Theoretical Study on the Polarographic Limiting Currents. I. Revised Equation for the Diffusion Currents*

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Criticism of the Revised Equations Already Reported

Recently H. Strehlow and M. von Stackelberg,⑴ J. J. Lingane and B. A. Loveridge⑵ and T. Kambara, M. Suzuki and I. Tachi,⑶ taking the curvature of dropping mercury electrode into consideration, derived the following revised expression of Ilkovič equation representing the mean diffusion current $\overline{i_d}(\mu A)$.

$$\overline{i_d}=607n^*CD^{1/2}m^{2/3}\tau^{1/6}(1+AD^{1/2}m^{-1/3}\tau^{1/6}) \tag{1}$$

In this equation, $n, {}^*C, D, m$ and τ are the number of electrons associated with the electrode reaction, the concentration of depolarizer in the bulk of solution in millimol/l, the diffusion constant of depolarizer in cm.^{2}/sec., the rate of flow of mercury in mg./sec. and the drop time in sec., respectively; A is a coefficient of interest to be discussed.

Strehlow and von Stackelberg have obtained the value $A=17$, upon solving the so-called Stackelberg's integral equation⑷ representing the "differential thickness of diffusion layer" denoted by δ.⑸ It seems, however, that the conclusion $A=17$ has not a good theoretical ground owing to the error contained in the integral equation employed by them, as given below. They define the "integral thickness of diffusion layer", denoted by $\varDelta$, by the relationship:

$$\varDelta=\frac{2}{{}^*C}\int_{r_0}^{\infty}({}^*C-C)dr \tag{2}$$

and upon assuming that $4\pi r_0^2\cdot\varDelta$ is proportional to the total amount of reduction product, they derive

$$\varDelta=\frac{2D}{r_0^2}\int_0^t r_0^2\delta^{-1}dt \tag{3}$$

where t is the time. These assumptions stated by them are not right in tri-dimensional problem, although they are legitimate in unidimensional one. This can be readily seen, when we treat a stationary spherical electrode, in which the quantity $4\pi r_0^2\varDelta$ is clearly not proportional to the amount of reduction product, and thus Eq. (3) does not hold. In order to define the integral thickness of diffusion layer in such a rational way, as Eq. (3) can hold in the case of stationary spherical electrode, we should use the following equation instead of Eq. (2).

$$\varDelta'=\frac{2}{{}^*Cr_0^2}\int_{r_0}^{\infty}({}^*C-C)r^2dr \tag{4}$$

It can be shown that in the case of diffusion at a stationary spherical electrode $\varDelta'$ and δ are given by

$$\varDelta'=4\sqrt{\frac{Dt}{\pi}}\left(1+\frac{\sqrt{\pi Dt}}{2r_0}\right) \tag{5}$$

$$\frac{1}{\delta}=\frac{1}{r_0}+\frac{1}{\sqrt{\pi Dt}} \tag{6}$$

Elimination of t from Eqs. (5) and (6) leads to the relationship between $\varDelta'$ and δ, which holds for the stationary electrode of spherical form; thus it is found that

$$\varDelta'=\frac{4}{\pi}\frac{r_0\delta}{r_0-\delta}\left(1+\frac{\delta}{2(r_0-\delta)}\right) \tag{7}$$

If we assume that Eq. (7) holds for the diffusion at the dropping electrode, upon eliminating $\varDelta'$ from Eqs. (3) and (7), we obtain the following integral equation:

$$\pi D\int_0^t r_0^2\delta^{-1}dt=r_0^3\left\{2\frac{\delta}{r_0-\delta}+\left(\frac{\delta}{r_0-\delta}\right)^2\right\} \tag{8}$$

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⑴ H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

⑵ J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.* **72**, 438 (1950).

⑶ T. Kambara, M. Suzuki and I. Tachi, This Bnlletin **23**, 219 (1950).

⑷ M. von Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

⑸ The differential thickness of diffusion layer is defined as follows:

$$\delta={}^*C/(\partial C/\partial r)_{r=r_0}$$

In this equation, C, r_0 and r are the concentration of depolarizer at an arbitrary point in the diffusion layer, the radius of mercury drop and tbe distance of any point from the center of drop, respectively.

This equation is the Stackelberg's integral equation determining the thickness δ in the case of spherical diffusion at a mercury drop expanding symmetrically. This equation has been already derived by Kambara, Suzuki and Tachi,(3) and upon solving this equation by means of an approximate calculation, they have shown the value of A to be 29.3.(6) The present author expands the quantity δ into the power series of $(m^{-1/3}D^{1/2}t^{1/6})$; i. e.

$$\delta=(D^{1/2}t^{1/2})\sum_{j=0}^{\infty}\beta_j(m^{-1/3}D^{1/2}t^{1/6}),$$

and then by comparing the means of comparison of coefficients, the β's are determined; thus Eq. (8) can be solved more precisely and the value of $A=31.2$ is obtained.

The above stated procedures are all based on the assumption that Stackelberg's integral equation, i. e. Eq. (7) showing the relationship between the differential and integral thicknesses of diffusion layer at a stationary spherical electrode, is valid even in the case of a dropping electrode. However, this assumption seems to have no theoretically concrete basis.

On the other hand, the intuitive consideration of Lingane and Loveridge(2) gave the value $A=39$. Kambara and Tachi(7) approximately solved the differential equation proposed by D. MacGillavry and E. K. Rideal(8) and the result was $A=39$; but the accuracy of this approximate calculation seems considerably inferior.

On account of these circumstances, it may be significant to consider here again the theoretical revision of Ilkovič equation. In this paper the solution of MacGillavry-Rideal differential equation by means of the method, that has been employed in the field of hydrodynamics by Th. von Kárman(9) and K. Pohlhausen(10) in order to evaluate the velocity distribution in the boundary layer, will be demonstrated and the expression for the limiting diffusion current will be shown. Further, the shielding effect of capillary will be considered theoretically. Finally, the revised Ilkovič equation representing the diffusion current in amalgam polarography will be also shown.

Theoretical Derivation of the Revised Equation for the Diffusion Current

The movement of solution in the vicinity of mercury drop appears to be very complicated; now let us assume that the solution around the mercury drop is pushed away by the concentric expansion of drop, the volume of which increases at a constant rate. Then we can find $C(r,t)$ the concentration of depolarizer in the diffusion layer, by solving the following MacGillavry-Rideal differential equation:

$$\frac{\partial C}{\partial t}=D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C}{\partial r} \qquad (9)$$

where

$$a=(3m/4\pi d,^{1/3}$$

In this equation d represents the density of mercury at 25°C.

The initial and boundary conditions are clearly given by

$$C={}^*C \quad \text{for} \quad t=0,\ r>r_0;$$
$$C=0 \quad \text{for} \quad r=r_0,\ t>0;$$
$$C={}^*C,\ r^2\frac{\partial C}{\partial r}=0 \quad \text{for} \quad r\to\infty,\ t>0.$$

${}^*C$ represents here the concentration of depolarizer in the bulk of solution, and the radius of mercury drop r_0 is given by

$$r_0=at^{1/3}=\left(\frac{3}{4\pi d}\right)^{1/3}m^{1/3}t^{1/3}=0.260m^{1/3}t^{1/2}(\text{mm})$$

Upon multiplying the both sides of Eq. (9) by r^2, and integrating the equation thus obtained with respect to r from r_0 to infinity, it can be readily seen that

$$\frac{\partial}{\partial t}\int_{r_0}^{\infty}({}^*C-C)r^2dr=Dr_0{}^2\left(\frac{\partial C}{\partial r}\right)_{r=r_0}.$$

Since the diffusion constant of depolarizer is very small, the inhomogeneity of concentration distribution occurs only in the vicinity of electrode surface; therefore, the integration interval from r_0 to infinity shown in the above equation may be replaced by that from r_0 to $\delta'(t)$, resulting in no appreciable deviation. Here, $\delta'(t)$ is a function of time, and represents the thickness of layer, in which the inhomogeneity of concentration arises, i. e. the thickness of diffusion layer. Writing

$$r=r_0+x,$$

then it is found that

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(6) T. Kambara and I. Tachi, This Bulletin, **25**, 284 (1952).

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

(8) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(9) Th. von Karman, *Z. angew. Math. u. Mech.*, **1**, 233 (1921).

(10) K. Pohlhausen, ibid., **1**, 252 (1921).

$$\frac{\partial}{\partial t}\int_0^{\delta'}(*C-C)(r_0+x)^2dx = Dr_0^2\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{10}$$

This equation corresponds to the integro-differential equation of von Kárman in hydrodynamics; in order to solve this equation, we will at first expand the quantity $*C-C$ in the power series of x; i. e.

$$*C-C = *C\frac{x}{r_0+x}\left(1+\sum_{j=1}^{l}A_jx^j\right) \tag{11}$$

When the l unknown coefficients A_j $(j=1, 2, \ldots, l)$ are determined as functions of δ' and r_0 with the aid of l suitable boundary conditions, then insertion of Eq. (11) into Eq. (10) gives an ordinary differential equation of first order demonstrating δ'. Upon integrating the differential equation thus obtained, we can find δ' as a function of time, from which the proper expression for the diffusion current is derived.

(i) At first we will put $l=6$; then the following boundary conditions are found, by which A_j $(j=1, 2, \ldots, 6)$ are to be determined.

$$\left.\begin{aligned}&(C)_{x=\delta'}=*C;\ \left(\frac{\partial C}{\partial x}\right)_{x=\delta'}=0;\\&\left(\frac{\partial^2 C}{\partial x^2}\right)_{x=\delta'}=0;\ \left(\frac{\partial^3 C}{\partial x^3}\right)_{x=\delta'}=0;\\&\left(\frac{\partial^4 C}{\partial x^4}\right)_{x=\delta'}=0;\\&\left[\frac{\partial^2\{(r_0+x)C\}}{\partial x^2}\right]_{x=0}=0\end{aligned}\right\} \tag{12}$$

The first five equations result from the fact that the concentration C in the diffusion layer should vary as continually as possible and be connected with the bulk concentration $*C$ at $x=\delta'$. The last condition is obtained when the relation $r=r_0+x$ is inserted into Eq. (9) and then $x=0$ is put therein. Upon determining the coefficients A_j by the aid of conditions shown by Eq. (12), it is found that $*C-C$ is given by

$$\begin{aligned}*C-C=*C\frac{r_0}{r_0+x}\Bigg\{&1-3\left(\frac{x}{\delta'}\right)+10\left(\frac{x}{\delta'}\right)^3\\&-15\left(\frac{x}{\delta'}\right)^4+9\left(\frac{x}{\delta'}\right)^5-2\left(\frac{x}{\delta'}\right)^6\Bigg\}\end{aligned} \tag{13}$$

Insertion of Eq. (13) into Eq. (10) gives the following ordinary differential equation of first order, by which δ' is to be determined.

$$\frac{d}{dt}\left(\frac{3}{14}r_0^2\delta'+\frac{1}{28}r_0\delta'^2\right)=Dr_0^2\left(\frac{1}{r_0}+\frac{3}{\delta'}\right) \tag{14}$$

Now writing

$$\delta'=(D^{1/2}t^{1/2})\sum_{j=0}^{\infty}\alpha_j(a^{-1}D^{1/2}t^{1/6})^j$$

and inserting this equation into Ep. (14), we can determine α_j's by the method of comparison of coefficients; thus the solution of Eq. (14) is given by the equation in form of following power series.

$$\begin{aligned}\delta'=(D^{1/2}t^{1/2})\Bigg\{&2\sqrt{3}+\frac{4}{5}(a^{-1}D^{1/2}t^{1/6})\\&-\frac{19}{75}\sqrt{3}(a^{-1}D^{1/2}t^{1/6})^2\\&+\frac{856}{6375}(a^{-1}D^{1/2}t^{1/6})^3-\ldots\ldots\Bigg\}\end{aligned} \tag{15}$$

Since the diffusion current i_d is equal to the number of mols of depolarizer reaching the surface of dropping electrode in unit time multiplied by nF, it is found that

$$\begin{aligned}i_d&=4\pi r_0^2\cdot nF\cdot D\left(\frac{\partial C}{\partial r}\right)_{r=r_0}\\&=4\pi r_0^2\cdot nF\cdot D\cdot *C\left(\frac{1}{r_0}+\frac{3}{\delta'}\right)\end{aligned}$$

When the expression for δ' given by Eq. (15) is inserted into the above equation, then we obtain the following equation showing the instantaneous diffusion current, in which the usual conventional units are employed.

$$\begin{aligned}i_d=709\,n{*C}D^{1/2}m^{2/3}t^{1/6}\{&1+35.5(D^{1/2}m^{-1/3}t^{1/6})\\&+266(D^{1/2}m^{-1/3}t^{1/6})^2-\ldots\ldots\}\end{aligned} \tag{16}$$

Accordingly the mean diffusion current is shown by

$$\begin{aligned}\bar{i}_d=608n{*C}D^{1/2}m^{2/3}\tau^{1/6}\{&1+31.1\,(D^{1/2}m^{-1/3}\tau^{1/6})\\&+207(D^{1/2}m^{-1/3}\tau^{1/6})^2-\ldots\ldots\}\end{aligned} \tag{17}$$

(ii) In order to execute the calculation of higher order approximation, the value $l=10$ will be chosen; for the determination of A_j $(j=1, 2, \ldots, 10)$ to the six boundary conditions shown by Eq. (12) the following four conditions will be added.

$$\left.\begin{aligned}&\left(\frac{\partial^5 C}{\partial x^5}\right)_{x=\delta'}=0;\ \left(\frac{\partial^6 C}{\partial x^6}\right)_{x=\delta'}=0;\\&\left(\frac{\partial^7 C}{\partial x^7}\right)_{x=\delta'}=0;\\&\left[\frac{\partial^4}{\partial x^4}\{(r_0+x)C\}\right]_{x=0}+4\frac{a^3}{D}\frac{1}{r_0^3}\left(\frac{\partial C}{\partial x}\right)_{x=0}=0\end{aligned}\right\} \tag{18}$$

The last condition can be obtained, when r in Eq. (9) is replaced by (r_0+x) and then equation thus obtained is twice differentiated with respect to x and further $x=0$ is put therein.

When the quite analogous mathematical procedures shown in the case of $l=6$ are carried out, then we find the following equation representing the instantaneous and mean diffusion current; i. e.

$$i_d=709n^*CD^{1/2}m^{2/3}t^{1/6}\{1+36.3(D^{1/2}m^{-1/3}t^{1/6})+343(D^{1/2}m^{-1/3}t^{1/6})^2-\dots\} \qquad (19)$$

$$\bar{i}_d=608n^*CD^{1/2}m^{2/3}\tau^{1/6}\{1+31.7\,(D^{1/2}m^{-1/3}\tau^{1/6})+267(D^{1/2}m^{-1/3}\tau^{1/6})^2-\dots\}. \qquad (20)$$

Although the accuracy of mathematical treatment can be increased with the increasing greater value of l, the numerical calculation thereof becomes more and more complicated. Furthermore, the comparison of Eq. (16) with (19) and (17) with (2) clearly indicates that the coefficients of the first, second and third terms, appearing in the above stated two calculations, show no considerable differences. Hence the approximate calculation with $l=10$ may be satisfactorily precise.

NOTE:—In the case of uni-dimensional diffusion, coresponding to the Ilkovič equation, the solution can, as well known, be obtained rationally; when the above developed approximate treatment is applied to this case with the value $l=10$, the following equations for the instantaneous and mean diffusion current are derived.

$$i_d=709n^*CD^{1/2}m^{2/3}t^{1/6}$$
$$\bar{i}_d=608n^*CD^{1/2}m^{2/3}\tau^{1/6}$$

Comparison of these equations with the Ilkovič equation indicates that the coefficients 707 and 607 obtained by Ilkovič are converted into 709 and 608, respectively, by the present approximate method. Therefore the above derived coefficients 709 and 608, which appear in Eqs. (16), (17), (19) and (20) showing the instantaneous and mean diffusion current, may be replaced by the values 707 and 607, respectively.

Shielding Effect of the Capillary Tube

In the above quoted mathematical treatment, it is assumed that the mercury drop hangs freely in solution and expands concentrically. In fact, however, at the upper end of drop the capillary tube exists, and accordingly the diffusion of depolarizer from the region neighbouring the upper part of drop is prevented.

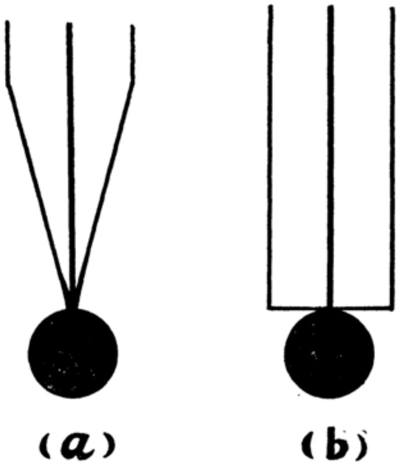

Fig. 1.

In the case of the tapering capillary tube as illustrated in Fig. 1 (a), the shielding effect of capillary may be considerably lessened; but with the capillary of thick wall as shown in Fig. 1 (b) this effect should be taken into account.

Next we will consider how the diffusion current will be affected by the shielding effect due to such a capillary as shown in Fig. 1(b). In order to treat this problem precisely, we must integrate the differential equation representing the cylindrically symmetric diffusion with the boundary conditions which are so complicated that it appears almost impossible. Hence we may be satisfied with the treatment based on the simplified model as follows.

Since the total current I, which has flowed in the time interval from $t=0$ to $t=t$, is obviously equal to the number of mols of depolarizer, which have disappeared from the solution in the same time interval, multiplied by nF, the diffusion current i_d is given by

$$i_d=\frac{dI}{dt}=nF\frac{d}{dt}\iiint_V(^*C-C)r^2\sin\theta\,dr\,d\theta\,d\varphi \qquad (21)$$

where the region of integration V covers all the space in diffusion layer. In the preceding treatment, the region of integration is regarded to be the spherical shell surrounded by two spheres of radii r_0 and $r_0+\delta'$, owing to the assumption of free existence of mercury drop in solution. The upper part of this spherical shell, however, is in fact partly covered by the lower tip of capillary tube, as illustrated by the shaded portion in Fig. 2, and so the decrease in the concentration of depolarizer in this shielded part has no effect on the current

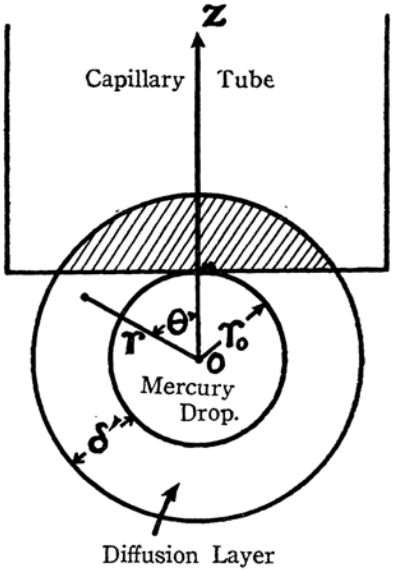

Fig. 2.—Schematic representation of shielding effect due to capillary tube.

intensity. Hence, in order to consider the shielding effect of capillary, the proper region of integration must be limited to the part of spherical shell which is really occupied by solution. Therefore, as to the three variables, r, θ and φ, the limits of integration should be $r_0 \rightarrow r_0+\delta'$, $\cos^{-1}(r_0/r) \rightarrow \pi$ and $0 \rightarrow 2\pi$, respectively. With these considerations, Eq. (21) is written in the form:

$$i_d = nF\frac{d}{dt}\int_0^{2\pi} d\varphi \int_{r_0}^{r_0+\delta'} ({}^*C-C)r^2 dr \times \int_{\cos^{-1}\frac{r_0}{r}}^{\pi} \sin\theta d\theta$$

Upon executing the calculation with the value $l=10$ after inserting the expression for ${}^*C-C$ given by Eq. (11) into the above equation, we can obtain the following equation for diffusion current.

$$i_d = 709n{}^*CD^{1/2}m^{2/3}t^{1/6}\{1+23.5(D^{1/2}m^{-1/3}t^{1/6}) +62.9(D^{1/2}m^{-1/3}t^{1/6})^2-\ldots\} \qquad (22)$$

Whence the mean diffusion current is found to be

$$\bar{i}_d = 608n{}^*CD^{1/2}m^{2/3}\tau^{1/6}\{1+20.6(D^{1/2}m^{-1/3}\tau^{1/6}) +49.0(D^{1/2}m^{-1/3}\tau^{1/6})^2-\ldots\} \qquad (23)$$

Revised Equation for the Diffusion Current in Amalgam Polarography

Next, employing the similar mathematical procedure as is already shown above, we will derive the revised Ilkovič equation showing the diffusion current observed in amalgam polarography.

Although the movement of mercury in the drop electrode seems very complicated, the diffusion process of amalgamated metal may be regarded to proceed in a spherical mercury drop expanding concentrically, provided that the rate of flow of mercury is not seriously great. Then the distribution of concentration $C_M(r, t)$ of amalgamated metal in the mercury drop is represented by the following equation.

$$\frac{\partial C_M}{\partial t} = D_M\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_M}{\partial r}\right) - \frac{a^3}{3r^2}\frac{\partial C_M}{\partial r} \qquad (r \leqq r_0) \qquad (24)$$

Here, D_M is the diffusion constant (cm.^{2}/sec.) of amalgamated metal in mercury.

Further the initial and boundary conditions are given by

$$\left.\begin{array}{lll} C_M = {}^*C_M & \text{for} & t=0 \ (r<r_0); \\ C_M = 0 & \text{for} & r=r_0 \ (t>0); \\ C_M = {}^*C_M, \ \dfrac{\partial C_M}{\partial r}=0 & \text{for} & r=0 \ (t>0) \end{array}\right\} \qquad (25)$$

where ${}^*C_M$ represents the concentration of amalgamated metal in the bulk of mercury.

Multiplying the Eq. (24) by r^2 and then integrating with respect to r from zero to r_0, it can be readily seen that

$$\frac{\partial}{\partial t}\int_0^{r_0}({}^*C_M-C_M)r^2 dr = -D_M r_0^2\left(\frac{\partial C_M}{\partial r}\right)_{r=r_0}$$

Since it may be assumed that the thickness of diffusion layer $\delta'_M(t)$ is much smaller than r_0, the integration from zero to r_0 may be replaced by that from $r_0-\delta'_M$ to r_0; then putting $r=r_0-x$, we have

$$\frac{\partial}{\partial t}\int_0^{\delta'_M}({}^*C_M-C_M)(r_0-x)^2 dx = D_M r_0^2\left(\frac{\partial C_M}{\partial x}\right)_{x=0}. \qquad (26)$$

As shown by Eq. (11), the quantity ${}^*C_M-C_M$ will be expanded into the power series of x; i. e.

$${}^*C_M-C_M = {}^*C_M\frac{r_0}{r_0-x}\left(1+\sum_{j=1}^{l}B_j x^j\right) \qquad (27)$$

Then, taking $l=10$, and employing the similar boundary conditions as shown by Eqs. (12) and (18), we can determine the coefficients B_j $(j=1, 2, \ldots, 10)$ as the functions of δ'_M and r_0. Next, insertion of Eq. (27) into Eq.

(26) gives then an ordinary differential equation of first order, by which δ'_M is demonstrated; upon integrating this equation, we can obtain δ'_M as a function of t. The diffusion current can be easily found therefrom, and the result is

$$i_d = -709n^* C_M D_M{}^{1/2} m^{2/3} t^{1/6} \times \{1 - 34.9(D_M{}^{1/2} m^{-1/3} t^{1/6}) + 199(D_M{}^{1/2} m^{-1/3} t^{1/9})^2 - \ldots\ldots\} \quad (28)$$

Further the mean diffusion current is manifested by

$$\bar{i}_d = -608n^* C_M D_M{}^{1/2} m^{2/3} \tau^{1/6} \times \{1 - 30.5(D_M{}^{1/2} m^{-1/3} \tau^{1/6}) + 155(D_M{}^{1/2} m^{-1/3} \tau^{1/6})^2 - \ldots\ldots\} \quad (29)$$

In the case of amalgam polarography, since the diffusion layer is built up inside the mercury drop, the shielding effect due to capillary tube is expected to be of little importance, so that it may be ignored.

Comparison with Experimental Data

(A) Mean Diffusion Current.— Recently, in order to verify the validity of the revised Ilkovič equation, many investigators have carried out precise experiments, in which the drop time and the rate of outflow of mercury are variously changed with many capillaries of different characteristics; these experiments shows that Eq. (1) holds for the drop time longer than the critical drop time. And as for the numerical value of the coefficient A appearing in the second term of Eq. (1), the experimental results can be classified into the following two cases. I. e., Lingane with Loveride(11) and L. Meites with T. Meites(12) have found the result $A=31.5\pm4.6$, in the case with reductions of several ionic species. On the other hand, von Stackelberg and his collaborators(13) have found that $A=17\pm3$ agrees well with the results; it must be noted here especially that W. Hans and W. Jensch(14) have found that $A=16.1\pm1.5$ is adequate according to their elaborated studies on the polarographic reduction of hydrogen ion. The result observed by the former group of investigators, i. e. $A=31.5\pm4.6$, is in good agreement with Eq. (20), in which the shielding effect of capillary tube is ignored, while $A=17\pm3$ observed by the latter group is in fairly good harmony with Eq. (23), in which the shielding effect is taken into consideration. Which is then more adequate of these two numerical values proposed for the coefficient A? This will be judged by many accurate experimental studies in future.

As to the case of amalgam polarography, Strehlow and von Stackelberg(1) have experimented with cadmium amalgam, and shown that Eq. (29) holds when no phenomenon of "Spüleffekt" appears. Further, R. C. Turner and C. A. Winkler(15) have also confirmed the fact that in the case of lead and cadmium amalgam Eq. (29) agrees well with the experimental findings when m is lesser than 1.2 mg./sec.

(B) Current-Time Curve.—With variable ionic species, the diffusion current-time curve during one drop-life has been investigated oscillographically by Mc Kenzie,(16) Taylor, Smith and Cooter,(17) Mac Donald and Wetmore,(18) and Kambara, Suzuki and Tachi.(3) According to these experiments, although at the last two thirds of drop-life Eq. (22) holds semi-quantitatively, the current intensity at the first one third of drop-life is found to be very small; i. e. a perfect deviation from Eq. (22) is reported. The extraordinary small current flowing in the youth of drop-life will be explained by considering some or all of the following facts, that have been ignored in the above mathematical treatment. (1) In the present calculation, it is assumed that m is constant; but it is well known that m may become considerably small in the youth of drop-life, because the back pressure due to the interfacial tension must increase with the decreasing radius of drop.(19) (2) Owing to the electrolytic reaction at the preceding drop, the succeeding drop is dipped into the solution of lower concentration of depolarizer than that of bulk; i. e. there exists at the beginning of renewed drop-life already a diffusion layer around the drop.(20) (3) At the very infancy of drop-life the diffusion layer is so thin, that the rate-determining process depends not

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(11) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **66**, 1425 (1944); *Anal. Chem.*, **21**, 52 (1949). Cf. *Reference* (2).

(12) L. Meites and T. Meites, *J. Am. Chem. Soc.*, **72**, 3686 (1950), **73**, 395 (1951).

(13) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950) H. Strehlow, O. Madrich and M. von Stackelberg, ibid., **55**, 244 (1951).

(14) W. Hans and W. Jensch, ibid. **56**, 648, (1952).

(15) R. C. Turner and C. A. Winkler, *Cad. J. Chem.*, **29**, 469 (1951), *Chem. Abst.* **46**, 3421 (1952).

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

(17) J. K. Taylor, R. C. Smith and I. L. Cooter, *J. Reserch Natl. Bur. Standards*, **42**, 387 (1949).

(18) J. J. MacDonald and F. E. Wetmore, *Trans. Faraday Scc.*, **47**, 533 (1951).

(19) I. M. Kolthoff and J. J. Lingane, "Polarography" vol. 1, p. 76 (1952) Interscí. Publ.

(20) L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950).

solely on diffusion velocity and the rate of electrode process must be taken into account at the same time.[21]

(C) Ratio of the Mean Diffusion Current $\overline{i}_d$ to the Maximum Value of Instantaneous Current $i_{\max}$. — According to the Ilkovič equation, the ratio $\overline{i}_d/i_{\max}$. becomes $6/7=0.857$. On the other hand, according to the present revised equations (22) and (23) this is given by

$$\frac{\overline{i}_d}{i_{\max}}=\frac{6}{7}-2.5(D^{1/2}m^{-1/3}\tau^{1/6})$$
$$+45(D^{1/2}m^{-1/3}\tau^{1/6})^2-\ldots.$$

E. g., employing the numerical values given by $D=0.72\cdot10^{-5}$cm.^{2}/sec.; $m=2.305$ mg./sec.; $\tau=3.488$ sec., it is found that $\overline{i}_d/i_{\max}=0.851$, while the experimental value observed by Taylor, Smith and Cooter[17] is 0.813. Thus the revised equation approaches somewhat nearer to the experimental result than the original Ilkovič equation; neverthless neither of the two theories is seen to be in complete harmony with the experiments.

Summary

In order to integrate the MacGillavry-Rideal differential equation, representing the diffusion process at the dropping mercury electrode, the present author employed the von Kárman-Pohlhausen method. Thus the following revised expression of the Ilkovič equation showing the mean diffusion current is derived, in which the shielding effect due to the capillary tube is also treated theoretically.

$$\overline{i}_d=608n^*CD^{1/2}m^{2/3}\tau^{1/6}\{1+20.6(D^{1/2}m^{-1/3}\tau^{1/6})$$
$$+49.0(D^{1/2}m^{-1/3}\tau^{1/6})^2-\ldots.\}$$

The analogous treatment is also applied to the case of amalgam polarography, and the following equation for the mean diffusion current is obtained.

$$\overline{i}_d=-608n^*C_M{D_M}^{1/2}m^{2/3}\tau^{1/6}$$
$$\times\{1-30.5({D_M}^{1/2}m^{-1/3}\tau^{1/6})$$
$$+155({D_M}^{1/2}m^{-1/3}\tau^{1/6})^2-\ldots.\}$$

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[21] T. Kambara and I. Tachi, This Bulletin **25**, 135, 281 (1952); H. Matsuda, Presented at the 5 th Annual Meeting of Chem. Soc. of Japan, April 1952.