Polarographic Diffusion Current Observed with Square Wave Voltage. III. Applications of the Theory

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In Part I of this study,[1] the change of diffusion current produced by the discontinuous change of the electrode potential is discussed, and further in Part II the theory for the electrolysis with a square wave voltage is developed.[1] The conclusion thereof is, employing the same symbols as in the previous studies, that the concentration gradient of the depolarizer at the electrode surface is demonstrated by

$$\left(\frac{\partial C}{\partial x}\right)_{x=0}=\frac{{}^{*}C-{}^{\circ}_{1}C}{\sqrt{\pi Dt}}+\sum_{n=1}^{n}(-1)^{n+1}\frac{{}^{\circ}_{1}C-{}^{\circ}_{2}C}{\sqrt{\pi D(t-nT)}} \tag{1}$$

The instantaneous current intensity i, on the other hand, is shown by

$$i=nFqD(\partial C/\partial x)_{x=0}. \tag{2}$$

Now, writing

$$\alpha={}^{*}C-{}^{\circ}_{1}C\,;\quad \beta={}^{\circ}_{2}C-{}^{\circ}_{1}C\,; \tag{3}$$

$$k=nFq\sqrt{D/\pi}\,; \tag{4}$$

it is seen that

$$I=\frac{i}{k}=\frac{\alpha}{\sqrt{t}}+\sum_{n=1}^{n}(-1)^{n}\frac{\alpha}{\sqrt{t-nT}}\ . \tag{5}$$

Further, for the sake of convenience in the following discussions, some quantities will be introduced as follows. Let i_1 be the diffusion current observed when the electrolysis is

1) T. Kambara, This Bulletin, **27**, 523, 527 (1554).

continuously executed with the constant voltage E_1; then it is seen that

$$i_1=\frac{nFq\sqrt{D}}{\sqrt{\pi t}}\,({}^{*}C-{}^{\circ}_{1}C)=\frac{k\alpha}{\sqrt{t}}, \tag{6}$$

where ${}^{\circ}_{1}C$ is the equilibrium interfacial concentration of depolarizer corresponding to the voltage E_1. Therefore the mean value of the current intensity in the time interval from $t=0$ to $t=t_1$ is shown by

$$\bar{i}_1=\frac{1}{t_1}\int_0^{t_1} i_1\cdot dt=\frac{2k\alpha}{\sqrt{t_1}}. \tag{7}$$

An analogous discussion holds also for the electrolysis with the steady voltage E_2, where it is found that

$$i_2=\frac{k(\alpha-\beta)}{\sqrt{t}}; \tag{8}$$

$$\bar{i}_2=\frac{1}{t_1}\int_0^{t_1} i_2\cdot dt=\frac{2k(\alpha-\beta)}{\sqrt{t_1}}. \tag{9}$$

These can be readily seen, since ${}^{\circ}_{2}C$ implies the equilibrium interfacial concentration corresponding to the constant voltage E_2. Thus from these equations it follows that

$$\beta=\frac{\sqrt{t_1}}{2k}(\bar{i}_1-\bar{i}_2)=\frac{\sqrt{t}}{k}(i_1-i_2). \tag{10}$$

Next, some conclusions derived from the theory will be compared with several experimental findings in the section below.

Experiment of Madame Fournier

In the recording of polarographic current-voltage curve, Fournier[2] has experimented while a suitable alternating voltage is superposed onto the constant voltage, which increases negatively as is usual in polarography. The result of her experiment is well understood when the superposed sine-wave voltage is regarded to be equivalent to a square wave voltage of suitable amplitude and frequency. Now, we will compute the mean current which flows during the time interval shown by

$$t_1=2mT, \quad (m\text{: an integer}) \tag{11}$$

where T represents, as in the previous papers, the half-period, and in the case of the dropping mercury electrode t_1 corresponds to the drop time. Eq. (5) can be written as

$$I=\frac{\alpha}{\sqrt{t}}+\beta\Big(\frac{-1}{\sqrt{t-T}}+\frac{1}{\sqrt{t-2T}}+\frac{-1}{\sqrt{t-3T}}+\cdots\cdots+\frac{1}{\sqrt{t-(2m-2)T}}+\frac{-1}{\sqrt{t-(2m-1)T}}\Big)$$

Thus the integrated value of I is given by

$$\int_0^{t_1} I\cdot dt=\int_0^{t_1}\frac{\alpha}{\sqrt{t}}dt+\beta\Big(\int_T^{t_1}\frac{-dt}{\sqrt{t-T}}+\int_{2T}^{t_1}\frac{dt}{\sqrt{t-2T}}+\cdots\cdots+\int_{(2m-2)T}^{t_1}\frac{dt}{\sqrt{t-(2m-2)T}}+\int_{(2m-1)T}^{t_1}\frac{-dt}{\sqrt{t-(2m-1)T}}\Big),$$

where the lower limits of the integrals take the values: 0, T, $2T$, ……, etc., because each term containing $(t-nT)^{-1/2}$ in the summation in Eq. (5) must vanish away for $t<nt$ owing to the property of the translated function. Upon executing the integrations, it is found that

$$\int_0^{t_1} I\cdot dt=2\alpha\sqrt{2mT}-2\beta\sqrt{T}\,(\sqrt{2m-1}+\sqrt{2m-3}+\cdots\cdots+\sqrt{3}+\sqrt{1})+2\beta\sqrt{T}\,(\sqrt{2m-2}+\sqrt{2m-4}+\cdots\cdots+\sqrt{4}+\sqrt{2}).$$

For the large value of m, the approximate values of the series appearing in this equation can be estimated by performing integration instead of the summation as follows.

$$\sum_{m=1}^{m}\sqrt{2m-1}\simeq\int_1^m\sqrt{2}\Big(m-\frac{1}{2}\Big)^{1/2}\cdot dm=\frac{2\sqrt{2}}{3}\Big\{\Big(m-\frac{1}{2}\Big)^{3/2}-\Big(\frac{1}{2}\Big)^{3/2}\Big\};$$

$$\sum_{m=2}^{m}\sqrt{2m-2}\simeq\int_2^m\sqrt{2}\,(m-1)^{1/2}\cdot dm=\frac{2\sqrt{2}}{3}\Big\{(m-1)^{3/2}-1\Big\}.$$

Hence we obtain

$$\int_0^{2mT} I\cdot dt\simeq 2\alpha\sqrt{2mT}-2\beta\sqrt{T}\cdot\frac{2\sqrt{2}}{3}\Big\{\Big(m-\frac{1}{2}\Big)^{3/2}-(m-1)^{3/2}+1-\Big(\frac{1}{2}\Big)^{3/2}\Big\}.$$

Therefore, upon regarding m to be very large and applying the familiar binomial theorem, the mean value of Fournier current is shown by

$$\bar{i}_F=\frac{k}{2mT}\int_0^{2mT} I\cdot dt=\frac{2k\alpha}{\sqrt{2mT}}-\frac{4k\beta}{3}\cdot\frac{\sqrt{2T}}{2mT}\Big(\frac{3\sqrt{m}}{4}+\frac{\sqrt{8}-1}{\sqrt{8}}\Big). \tag{12}$$

Inserting Eqs. (7), (10) and (11) into (12) gives

$$\bar{i}_F=\bar{i}_1-\frac{2}{3}(\bar{i}_1-\bar{i}_2)\Big\{\frac{3}{4}+\frac{\sqrt{8}-1}{\sqrt{8m}}\Big\},$$

which, again owing to the large value of m, can be simplified into

$$\bar{i}_F=\frac{1}{2}(\bar{i}_1+\bar{i}_2). \tag{13}$$

On the other hand, the equation for the polarographic wave due to the reversible electrode reaction is, upon employing the usual notations, demonstrated by

$$\left.\begin{aligned}\bar{i}&=\frac{\bar{i}_d}{2}(1+\tanh\xi);\\ \xi&=\frac{1}{2}\cdot\frac{nF}{RT}(-E+E_{1/2}).\end{aligned}\right\} \tag{14}$$

In the Fournier's investigation, it can be written that

$$E_1=E-\varDelta E;\quad E_2=E+\varDelta E;\ (\varDelta E>0) \tag{15}$$

i. e.

2) M. Fournier, *Compt. rend.*, **232**, 1673 (1951).

$$\left.\begin{aligned}\xi_1=\xi-\Delta\xi\,;\quad \xi_2=\xi+\Delta\xi\,;\\ \Delta\xi=\frac{1}{2}\cdot\frac{nF}{RT}\cdot\Delta E.\end{aligned}\right\}\qquad(16)$$

Accordingly the Fournier's current-voltage curve is manifested by

$$\bar{i}_F=\frac{\bar{i}_d}{4}\{2+\tanh(\xi-\Delta\xi)+\tanh(\xi+\Delta\xi)\}.\qquad(17)$$

Then, since we have

$$\tanh\xi=-\tanh(-\xi),$$

it is found that the curve:

$$\bar{i}_F-\frac{\bar{i}_d}{2}=\frac{\bar{i}_d}{4}\{\tanh(\xi-\Delta\xi)+\tanh(\xi+\Delta\xi)\}$$

$$=-\frac{\bar{i}_d}{4}\{\tanh(-\xi-\Delta\xi)+\tanh(-\xi+\Delta\xi)\}$$

has a point of symmetry shown by

$$\bar{i}_F=\bar{i}_{d/2}\,;\quad \xi=0\,;\quad E=E_{1/2}\,;\qquad(18)$$

which is, of course, identical with the usual half-wave point.

Further the following relations are also found:

$$\left.\begin{aligned}\bar{i}_F=\bar{i}_d\quad\text{for}\quad E=-\infty\,;\ \xi=\infty\,;\\ \bar{i}_F=0\quad\text{for}\quad E=\infty\,;\quad \xi=-\infty\,;\end{aligned}\right\}\qquad(19)$$

Next the inclination of the Fournier's polarogram at the half-wave potential is given by

$$-\left(\frac{d\bar{i}_F}{dE}\right)_{E=E1/2}=\frac{\bar{i}_d nF}{4RT}\cdot\frac{1}{\cosh^2\Delta\xi}\,;\qquad(20)$$

whereas that of the ordinary polarogram is, as is well known, given by

$$-\left(\frac{d\bar{i}}{dE}\right)_{E=E1/2}=\frac{\bar{i}_d nF}{4RT}.\qquad(21)$$

Thus it can be concluded that the inclination is made less steep by the superposition of an alternating voltage. The above derived theoretical conclusions have all been confirmed experimentally by Fournier in the case of reversible electrode reaction, e. g. the cathodic reduction of monovalent metal ion; the general aspect of Fournier current is illustrated in Fig. 1.

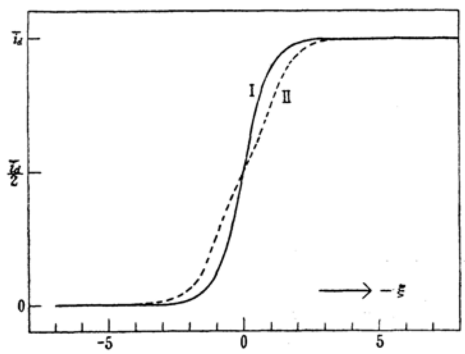

Fig. 1. Curve I shows the ordinary polarogram, and curve II shows the Fournier's polarogram drawn theoretically with the value $\Delta\xi=2$ [Cf. Eqs. (14)–(17)].

Kalousek Apparatus

In the apparatus designed by Kalousek,[3] the electrolysis is performed by applying a square wave voltage; viz. at first the electrolysis is carried out with the potential E_1 for T sec. and then the potential is discontinuously changed to a more positive value E_2; i. e.

$$E_2>E_1,\qquad(22)$$

and it may be supposed that the reversibility of the electrode process is to be judged by the intensity of the oxidation current. And thus in this apparatus, it is so designed that only the current flowing during the application of the more positive potential E_2 is recorded by the galvanometer. In order to clear up the observations obtained with this apparatus, at first, we must compute the integrated value of the current, which flows in the half-period shown by

$$E=E_2\,;\ (2m+1)T<t<(2m+2)T\ \ (m\text{: integer})\qquad(23)$$

It follows from Eq. (5) that

$$\int_{(2m+1)T}^{(2m+2)T}I\cdot dt=\int_{(2m+1)T}^{(2m+2)T}\frac{\alpha}{\sqrt{t}}\cdot dt$$

$$+\sum_{n=1}^{2m+1}\int_{(2m+1)T}^{(2m+2)T}(-1)^n\cdot\frac{\beta}{\sqrt{t-nT}}\cdot dt$$

$$=2\alpha(\sqrt{2m+2}-\sqrt{2m-1})\sqrt{T}$$

$$+2\beta\sqrt{T}(\sqrt{2m}+\sqrt{2m-2}+\cdots\cdots+\sqrt{2})$$

$$-2\beta\sqrt{T}(\sqrt{2m-1}+\sqrt{2m-3}+\cdots\cdots+\sqrt{3}+\sqrt{1})$$

$$-2\beta\sqrt{T}(\sqrt{2m+1}+\sqrt{2m-1}+\cdots\cdots+\sqrt{3}+\sqrt{1}).$$

$$+2\beta\sqrt{T}(\sqrt{2m}+\sqrt{2m-2}+\cdots\cdots+\sqrt{2})$$

As shown in the preceding section, for the large value of m, it can be written that

$$\sum_{m=1}^{m}m^{1/2}\simeq\int_1^m m^{1/2}\cdot dm=\frac{2}{3}(m^{3/2}-1)\,;$$

$$\sum_{m=1}^{m}(2m-1)^{1/2}\simeq\int_1^m(2m-1)^{1/2}\cdot dm=\frac{1}{3}\{(2m-1)^{3/2}-1\}\,;$$

$$\sum_{m=1}^{m}(2m+1)^{1/2}\simeq\int_1^{m+1}(2m+1)^{1/2}\cdot dm=\frac{1}{3}\{(2m+1)^{3/2}-1\}\,;$$

i. e. the summation is replaced approximately by integration. Thus with the aid of binomial theorem, it is seen that

$$\int_{(2m+1)T}^{(2m+2)T}I\cdot dt=2\alpha\sqrt{T}(\sqrt{2m+2}-\sqrt{2m+1})$$

$$+\frac{4\beta\sqrt{2T}}{3}\left\{2m^{3/2}-2-\left(m-\frac{1}{2}\right)^{3/2}-\left(m+\frac{1}{2}\right)^{3/2}\right.$$

$$\left.+\frac{1}{\sqrt{2}}\right\}\simeq2\alpha\sqrt{T}(\sqrt{2m+2}-\sqrt{2m+1})$$

$$+\frac{4\beta\sqrt{2T}}{3}\left(\frac{1}{\sqrt{2}}-2\right).\qquad(23)$$

Now we must evaluate the integrated value of the total current which flows under the application of potential E_2 during the time interval given by

$$t_1=2(m+1)T.\qquad(24)$$

Then it is seen that

3) M. Kalousek, *Collection Czech. Chem. Communs.*, **13**, 105 (1948).

$$\sum_{m=0}^{m}\int_{(2m+1)T}^{(2m+2)T} I\cdot dt=\sum_{m=0}^{m}2\alpha\sqrt{T}(\sqrt{2m+2}-\sqrt{2m+1}$$
$$+(m+1)\frac{4\beta}{3}\sqrt{2T}\left(\frac{1}{\sqrt{2}}-2\right),$$

where it can be shown approximately that

$$\sum_{m=0}^{m}(\sqrt{2m+2}-\sqrt{2m+1})$$
$$\simeq\frac{2\sqrt{2}}{3}\left(\frac{3}{4}m^{1/2}-\frac{\sqrt{8}-1}{\sqrt{8}}\right)\simeq\left(\frac{m}{2}\right)^{1/2},$$

in which the summation is again replaced by integration. Therefore the Kalousek's mean current which flows during the half periods, in which the potential E_2 is applied, is demonstrated by

$$\bar{i}_K=k\sum_{m=0}^{m}\int_{(2m+1)T}^{(2m+2)T} I\cdot dt\Big/t_1$$
$$=\frac{k\alpha}{\sqrt{t_1}}\left(\frac{m}{m+1}\right)^{1/2}-\frac{4k\beta}{3}\left(2-\frac{1}{\sqrt{2}}\right)\frac{1}{\sqrt{2t_1T}}, \qquad (25)$$

where the quantity $\sqrt{m/m+1}$ can be regarded to be nearly unity for the large value of m. Hence, upon inserting Eqs. (7) and (10) into this equation, it is seen that

$$\left.\begin{aligned}\bar{i}_K&=\frac{1}{2}\bar{i}_1=\frac{s}{\sqrt{2T}}(\bar{i}_1-\bar{i}_2)\,;\\ s&=\frac{2}{3}\left(2-\frac{1}{\sqrt{2}}\right)=1.195\end{aligned}\right\} \qquad (26)$$

Eurther the frequency of applied square wave voltage will be introduced according to

$$f=1/2T, \qquad (27)$$

which is equal to the number of revolutions of rotating switch per second. Then it is manifest that

$$\bar{i}_K=\frac{1}{2}\bar{i}_1-s\sqrt{f}(\bar{i}_1-\bar{i}_2), \qquad (28)$$

which is the fundamental equation for the Kalousek current provided that the electrode reaction proceeds reversibly.

The changes of the cathode potential with time due to the employment of Kalousek apparatus Ia, II and III are schematically illustrated in Fig. 2. In the case of apparatus I, it is so designed that the potential E_2 is always kept more positive by a constant value ΔE than the potential E_1; i. e.

$$E_2=E_1+\Delta E. \qquad (29)$$

Accordingly it can be readily found that

$$\bar{i}_1-\bar{i}_2=\Delta\bar{i}=(d\bar{i}/dE)\cdot(-\Delta E), \qquad (30)$$

and further it is clear that the potential E_1 is increased negatively with time, as is usual in polarography. Thus $\bar{i}_1$ is shown by Eq. (14) demonstrating the ordinary polarographic wave. Therefore, it can be readily seen that

$$\bar{i}_K(I\alpha)=\frac{1}{2}\bar{i}-s\sqrt{f}\left(\frac{d\bar{i}}{dE}\right)\cdot(-\Delta E)\,; \qquad (31)$$

viz. the curve observed with the apparatus Ia is the superposition of two currents, namely (1) the current-voltage curve registered with the half decreased sensitivity of a galvanometer, and (2) the derivative curve thereof multiplied by the factor $(-s\sqrt{f})$. It is derived from Eq. (31) that a deep valley due to the oxidation current should be observed near the half-wave potential, which is in complete accordance with Kalousek's findings. Further it is seen that at a sufficiently negative potential, the Kalousek current is just one half the limiting diffusion current (cf. Fig. 3).

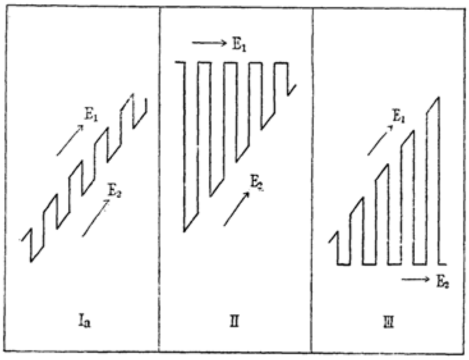

Fig. 2. Changes of the electrode potential with time in the Kalousek's apparatus.

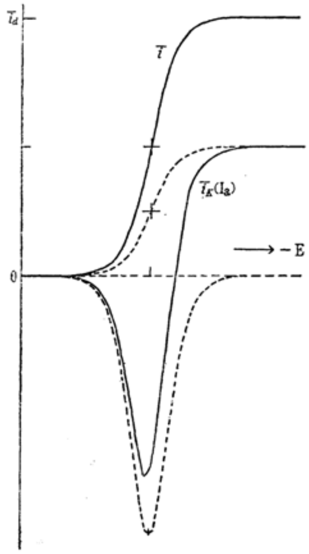

Fig. 3. Kalousek polarogram Ia.

Next in the apparatus II, the potential E_1 is fixed at such a negative value that the limiting current $\bar{i}_d$ is observable, whereas E_2 is increased negatively. Thus from Eq. (28) it follows that

$$\bar{i}_K(\mathrm{II})=\left(\frac{1}{2}-s\sqrt{f}\right)\bar{i}_d+s\sqrt{f}\,\bar{i}. \qquad (32)$$

This conclusion shown in Fig. 4 is quite in harmony with the experiment.

Eurther, in the apparatus III, the potential E_2 is fixed at such a positive value that no appreciable reduction occurs, i. e.

$$\bar{i}_2=0,$$

whereas E_1 is increased negatively. Thus it is seen that

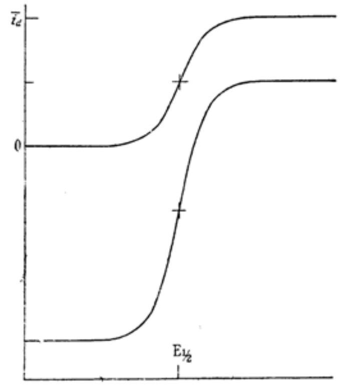

Fig. 4. Kalousek polarogram II.

$$\bar{i}_K(\mathrm{III}) = -\left(s\sqrt{f} - \frac{1}{2}\right)\bar{i}. \qquad (33)$$

This equation also agrees well with the Kalousek's observation, and is illustrated in Fig. 5.

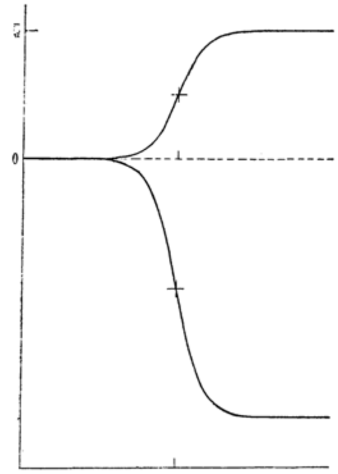

Fig. 5. Kalousek polarogram III.

Ishibashi-Fujinaga Apparatus

In I–F apparatus[4] aiming at the differential polarography and the increased sensitivity, a square wave voltage is applied by means of a rotating switch as in the Kalousek apparatus; furthermore, the rotating current alternator makes the current, flowing under the application of potential E_2, run through the galvanometer in the reverse direction, which is opposite ta the direction of the current flowing while the potential is E_1. This is, as it were, a full-wave rectification of the electrolytic current observed with a square wave voltage. Thus, in order to treat this problem theoretically, it is needed to compute the mean current which flows in the half-period shown by

$$E = E_1;\ 2mT < t < (2m+1)T\ (m;\ \text{integer}) \qquad (34)$$

Therefore, at first, we must evaluate the quantity:

$$\sum_{m=0}^{m}\int_{2mT}^{(2m+1)T} I\cdot dt.$$

This calculation is to be executed as is seen in Eqs. (23) and (25); but this is much more simply performable as shown below. When the time interval given by

$$t_1 = (2m+2)T$$

is considerably long, it is already seen that (cf. Eq. (13))

$$\frac{1}{t_1}\int_0^{t_1} i\cdot dt = \bar{i}_F = \frac{1}{2}(\bar{i}_1 + \bar{i}_2).$$

On the other hand, there is no doubt that the following relationship holds.

$$\bar{i}_F = \frac{1}{t_1}\sum_{m=0}^{m}\left\{\int_{2mT}^{(2m+1)T} i\cdot dt + \int_{(2m+1)T}^{(2m+2)T} i\cdot dt\right\}, \qquad (35)$$

Thus it follows from the Eqs. (13), (26) and (35) that

$$\frac{1}{t_1}\sum_{m=0}^{m}\int_{2mT}^{(2m+1)T} i\cdot dt = \bar{i}_F - \bar{i}_K$$

$$= \frac{1}{2}\bar{i}_2 + s\sqrt{f}(\bar{i}_1 - \bar{i}_2). \qquad (36)$$

Hence the mean current observed with I–F apparatus is clearly given by

$$\bar{i}_{IF} = \frac{1}{t_1}\sum_{m=0}^{m}\left\{\int_{2mT}^{(2m+1)T} i\cdot dt - \int_{(2m+1)T}^{(2m+2)T} i\cdot dt\right\}$$

$$= \left(2s\sqrt{f} - \frac{1}{2}\right)(\bar{i}_1 - \bar{i}_2). \qquad (37)$$

In the differential apparatus, it is so arranged that

$$\Delta E = E_2 - E_1 = \text{const.}$$

Therefore, from Eq. (30) it follows that

$$\bar{i}_{IF}(\text{diff.}) = \left(2s\sqrt{f} - \frac{1}{2}\right)\cdot\left(\frac{d\bar{i}}{dE}\right)\cdot(-\Delta E). \qquad (38)$$

Thus the sensitivity of the derivative curve increases, when the revolution number of a rotating switch is elevated and when a large ΔE is chosen. It is seen that if $f = 16$ c./sec. the height of the peak of the derivative curve is about ten times greater than $\Delta\bar{i}$ corresponding to the given value of ΔE. Next in the I–F apparatus for the increased sensitivity, the potential E_2 is so chosen that no appreciable cathodic current flows; i.e.

$$\bar{i}_2 = 0. \qquad (39)$$

On the other hand, $\bar{i}_1$ is the current intensity corresponding to the ordinary polarographic wave and is given by Eq. (14). Hence it follows that

$$\bar{i}_{IF}(\text{incr.}) = \left(2s\sqrt{f} - \frac{1}{2}\right)\cdot\bar{i}; \qquad (40)$$

i. e. the observed polarogram exhibits the same effect, that is to be seen with the increased sensitivity of the galvanometer employed; such an effect of increasing the sensitivity, however, depends clearly on the reversibility of the electrode process.

Note—In the above discussions, in which the current intensities under several experimental conditions are well comprehensible from the present theoretical considerations, the reversibility

4) M. Ishibashi and T Fujinaga, This Bulletin, **25**, 68, 238 (1952).

of electrode reaction is always assumed. Accordingly deviations of experimental results from the theoretical conclusion are obviously due to the irreversible character of the process concerned; and hence the degree of such a deviation may be a rational measure of the irreversibility.

The above theory is developed based on the assumption that a stationary plane electrode is employed; thus it may not be quite adequate to apply the theory to the phenomenon obtained with a dropping electrode. But, since the equation for the diffusion current at a plane electrode differs from the Ilkovic equation only by a numerical factor, the present theory seems to be approximately correct. Were it possible to perform the calculation taking the effects due to the curvature and expansion of mercury drop into consideration, although mathematically very hard, it would be a strictly correct.

When in the above treatment the changes of the mercury drop surface given by

$$q=0.85\cdot m^{2/3}\cdot t^{2/3}$$

is employed, then we have the definite integral of the form:

$$\int_{nT}\frac{t^{2/3}\cdot dt}{\sqrt{t-nT}}=\int_{0}\frac{(t'+nT)^{2/3}}{\sqrt{t'}}\cdot dt',$$

which can not be evaluated rationally. But in this integral the effect of the denominator is far greater than that of numerator, so that the error produced by the assumption that the surface area is independent of time may not be very serious.

Summary

The theoretical treatment given in the previous works on the electrolysis with square wave voltage is here applied to the elucidation of experimental results. Thus the experiment by Madame Fournier is satisfactorily explained, and further the findings obtained with Kalousek's and Ishibashi-Fujinaga's apparatus are also rationally clarified.

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