controlled by the electrode reaction and is manifested by

$$D_1\frac{\partial C_1}{\partial x}=k_1{}^\circ C_1-k_2{}^\circ C_2=-D_2\frac{\partial C_2}{\partial x}$$
$$\text{when}\quad x=0,\ t>0, \tag{4}$$

where k_1 and k_2 are the specific rates of the forward and reverse reactions, respectively, and ${}^\circ C_1$ and ${}^\circ C_2$ represent the concentrations of the depolarizer and the reaction product at the electrode surface ($x=0$), and are the functions of time t. In some cases, k_1 or k_2 includes the product of the concentrations of the chemical species which take part in the reaction. This boundary condition results from the conception that the rate of depolarization process is given by

$$v_1=k_1\cdot{}^\circ C_1$$

and that the rate of reverse process is given by

$$v_2=k_2\cdot{}^\circ C_2.$$

In general this condition depends on the mechanism of the electrode reaction and is written in the form:

$$D_1\frac{\partial C_1}{\partial x}=k_1'\cdot{}^\circ C_1^{\,n_1}-k_2'\cdot{}^\circ C_2^{\,n_2}=-D_2\frac{\partial C_2}{\partial x}$$
$$\text{when}\quad x=0,\ t>0. \tag{4 a}$$

The physical meaning of Eqs. (1) and (4) can be readily seen, *i. e.*, the depolarizer and the reaction product move according to the law of diffusion, but their amount which penetrate the plane $x=0$, *i. e.* the velocity of the electrode reaction is governed by the law of chemical kinetics, and the flow of materials must be continuous even at the plane $x=0$.

In order to integrate the system of differential equations (1), we will employ the Laplace transformation(3) defined by

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

Then it is found that

$$\mathfrak{L}\,\frac{\partial C_i}{\partial t}=\left[p\cdot C_i\cdot e^{-pt}\right]_0^\infty+p^2\int_0^\infty e^{-pt}\cdot C_i\cdot dt$$
$$=-p{}^*C_i+pu_i. \qquad (\text{for } i=1,\ 2.)$$

Hence we obtain the following system of ordinary differential equations

$$\left.\begin{aligned}\frac{p}{D_1}(u_1-{}^*C_1)&=\frac{\partial^2 u_1}{\partial x^2};\\ \frac{p}{D_2}(u_2-{}^*C_2)&=\frac{\partial^2 u_2}{\partial x^2}.\end{aligned}\right\} \tag{5}$$

The general integral of these two equations are:

$$\left.\begin{aligned}u_1&={}^*C_1+A_1\cdot\exp\left(\sqrt{\frac{p}{D_1}}\,x\right)\\ &\qquad+B_1\cdot\exp\left(-\sqrt{\frac{p}{D_1}}\,x\right);\\ u_2&={}^*C_2+A_2\cdot\exp\left(\sqrt{\frac{p}{D_2}}\,x\right)\\ &\qquad+B_2\cdot\exp\left(-\sqrt{\frac{p}{D_2}}\,x\right).\end{aligned}\right\} \tag{6}$$

Since u_1 and u_2 must be finite even at $x\to\infty$, two constants A_1 and A_2 must be zero; *i. e.*,

$$A_1=A_2=0 \tag{7}$$

and

$$\left.\begin{aligned}u_1&={}^*C_1+B_1\cdot\exp\left(-\sqrt{\frac{p}{D_1}}\,x\right);\\ u_2&={}^*C_2+B_2\cdot\exp\left(-\sqrt{\frac{p}{D_2}}\,x\right)\end{aligned}\right\} \tag{8}$$

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(3) K. W. Wagner, "Operatorenrechnung nebst Anwendungen in Physik und Technik." (1940); Japanese Translation by H. Tahara (1943) Kagaku-Shinko-Sha.

Differentiation of these equations gives

$$\left.\begin{aligned}\frac{\partial u_1}{\partial x}&=-B_1\sqrt{\frac{p}{D_1}}\exp\left(-\sqrt{\frac{p}{D_1}}x\right)\ ;\\ \frac{\partial u_2}{\partial x}&=-B_2\sqrt{\frac{p}{D_2}}\exp\left(-\sqrt{\frac{p}{D_2}}x\right)\ .\end{aligned}\right\}\quad(9)$$

Hence from the Eqs. (4) and (9), it is found that

$$\begin{aligned}-B_1\sqrt{pD_1}&=k_1({}^*C_1+B_1)\\ &-k_2({}^*C_2+B_2)=B_2\sqrt{pD_2}.\qquad(10)\end{aligned}$$

Thus the two integral constants B_1 and B_2 are found to be

$$\left.\begin{aligned}B_1&=-\frac{k_1{}^*C_1-k_2{}^*C_2}{\sqrt{pD_1}+k_1+k_2\sqrt{\dfrac{D_1}{D_2}}}\ ;\\ B_2&=\frac{k_1{}^*C_1-k_2{}^*C_2}{\sqrt{pD_2}+k_2+k_1\sqrt{\dfrac{D_2}{D_1}}}.\end{aligned}\right\}\quad(11)$$

Accordingly it is shown that

$$\left.\begin{aligned}u_1&={}^*C_1-\frac{\alpha\sqrt{D_2}}{\lambda}\cdot\frac{\lambda}{\lambda+\sqrt{lp}}\\ &\qquad\cdot\exp\left(-a_1\sqrt{lp}\right);\\ u_2&={}^*C_2+\frac{\alpha\sqrt{D_1}}{\lambda}\cdot\frac{\lambda}{\lambda+\sqrt{lp}}\\ &\qquad\cdot\exp\left(-a_2\sqrt{lp}\right);\end{aligned}\right\}\quad(12)$$

where

$$\left.\begin{aligned}&l=D_1D_2;\quad \alpha=k_1{}^*C_1-k_2{}^*C_2;\\ &\lambda=k_1\sqrt{D_2}+k_2\sqrt{D_1};\\ &a_1=\frac{x}{D_1\sqrt{D_2}};\quad a_2=\frac{x}{D_2\sqrt{D_1}}.\end{aligned}\right\}\quad(13)$$

Now let us perform the inverse transformation of Eq. (12) in order to evaluate the quantity C_1 and C_2; for this purpose, the following theorem is valid⑶:

If $$\mathfrak{L}^{-1}f(p)=A(t),$$

it is found that

$$\mathfrak{L}^{-1}f(lp)=A(t/l),\qquad(14)$$

where l is a coefficient. Further it is known that

$$\left.\begin{aligned}&\mathfrak{L}^{-1}\frac{\lambda}{\lambda+\sqrt{p}}\cdot\exp\left(-a\sqrt{p}\right)\\ &\quad=1-\operatorname{erf}\frac{a}{2\sqrt{t}}-\Psi(t);\\ &\Psi(t)\equiv\exp\left(a\lambda+\lambda_2t\right)\\ &\quad\times\left\{1-\operatorname{erf}\left(\frac{a}{2\sqrt{t}}+\lambda\sqrt{t}\right)\right\}\ ,\end{aligned}\right\}\quad(15)$$

where erf ξ is the Gauss' error function defined by

$$\operatorname{erf}\xi\equiv\frac{2}{\sqrt{\pi}}\int_0^{\xi}\exp\left(-z^2\right)\cdot dz.$$

Accordingly it is found finally that

$$\left.\begin{aligned}\mathfrak{L}^{-1}u_1&=C_1={}^*C_1-\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_1}}\\ &\times\left[1-\operatorname{erf}\frac{x}{2\sqrt{D_1t}}-\exp\left(\frac{sx}{\sqrt{D_1}}+s^2t\right)\right.\\ &\left.\times\left\{1-\operatorname{erf}\left(\frac{x}{2\sqrt{D_1t}}+s\sqrt{t}\right)\right\}\right]\ ;\\ \mathfrak{L}^{-1}u_2&=C_2={}^*C_2+\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_2}}\\ &\times\left[1-\operatorname{erf}\frac{x}{2\sqrt{D_2t}}-\exp\left(\frac{sx}{\sqrt{D_2}}+s^2t\right)\right.\\ &\left.\times\left\{1-\operatorname{erf}\left(\frac{x}{2\sqrt{D_2t}}+s\sqrt{t}\right)\right\}\right]\ ;\end{aligned}\right\}\quad(16)$$

where s is given by

$$s=\frac{k_1}{\sqrt{D_1}}+\frac{k_2}{\sqrt{D_2}}.\qquad(17)$$

Hence it is obvious that the concentrations at the interface ($x=0$) are shown by

$$\left.\begin{aligned}{}^\circ C_1&={}^*C_1-\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_1}}\\ &\quad\times\left\{1-\exp s^2t\cdot\left(1-\operatorname{erf}s\sqrt{t}\right)\right\};\\ {}^\circ C_2&={}^*C_2+\frac{k_1{}^*C_1-k_2{}^*C_2}{s\sqrt{D_2}}\\ &\quad\times\left\{1-\exp s^2t\cdot\left(1-\operatorname{erf}s\sqrt{t}\right)\right\}.\end{aligned}\right\}\quad(18)$$

Applications of the Theory

(1) In the case that the Reverse Reaction dose not Take Place.—In this case k_2 equals zero, and from Eqs. (16) and (18) it is seen that

$$\begin{aligned}\lim_{k_2\to0}C_1&={}^*C_1\left[\operatorname{erf}\left(\frac{x}{2\sqrt{D_1t}}\right)\right.\\ &\quad+\exp\left(\frac{k_1{}^2}{D_1}t+\frac{k_1}{D_1}x\right)\\ &\quad\left.\times\left\{1-\operatorname{erf}\frac{x}{2\sqrt{D_1t}}+\frac{k_1\sqrt{t}}{\sqrt{D_1}}\Big)\right\}\right]\ ;\qquad(19)\end{aligned}$$

$$\lim_{k_2\to 0}{}^\circ C_1={}^*C_1\cdot\exp\left(\frac{k_1{}^2}{D_1}t\right)\times\left\{1-\mathrm{erf}\left(\frac{k_1}{\sqrt{D_1}}\sqrt{t}\right)\right\}. \qquad (20)$$

This result can be obtained when we solve the equation

$$\partial C_1/\partial t=D_1\cdot\partial^2C_1/\partial x^2 \qquad (1)$$

with the conditions

$$C_1={}^*C_1 \quad \text{when} \quad t=0,\quad x>0;$$

$$D_1\frac{\partial C_1}{\partial x}=k_1\cdot C_1 \quad \text{when} \quad t>0,\quad x=0.$$

I.e., it can be readily found that the solution given by Fürth⁽⁴⁾ is quite in harmony with Eq. (19).

(2) The final Concentrations at the Electrode Surface.—For large value of ξ, it can be shown that

$$\sqrt{\pi}\,(1-\mathrm{erf}\,\xi)=2\left(\int_0^\infty-\int_0^\xi\right)\sim\exp\,(-\xi^2)\times\left(\frac{1}{\xi}-\frac{1}{2\xi^3}+\frac{3}{4\xi^5}-\cdots\right), \qquad (21)$$

i. e.,

$$\exp\xi^2\cdot(1-\mathrm{erf}\,\xi)\sim\frac{1}{\sqrt{\pi}}\times\left(\frac{1}{\xi}-\frac{1}{2\xi^3}+\frac{3}{4\xi^5}-\cdots\right). \qquad (22)$$

Hence it follows that

$$\lim_{t\to\infty}{}^\circ C_1=\frac{k_2({}^*C_1\sqrt{D_1}+{}^*C_2\sqrt{D_2})}{k_1\sqrt{D_2}+k_2\sqrt{D_1}}={}^\circ C_1(\text{fin.}), \qquad (23)$$

$$\lim_{t\to\infty}{}^\circ C_2=\frac{k_1({}^*C_1\sqrt{D_1}+{}^*C_2\sqrt{D_2})}{k_1\sqrt{D_2}+k_2\sqrt{D_1}}={}^\circ C_2(\text{fin.}), \qquad (24)$$

and accordingly it is found that

$$\lim_{t\to\infty}\frac{{}^\circ C_1}{{}^\circ C_2}=\frac{{}^\circ C_1(\text{fin.})}{{}^\circ C_2(\text{fin.})}=\frac{k_2}{k_1}=K, \qquad (25)$$

where k_1, k_2, and the equilibrium constant K depend on the electrode potential. Thus it is found that the depolarizer and the reaction product finally reach to their equilibrium concentrations.

(3) Electro-deposition of Solid Metal or Alloy on a Solid Cathode.—In this case the concentration of the deposited material is considered to show a constant value ${}^\circ C_s$. Hence we must solve the equation

$$\partial C_1/\partial t=D_1\cdot\partial^2C_1/\partial x^2 \qquad (1)$$

with the initial condition given by Eq. (3) and with the boundary condition given by

$$D_1\frac{\partial C_1}{\partial x}=k_1\cdot C_1-k_2\cdot{}^\circ C_s \quad \text{when} \quad t>0,\ x=0. \qquad (4b)$$

And it is found finally that

$$C_1={}^*C_1-\frac{k_1{}^*C_1-k_2{}^\circ C_s}{k_1}\left[1-\mathrm{erf}\frac{x}{2\sqrt{D_1t}}-\exp\left(\frac{k_1x}{D_1}+\frac{k_1{}^2t}{D_1}\right)\times\left\{1-\mathrm{erf}\left(\frac{x}{2\sqrt{D_1t}}+\frac{k_1}{\sqrt{D_1}}\sqrt{t}\right)\right\}\right]. \qquad (26)$$

Hence it follows that

$$\lim_{t\to\infty}{}^\circ C_1=\frac{k_2}{k_1}{}^\circ C_s, \qquad (27)$$

i. e., when the considerable time has elapsed after the beginning of electrolysis, the equilibrium concentration is established at the interface.

(4) Current-Time Curves.—

(a) Stationary Electrode.—Ilkovic etc⁽⁵⁻¹¹⁾ have solved the differential equation

$$\partial C_1/\partial t=D_1\cdot\partial^2C_1/\partial x^2 \qquad (1)$$

with the condition

$$\left.\begin{aligned}C_1&={}^*C_1 && \text{when} \quad t=0,\quad x>0;\\ C_1&={}^\circ C_1\ (\text{fin.}) && \text{when} \quad t>0,\quad x=0,\end{aligned}\right\} \qquad (28)$$

and the result is

$$C_1={}^\circ C_1\,(\text{fin.})+\{{}^*C_1-{}^\circ C_1\,(\text{fin.})\}\cdot\mathrm{erf}\frac{x}{2\sqrt{D_1t}}, \qquad (29)$$

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(4) R. Fürth, "Wärmeleitung und Diffusion" in "Die Differential und Integralgleichungen der Mechanik und Physik." Bd. II. Herausgegeben von Ph. Frank und R. v. Mises. (1927) S, 234.

(5) D. Ilkovic. *Collection Czech. Chem. Communs.*, **6**, 498 (1934).

(6) D. Ilkovic, *Jour. chim. physique*, **35**, 129 (1938).

(7) D. MacGillavry and E. K. Rideal, *Rec. trav. chim. Pays-Bas*, **56**, 1013 (1937).

(8) M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

(9) H. Strehlow und M. v. Stackelberg, *Ibid.*, **54**, 51 (1950).

(10) T. Kambara, M. Suzuki and I. Tachi, *This Bulletin*, **23**, 219 (1950).

(11) T. Kambara and I. Tachi, *This Bulletin*, **23**, 225 (1950).

where it is supposed that the concentration of the depolarizer at the electrode surface shows a constant value $^{\circ}C_1\,(\text{fin.})$ according to the electrode potential immediately after the commencement of the electrolysis. From Eq. (29), it follows that

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = \frac{{}^*C_1 - {}^{\circ}C_1\,(\text{fin.})}{\sqrt{\pi D_1 t}}, \qquad (30)$$

and therefore if q is the surface area of the electrode, and nF (F: Faraday) is the electricity required for the electrolysis of one mol of the depolarizer, it can be seen that the instantaneous current intensity i is given by

$$i = nFqD_1\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = nFqD_1\frac{{}^*C_1 - {}^{\circ}C_1(\text{fin.})}{\sqrt{\pi D_1 t}}, \qquad (31)$$

i. e., it is shown that

$$i \propto t^{-1/2} \qquad (32)$$

Hence just at the beginning of the electrolysis the current intensity is given by

$$i_{t=0} = \infty, \qquad (33)$$

which is clearly an inadequate result.

According to the above-developed theory it is seen that

$$i/nFq = k_1{}^{\circ}C_1 - k_2{}^{\circ}C_2 = (k_1{}^*C_1 - k_2{}^*C_2) \times \exp s^2t\cdot(1-\operatorname{erf} s\sqrt{t}), \qquad (34)$$

and therefore it follows that

$$i_{t=0} \simeq nFq(k_1{}^*C_1 - k_2{}^*C_2), \qquad (35)$$

which is a quite rational conclusion. On the other hand, when the long time has elapsed after the commencement of electrolysis, it is shown from Eq. (22) that

$$i \simeq nFq\left({}^*C_1 - \frac{k_2}{k_1}{}^*C_2\right)\cdot\frac{D_1}{\sqrt{\pi D_1 t}} \times \frac{1}{1+\dfrac{k_2}{k_1}\sqrt{\dfrac{D_1}{D_2}}}.$$

Further, it is seen from Eq. (23) that

$${}^*C_1 - {}^{\circ}C_1\,(\text{fin.}) = \frac{k_1{}^*C_1\sqrt{D_2} - k_2{}^*C_2\sqrt{D_2}}{k_1\sqrt{D_2} + k_2\sqrt{D_1}} = \left({}^*C_1 - \frac{k_2}{k_1}\,{}^*C_2\right)\Big/\left(1+\frac{k_2}{k_1}\sqrt{\frac{D_1}{D_2}}\right),$$

and hence it can be found that

$$i \simeq nFqD_1\{{}^*C_1 - {}^{\circ}C_1\,(\text{fin.})\}/\sqrt{\pi D_1 t}, \qquad (36)$$

which perfectly coincides with Eq. (31). Analogously it can be readily found that

$$i \simeq nFqD_2\{{}^{\circ}C_2\,(\text{fin.}) - {}^*C_2\}/\sqrt{\pi D_2 t}. \qquad (36a)$$

It may be concluded that the boundary condition given by Eq. (28), and also the expessions shown by Eqs. (30) and (31) are merely approximate formulae representing the limiting case of our general theory.

On the contrary, when the electrode process is the rate-determining step, it is seen that k_1 and k_2 are much smaller than $\sqrt{D_1}$ and $\sqrt{D_2}$ and so the quantity s given by Eq. (17) is vanishingly small, *i. e.*

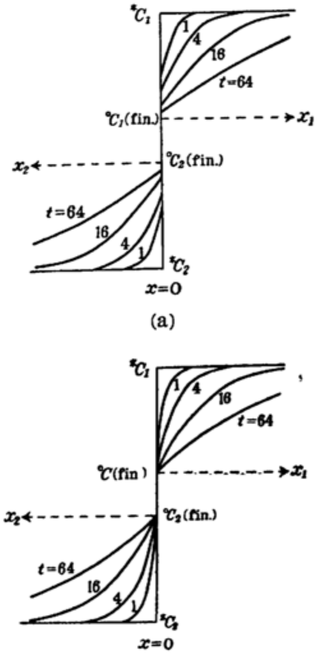
$$s \doteqdot 0. \qquad (37)$$

Then it can be seen from Eq. (34) that

$$i \simeq nFq(k_1{}^*C_1 - k_2{}^*C_2). \qquad (38)$$

This equation indicates that the overall reaction rate is nearly equal to the rate of electrode reaction.

In Fig. 1 (a) is shown the change of concentrations of the depolarizer and the product with time according to the conditions given by



(a)

(b)

Fig. 1.—Schematic representation of the structure of diffusion layer. Variation of C–x curves with time.
Curve (a): The present theory. Curve (b): Ilkovic theory.

Eqs. (3) and (4), and in Fig. 1 (b) is illustrated the change which is controlled by the conditions given by Eq. (28). The change of the diffusion current with time is illustrated in Fig. 2; curve (a) represents the current intensity given by Eq. (34) and the curve (b) shows that given by Eq. (36). In the Table are given the numerical values employed therefor.

Table

Numerical Values of Functions Appearing in Eqs. (34), (36), (42) and (47)

s^2t	$s\sqrt{t}$	$f_1(t)$*	$f_2(t)$*	$f_3(t)$*	$f_4(t)$*
0	0	1.000,0	∞	1.000,0	0
0.000,001	0.001	0.998,9	564.19	0.999,6	5.642
0.000,004	0.002	0.997,7	282.10	1.000,4	7.106
0.000,009	0.003	0.996,6	188.06	1.002,6	8.135
0.000,016	0.004	0.995,5	141.05	1.006,1	8.955
0.000,1	0.01	0.988,8	56.419	1.053,7	12.15
0.000,4	0.02	0.977,8	28.210	1.223,7	15.31
0.000,9	0.03	0.967,0	18.806	1.483,4	17.53
0.001,6	0.04	0.956,4	14.105	1.808,4	19.30
0.002,5	0.05	0.946,0	11.284	2.180,5	20.79
0.003,6	0.06	0.935,8	9.403	2.588,3	22.11
0.004,9	0.07	0.925,7	8.060	3.022,3	23.25
0.006,4	0.08	0.915,8	7.052	3.477,1	24.32
0.008,1	0.09	0.906,0	6.268	3.950,3	25.28
0.01	0.1	0.896,5	5.641,9	4.434	26.18
0.04	0.2	0.809,0	2.821,0	9.617	32.99
0.09	0.3	0.734,6	1.880,6	14.861	37.77
0.16	0.4	0.670,8	1.410,5	19.846	41.57
0.25	0.5	0.615,7	1.128,4	24.499	44.78
0.36	0.6	0.567,8	0.940,3	28.763	47.63
0.49	0.7	0.525,9	0.806,0	32.729	50.09
0.64	0.8	0.489,1	0.705,2	36.365	52.39
0.81	0.9	0.456,5	0.626,8	39.708	54.46
1.00	1.0	0.427,6	0.564,2	42.759	56.42
1.21	1.1	0.401,7	0.512,9	45.573	58.19
1.44	1.2	0.378,9	0.470,2	48.284	59.92
1.69	1.3	0.357,6	0.434,0	50.762	61.60
1.96	1.4	0.338,7	0.403,0	53.039	63.11
2.25	1.5	0.321,5	0.376,1	55.202	64.57
2.56	1.6	0.305,9	0.352,6	57.241	65.97
2.89	1.7	0.291,7	0.331,9	59.171	67.33
3.24	1.8	0.278,6	0.313,4	60.998	68.63
3.61	1.9	0.266,5	0.296,9	62.667	69.82
4.00	2.0	0.255,5	0.282,1	64.386	71.08
4.84	2.2	0.235,2	0.256,5	67.282	73.35
5.76	2.4	0.219,0	0.235,1	70.377	75.55
6.76	2.6	0.207,0	0.217,0	74.018	77.58

* $f_1(t)=\exp s^2t\cdot(1-\mathrm{erf}\, s\sqrt{t})$;

$f_2(t)=\dfrac{1}{\sqrt{\pi s^2 t}}$;

$f_3(t)=\left(1+\dfrac{v}{V_0}t\right)^{2/3}\cdot\exp s^2t\cdot(1-\mathrm{erf}\, s\sqrt{t})$;

$f_4(t)=\left(\dfrac{v}{V_0}t\right)^{2/3}\cdot\dfrac{1}{\sqrt{\pi s^2 t}}$;

$v/V_0=10^3$.

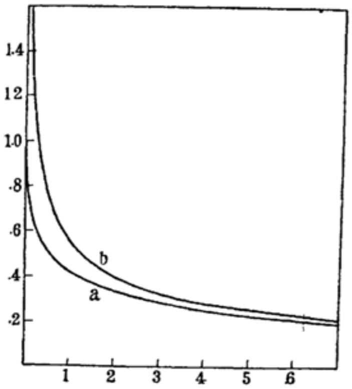


Fig. 2.—Current-time curve at the stationary electrode.

There is no doubt that the general formula for the linear diffusion current, *i.e.* Eq. (34), is reduced to the hitherto employed old formulae shown by Eq. (36) or Eq. (38) according to the simplification that the overall reaction rate is equal to either the rate of diffusion or the rate of electrode process; this is reasonably comparable to the relation between Eq. (iii) and the Eqs. (iii-a) and (iii-b).

(b) Dropping Mercury electrode.—Investigations by MacNevin with Balis⁽¹²⁾ and by Smith⁽¹³⁾ show that at the instant when the growth of the new drop has just begun, the new drop exposes a residual surface. Ilkovic⁽¹⁴⁾ describes in his paper on the theory of polarographic maxima that at the beginning of the growth of the new drop, its radius would be equal to the internal radius of the capillary. Taking these opinions into account, it may be supposed that the volume of the mercury drop V is given by

$$V = V_0 + vt, \qquad (39)$$

where V_0 is the residual volume at $t=0$ and v is the rate of flow of mercury out of the capillary in ccm/sec. Accordingly the radius of drop at any instant t is shown by

$$r=\{3(V_0+vt)/4\pi\}^{1/3},$$

and therefore the surface area q of drop is seen to be

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(12) W. M. MacNevin and E. W. Balis, *J. Am. Chem. Soc.*, **65**, 660 (1943).

(13) G. S. Smith, *Trans. Faraday Soc.*, **47**, 63 (1951).

(14) D. Ilkovic, *Collection Czech. Chem. Communs.*, **8**, 13 (1936).

$$q=4\pi\cdot(3/4\pi)^{2/3}\cdot(V_0+vt)^{2/3}, \tag{40}$$

and the residual surface area q_0 is demonstrated by

$$q_0=4\pi(3V_0/4\pi)^{2/3}. \tag{41}$$

Hence the instantaneous current intensity at the dropping electrode is manifested by

$$i=nF\cdot q_0\cdot\left(1+\frac{v}{V_0}t\right)^{2/3}\cdot(k_1{}^*C_1-k_2{}^*C_2)$$
$$\times\exp s^2t\cdot(1-\operatorname{erf} s\sqrt{t}). \tag{42}$$

From this equation, the current which flows at the instant when the preceding drop has just fallen off is given by

$$i_{t=0}\simeq nFq_0(k_1{}^*C_1-k_2{}^*C_2). \tag{43}$$

According to the Ilkovic theory, it is known that

$$i\infty t^{1/6},$$

and hence it follows that

$$i_{t=0}=0. \tag{44}$$

Many oscillographic observations,⁽¹⁰⁾ however, indicate that the current intensity at $t=0$ does not diminish away to zero, but shows a finite, although small, value. Differentiating Eq. (42) with respect to the time and putting $t=0$ gives

$$(\mathrm{d}i/\mathrm{d}t)_{t=0}=-\infty. \tag{45}$$

It is required by the Ilkovic theory that

$$(\mathrm{d}i/\mathrm{d}t)_{t=0}=+\infty, \tag{46}$$

which does not agree with the oscillogaphic findings. For the large value of t, since vt is much greater than V_0, it follows from Eqs. (22) and (42) that

$$i\simeq nF\cdot4\pi(3/4\pi)^{2/3}\cdot(vt)^{2/3}\cdot D_1$$
$$\{{}^*C_1-{}^\circ C_1\,(\text{fin.})\}/\sqrt{\pi D_1t}, \tag{47}$$

which is completely in accordance with the old theory of Ilkovic,⁽⁵⁾ neglecting the effect of compressions of the diffusion layer by the expansion of mercury drop.

It may be concluded that the instantaneous current at the dropping electrode starts from a certain small value given by Eq. (43) and at first decreases rapidly but soon it begins to increase as indicated by Eq. (42) and finally becomes asymptotically identical with that predicted by the Ilkovic theory. Such a course of current change as is reported by McKenzie⁽¹⁵⁾ and by us⁽¹⁰⁾ is first comprehensible from our theory which takes the diffusion process and the electrode reaction into consideration at the same time.

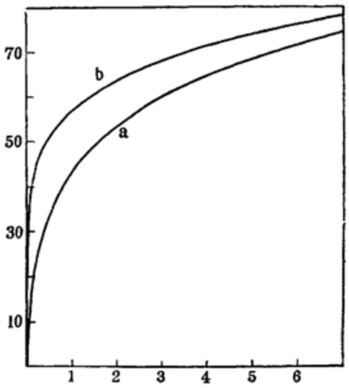

Fig. 3.—Current-time curve at the dropping electrode.

In the Table are given the numerical values of the functions appearing in Eqs. (42) and (47). For the sake of simplicity, it is assumed that $s=1$ and $v/V_0=10^3$. Randles⁽¹⁶⁾ gives the value 6×10^{-3} for the electrode reaction constant of zinc ion in potassium chloride solution. The internal radius of capillary electrode is said to be about 20~30 μ, and v under the ordinary condition is about 10^{-4} cc./sec. Curve (a) in Fig. 3 shows the theoretical current-time curve plotted according to Eq. (42) and curve (b) is drawn by Eq. (47). In the above considerations the effects produced by the convection of solution due to the expansion⁽⁵~⁸⁾ of drop and by the curvature⁽⁹~¹¹⁾ of mercury drop are ignored; it may be said, however, that the reason why the current intensity increases very slowly in the infancy of drop-life is cleared up.

Randles⁽¹⁶⁾ states that the rate constant k decreases remarkably with the addition of gelatine. On the other hand, it is well known that the mobility of an ion, and hence the diffusion coefficient, are hardly effected thereby.⁽¹⁷⁾ It is noteworthy that the polarographic current-time curve is much effected by the addition of gelatine, as observed by us⁽¹⁰⁾; this will be elucidated by the above theory which regards the electrode reaction as an ensemble of the diffusion and electrode process.

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(15) H. A. McKenzie, *J. Am. Chem. Soc.*, **70**, 3147 (1948).

(16) J. E. B. Randles, *Discuss. Faraday Soc.*, No. 1., 11 (1947).

(17) H. Ulich, "Elektrische Leitfähigkeit. Flüssigkeiten und Lösungen" in "Hand- und Jahrbuch der chemischen Physik" herausgegeben von A. Eucken und K. L. Wolf. Bd. 6/Abschnitt II. (1933) S. 150.

Note:—(1) The investigation by Koutecky and Brdicka[18] on the reaction current is the direct motive for the present paper. In their communication the numerical value of the integral defined by

$$f(y_1)=\int_0^{y_1} y^{2/3}\cdot\exp y\cdot(1-\mathrm{erf}\sqrt{y})\cdot dy$$

is tabulated, and this tabulation may be convenient for the study of the polarographic mean diffusion current; but it is pointed out that this table contains some miscalculations.[19]

(2) In the monograph by Frank and v. Mises,[20] the special case that is shown by

$$k_1=k_2=D^*;\ \ D_1=D_2=D;\ \ {}^*C_2=0:$$

is discussed. This condition corresponds to the problem of diffusion through a diaphragm, and its conclusion is immediately obtainable from Eq. (18).

Summary

The differential equation of linear diffusion was solved with the boundary condition controlled by the chemical kinetics. The result obtained gives the rate of the consecutive reaction consisting of the diffusion process and the electrode process. This theory can explain the course of the polarographic current-time curve very well.

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[18] J. Koutecky and R. Brdicka, *Collection Czech, Chem. Communs.*, **12**, 337 (1947).

[19] J. Koryta, *Proceedings of the I. Intern. Polarographic Congress in Prague*, Part 1., p. 794, 798. (1951)

[20] Reference 4, p. 237.