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Derivation of the Diffusion Equation and a Revision of Matsuda's Theory for Polarography

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DERIVATION OF THE DIFFUSION EQUATION AND A REVISION
OF MATSUDA'S THEORY FOR POLAROGRAPHY

BY

W. PATRICK RAHILLY

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Physics, South Dakota
State University

1965

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**DERIVATION OF THE DIFFUSION EQUATION AND A REVISION
OF MATSUDA'S THEORY FOR POLAROGRAPHY**

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Date

Head, Physics Department

Date

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INTRODUCTION

Many theories have been proposed to yield a current-time relationship in Polarography. The most widely accepted is that of Matsuda.¹ He assumes that the electrolyte can be separated into an inhomogeneous region about the mercury drop and a homogeneous region elsewhere. This assumption leads to a first order, nonlinear, ordinary differential equation directly solvable by substitution of a properly chosen series. But the series solution obtained is only a particular solution; for there exists, as one would expect, a family of solutions depending on a constant of integration.

In the literature, derivation of the diffusion equation has never been attacked from the standpoint that the diffusion processes are occurring with respect to the medium. The convection term in the accepted diffusion equation is introduced as a generalization to account for the growth of the mercury drop.²

This paper will show that the function describing the concentration of diffusing ions need not be broken up into two separate parts. Integration will be carried

¹H. Matsuda, Bull. Chem. Soc. Japan, 26, 342 (1953).

²J. M. Markowitz and P. J. Elving, Chem. Rev., 58, 1066 (1958).

out an infinite distance rather than from the surface of the mercury drop out distance $\underline{\theta}^1$. The series solution is only one of many solutions. A solution obtained by using an experimental value for an initial $\underline{\theta}$ will compare favorably with experiment. Also, derivation of a diffusion equation based on diffusion with respect to the medium will be given.

DERIVATION OF A DIFFUSION EQUATION

Assumptions

To begin with, some assumptions must be made in order to simplify the derivation. These assumptions are listed below:

1. The diffusion process takes place with respect to the medium. Each elementary step consists of movement of the solute from one equilibrium position in the medium to another.³
2. The dropping mercury electrode potential is large enough to deplete the region next to the electrode surface of a certain ion. In other words, the rate of reduction at the electrode depends only on the rate at which the reducible ion reaches the surface. Presumably, electron transfer to each surface ion is very fast.
3. The drop is motionless. Actually the center of gravity moves downward but this motion is negligible.
4. The mercury drop possesses spherical symmetry. This has been shown with high speed photographs

³S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Company, 517, (1941).

by MacNevin and Balis to be an accurate assumption.⁴

5. The pertinent solution about the drop exhibits spherical symmetry. This assumption is no better than a rough approximation. Certainly there exists a shielding effect due to the presence of the capillary. Derivation of a diffusion equation is made complicated by inclusion of the capillary in the theory.
6. The solution extends out an infinite distance. Antweiler has shown this to be a very good assumption.⁵

Two other assumptions that are cited in the literature are: The mass rate of flow of mercury is constant;⁶ and there is no depleted region around the newly forming drop.⁷ It will be shown that these need not be made in this derivation. To be more general, the diffusion coefficient will be taken as a function of the variables r and t .

⁴W. M. MacNevin and E. W. Balis, J. Am. Chem. Soc. 65, 660 (1943).

⁵Von H. J. Antweiler, Ztschr. Electrochem. 44, 888 (1938).

⁶J. J. Lingane, J. Am. Chem. Soc., 75, 788 (1953).

⁷J. M. Markowitz and P. J. Elving, J. Am. Chem. Soc., 81, 3518 (1959).

Derivation of the Diffusion Equation

Given a spherical surface in a medium where radial diffusion occurs, the moles, dN^s , that diffuse across in time dt equal

$$dN^s = A^s D^s \left(\frac{\partial C^s}{\partial r} \right) dt, \quad (1)$$

where A^s is the area of surface, D^s the diffusion coefficient at the surface and $\left(\frac{\partial C}{\partial r} \right)^s$ the gradient of the concentration evaluated at the surface.

Consider an infinitesimal spherical shell of thickness dr in the medium with a center common to the center of the mercury drop. Label the inner and outer surfaces g and f , respectively, as shown in Figure 1. The radius of the growing electrode is denoted by r_0 .

By Equation (1), the moles passing through surface f is given as

$$dN^f = A^f D^f \left(\frac{\partial C}{\partial r} \right)^f dt, \quad (2)$$

and for surface g , the number of moles is

$$dN^g = A^g D^g \left(\frac{\partial C}{\partial r} \right)^g dt. \quad (3)$$

Then the time rate of change of the concentration in the shell will be

$$\frac{\partial C}{\partial t} = \frac{dN^f - dN^g}{dV dt}, \quad (4)$$

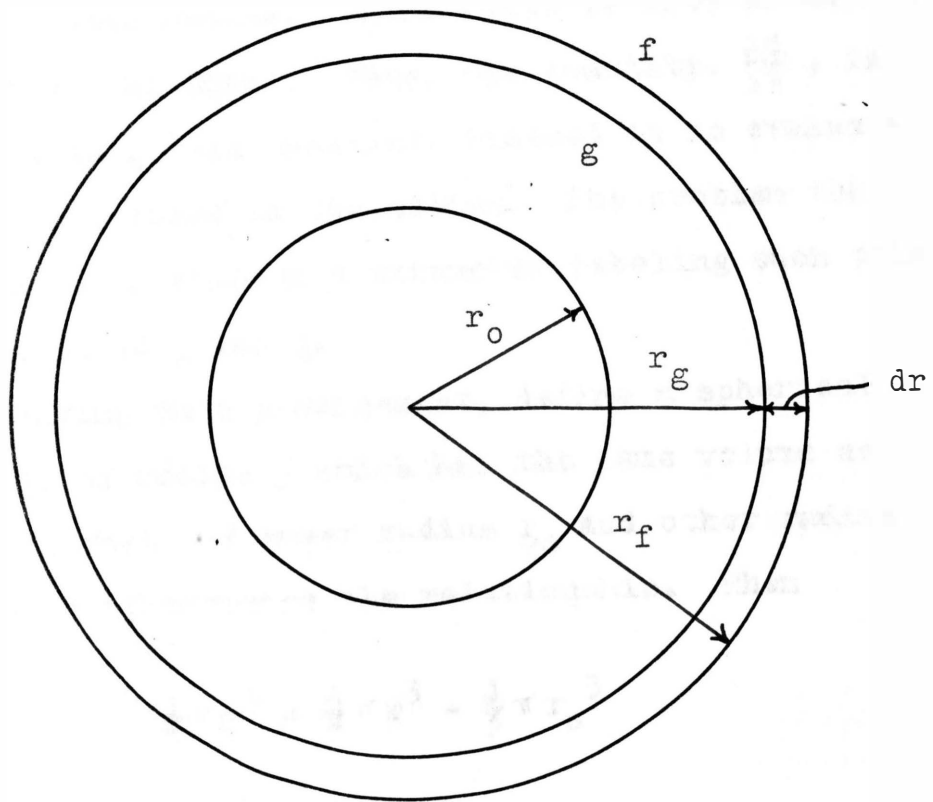


Figure 1. Description of Spherical Shell

where dV is the volume of the spherical shell.

If the mercury drop did not change size, then no problem would exist in deriving a diffusion equation. But the surfaces given move with the medium. Hence the quantities $(\frac{\partial C}{\partial r})^f$, $(\frac{\partial C}{\partial r})^g$, A^f , A^g , D^f and D^g cannot be taken with constant time; for this would freeze the surfaces at some radius. There would be flow of medium in and out of the shell. Thus, the quantity, $\frac{\partial C}{\partial t}$, is not taken with r held constant; instead it is evaluated between points fixed in the medium. The problem that now arises is to express a parameter labeling such points as a function of r and t .

In solving this predicament, define a spherical volume, ΔV , of radius ρ which has the same volume as a spherical shell of inner radius r_0 and outer radius r . Figure 2 illustrates the relationship. Then

$$\frac{4}{3}\pi\rho^3 = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi r_0^3$$

or

$$\rho^3 = r^3 - r_0^3. \quad (5)$$

Equation (5) gives a simple relation between ρ and the variables r , t . The coordinate ρ identifies a given element of solvent; for it can be argued that each given point in the medium will have a value ρ associated

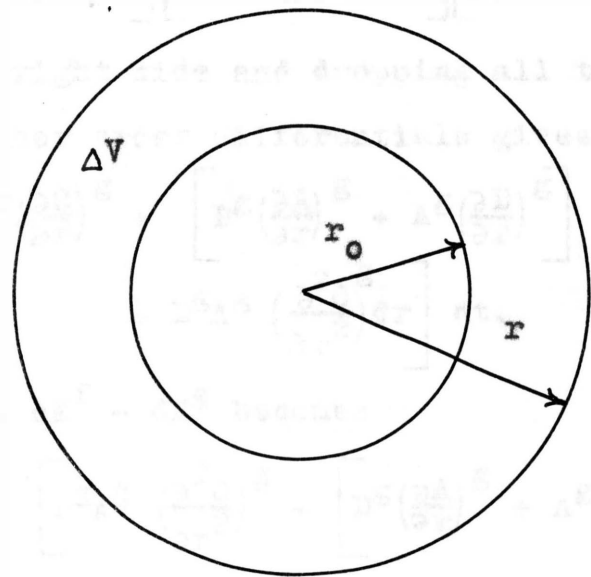
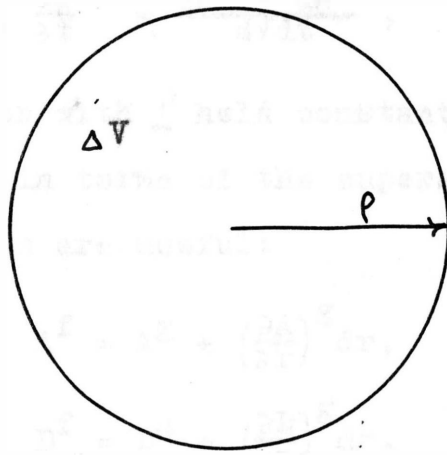


Figure 2. Definition of ρ

with it and this value will not change.

Now Equation (4) becomes

$$\frac{\partial C}{\partial t} = \frac{dN^f - dN^g}{dv dt}, \quad (6)$$

where $\frac{\partial C}{\partial t}$ is taken with ρ held constant.

To write dN^f in terms of the superscript g , the following equations are useful:

$$\begin{aligned} A^f &= A^g + \left(\frac{\partial A}{\partial r}\right)^g dr, \\ D^f &= D^g + \left(\frac{\partial D}{\partial r}\right)^g dr, \\ \left(\frac{\partial C}{\partial r}\right)^f &= \left(\frac{\partial C}{\partial r}\right)^g + \left(\frac{\partial^2 C}{\partial r^2}\right)^g dr. \end{aligned} \quad (7)$$

Then Equation (2) becomes

$$dN^f = \left[A^g + \left(\frac{\partial A}{\partial r}\right)^g dr \right] \left[D^g + \left(\frac{\partial D}{\partial r}\right)^g dr \right] \left[\left(\frac{\partial C}{\partial r}\right)^g + \left(\frac{\partial^2 C}{\partial r^2}\right)^g dr \right].$$

Expanding the right side and dropping all terms involving second and higher order differentials gives

$$\begin{aligned} dN^f &= \left[D^g A^g \left(\frac{\partial C}{\partial r}\right)^g + \left[D^g \left(\frac{\partial A}{\partial r}\right)^g + A^g \left(\frac{\partial D}{\partial r}\right)^g \right] \left(\frac{\partial C}{\partial r}\right)^g dr \right. \\ &\quad \left. + D^g A^g \left(\frac{\partial^2 C}{\partial r^2}\right)^g dr \right] dt. \end{aligned}$$

The difference $dN^f - dN^g$ becomes

$$\begin{aligned} dN^f - dN^g &= \left[D^g A^g \left(\frac{\partial^2 C}{\partial r^2}\right)^g + \left[D^g \left(\frac{\partial A}{\partial r}\right)^g + A^g \left(\frac{\partial D}{\partial r}\right)^g \right] \times \right. \\ &\quad \left. \left(\frac{\partial C}{\partial r}\right)^g \right] dr dt. \end{aligned} \quad (8)$$

The shell's volume is calculated as follows:

$$dV = \frac{4}{3} \pi r_f^3 - \frac{4}{3} \pi r_g^3$$

or

$$dV = \frac{4}{3} \pi (r_g + dr)^3 - \frac{4}{3} \pi r_g^3.$$

Expanding the first term on the right side and neglecting high-ordered differentials, the expression for dV becomes

$$dV = \frac{4}{3} \pi (r_g^3 + 3r_g^2 dr) - \frac{4}{3} \pi r_g^3$$

or

$$dV = 4 \pi r_g^2 dr. \quad (9)$$

The area of the surface g is

$$A^g = 4 \pi r_g^2 \quad (10)$$

and a change in area

$$\left(\frac{\partial A}{\partial r}\right)^g = 4 \pi (2r_g). \quad (11)$$

With Equations (8), (9), (10) and (11), Equation (6)

becomes

$$\frac{\partial C}{\partial t} = \frac{\left[4 \pi r_g^2 D^g \frac{\partial^2 C}{\partial r^2} + \left[D^g 4 \pi (2r_g) + 4 \pi r_g^2 \left(\frac{\partial D}{\partial r}\right)^g \right] \left(\frac{\partial C}{\partial r}\right)^g \right] dr dt}{4 \pi r_g^2 dr dt}$$

or

$$\frac{\partial C}{\partial t} = D^g \left(\frac{\partial^2 C}{\partial r^2} \right)^g + \left[D^g \frac{2}{r} + \left(\frac{\partial D}{\partial r} \right)^g \right] \left(\frac{\partial C}{\partial r} \right)^g. \quad (12)$$

Since all quantities on the right side of Equation (12) are evaluated at surface g , the superscripts can be dropped. Equation (12) is now written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2} + \left[D \frac{2}{r} + \left(\frac{\partial D}{\partial r} \right) \right] \left(\frac{\partial C}{\partial r} \right)$$

or

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D r^2 \left(\frac{\partial C}{\partial r} \right) \right]. \quad (13)$$

The left side is all that remains to be considered.

Writing $C = C(\rho, t) = C(r, t)$, and differentiating gives

$$dC = \left(\frac{\partial C}{\partial \rho} \right)_t d\rho + \left(\frac{\partial C}{\partial t} \right)_\rho dt \quad (14)$$

and

$$dC = \left(\frac{\partial C}{\partial r} \right)_t dr + \left(\frac{\partial C}{\partial t} \right)_r dt \quad (15)$$

Differentiating the relationship derived for $\underline{\rho}$ gives

$$3r^2 dr = 3\rho^2 d\rho + 3r_0^2 dr_0$$

or

$$dr = \frac{\rho^2}{r^2} d\rho + \frac{r_0^2}{r^2} dr_0$$

or

$$dr = \frac{\rho^2}{r^2} d\rho + \frac{r_0^2}{r^2} \left(\frac{dr_0}{dt} \right) dt. \quad (16)$$

Insert Equation (16) into Equation (15). Equating the result to Equation (14) and comparing coefficients of $d\rho$ and dt gives

$$\left(\frac{\partial C}{\partial \rho}\right)_t = \frac{\rho^2}{r^2} \left(\frac{\partial C}{\partial r}\right)_t$$

and

$$\left(\frac{\partial C}{\partial t}\right)_\rho = \left(\frac{\partial C}{\partial t}\right)_r + \frac{dr_o}{dt} \cdot \frac{r_o^2}{r^2} \left(\frac{\partial C}{\partial r}\right)_t.$$

Hence, Equation (13) becomes

$$\left(\frac{\partial C}{\partial t}\right)_r = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[Dr^2 \left(\frac{\partial C}{\partial r}\right) \right]_t - \frac{dr_o}{dt} \cdot \frac{r_o^2}{r^2} \left(\frac{\partial C}{\partial r}\right)_t,$$

or

$$\left(\frac{\partial C}{\partial t}\right)_r = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[Dr^2 \left(\frac{\partial C}{\partial r}\right) - r_o^2 \frac{dr_o}{dt} C \right]_t. \quad (17)$$

Taking the mass-rate of flow of mercury to be dependent on time yields

$$\frac{dV}{dt} = \frac{1}{d} m(t) \quad (18)$$

or

$$4\pi r_o^2 \frac{dr_o}{dt} = \frac{1}{d} m(t). \quad (19)$$

Integration gives

$$r_o^3 = \frac{3}{4\pi d} \int_0^t m(t) dt \quad (20)$$

where d is the density of mercury in gm/cm^3 and $m(t)$ has

the units of \underline{m}/sec . In keeping with the notation in the literature, Equation (20) is rewritten

$$r_0^3 = \frac{3m_0}{4\pi d} \int_0^t g(t) dt = \gamma_0 \int_0^t g(t) dt = \int_0^t \gamma(t) dt, \quad (21)$$

where $g(t)$ is some unitless function of time and γ_0 has the units of cm^3/sec .

Substitution of (21) into (17) gives finally

$$\left(\frac{\partial C}{\partial t}\right)_r = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[D r^2 \left(\frac{\partial C}{\partial r}\right) - \frac{\gamma(t)}{3} C \right]_t. \quad (22)$$

Equation (22) is valid for variation of \underline{D} with \underline{r} and \underline{t} , and mass rate of flow dependence on time.

Solving Equation (22) presents a formidable task. The most common method, separation of variables, is useless if \underline{m} has time dependence and \underline{D} varies with distance and time. For constant \underline{m} and \underline{D} , the separation method yields a second order, ordinary differential equation in \underline{r} involving an irregular singularity. Differential equations possessing such singularities are not easily solved. A series expansion for the solution, where the singularity has been removed by expanding about a chosen value of \underline{r} , does not give suitable results. The relationship for the coefficients in the series is complicated. Thus, integration over the separation constant is not possible. There is a way however, which is not strictly

correct in a mathematical sense, but does give acceptable results. This method is the integral solution employed by Matsuda.¹

SOLUTION OF THE DIFFUSION EQUATION

A procedure like that of Matsuda will be used in solving Equation (22).

The Integral Method

Equation (22) is now multiplied by $\underline{r^2 dr}$ and integrated from $\underline{r_0}$ to infinity to get

$$\int_{r_0}^{\infty} r^2 \left(\frac{\partial C}{\partial t} \right) dr = \int_{r_0}^{\infty} \frac{\partial}{\partial r} \left[D r^2 \left(\frac{\partial C}{\partial r} \right) - \frac{\gamma(t)}{3} C \right] dr$$

or

$$\int_{r_0}^{\infty} r^2 \left(\frac{\partial C}{\partial t} \right) dr = \left[D r^2 \left(\frac{\partial C}{\partial r} \right) - \frac{\gamma(t)}{3} C \right]_{r_0}^{\infty}. \quad (23)$$

If reduction of an ion takes place as soon as it reaches the mercury drop², then $\underline{C}(r_0, t) = 0$. If the concentration is uniform at some distance away from the electrode², then

$$\lim_{r \rightarrow \infty} C(r, t) = C_0$$

and

$$\lim_{r \rightarrow \infty} r^2 \left(\frac{\partial C}{\partial r} \right) = 0. \quad (24)$$

So, Equation (23) reduces to

$$\int_{r_0}^{\infty} r^2 \left(\frac{\partial C}{\partial t} \right) dr = -D(r_0, t) r_0^2 \left(\frac{\partial C}{\partial r} \right)_{r_0} - \frac{\gamma(t)}{3} C_0. \quad (25)$$

But with the relationships:

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C dr = \int_{r_0}^{\infty} r^2 \left(\frac{\partial C}{\partial t} \right) dr + \lim_{h \rightarrow \infty} h^2 C(h, t) \frac{dh}{dt} - r_0^2 C(r_0, t) \frac{dr_0}{dt}$$

or.

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C dr = \int_{r_0}^{\infty} r^2 \left(\frac{\partial C}{\partial t} \right) dr,$$

where $\frac{dh}{dt} = 0$, and

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C_0 dr = \int_{r_0}^{\infty} r^2 \left(\frac{\partial C_0}{\partial t} \right) dr + \lim_{h \rightarrow \infty} h^2 C(h, t) \frac{dh}{dt} - r_0^2 C_0 \frac{dr_0}{dt}$$

or

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C_0 dr = - r_0^2 C_0 \frac{dr_0}{dt} = - \frac{\gamma(t)}{3} C_0.$$

Equation (25) becomes

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C dr = -D(r_0, t) r_0^2 \left(\frac{\partial C}{\partial r} \right)_{r_0} + \frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C_0 dr$$

or

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 (C_0 - C) dr = D(r_0, t) r_0^2 \left(\frac{\partial C}{\partial r} \right)_{r_0}. \quad (26)$$

Equation (26) holds whether or not $\underline{\gamma}$ varies. It is also valid for a variable diffusion coefficient as long as $\underline{D}(r_0, t) = \underline{D}(t)$ and $\underline{D}(\infty, t) = \underline{D}_0$, where \underline{D}_0 is the limiting diffusion coefficient for large \underline{r} . The conditions imposed on $\underline{D}(r, t)$ are not objectionable because physically the

diffusion coefficient would be expected to vary with time at the surface of the drop and be constant for large distances from the electrode. The equality in Equation (26) will hold only if the \underline{C} in the equation is a solution of the diffusion equation. The correct solution of Equation (22) is not known, but the true form for \underline{C} is not of direct interest; for in the final analysis, only the gradient of \underline{C} evaluated at $\underline{r} = \underline{r}_0$ is important.

Choice of Concentration Function

The solution for the stationary spherical electrode has been discussed before.⁷ It is given by

$$C = C_0 - C_0 \frac{r'}{r} \operatorname{erfc} \left(\frac{r - r'}{\sqrt{4D_0 t}} \right) \quad (27)$$

where \underline{r}' is the radius of the stationary electrode. Equation (27) will be the choice for \underline{C} , but modified somewhat. A question may be raised as to why this is a reasonable selection. The answer is that the actual solution of Equation (22) would be of a similar form as Equation (27) because in both cases, the diffusion process is radial. In other words, from symmetry alone, the solution of Equation (22) should be similar to Equation (27). Matsuda chose a form for \underline{C} analogous to Equation (27).¹

The modifications to be made are based on the results previously obtained by Kidman.⁸ He argues that the temporal factor in the denominator of the complimentary error function should be replaced by $\underline{f}(t)$, where $\underline{f}(t)$ has the form

$$f(t) = at + b. \quad (28)$$

He gives \underline{b} meaning by stating that initially there exists a layer about the drop depleted of reducible ions because some of the layer about the previous drop is left behind. The coefficient of \underline{t} is given the same significance as the $3/7$ factor of Lingane and Loveridge.⁹

The corresponding change in Equation (27) will be to replace \underline{t} by $\underline{f}(t)$. The only other modification is the obvious one; \underline{r}' is replaced by radius \underline{r}_0 . With these alterations, Equation (27) is now written as

$$C = C_0 - C_0 \frac{r_0}{r} \operatorname{erfc} \left(\frac{r - r_0}{\sqrt{4D_0 f(t)}} \right) \quad (29)$$

Note that conditions (24) are satisfied.

Solution

Even with the aid of Equation (29), the solution of Equation (26) will be very much handicapped if the

⁸R. B. Kidman, A New Partial Differential Equation And A New Instantaneous Current-Time Curve for Polarography, M. S. Thesis, South Dakota State University, 32 (1964).

⁹J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc., 72, 438 (1950).

diffusion coefficient is to vary. To simplify matters considerably, $\underline{D}(r,t)$ will be taken as constant at the surface of the electrode and throughout the bulk of the electrolyte. Let $\underline{D}(r,t) = \underline{D}_0$ where, \underline{D}_0 is the value of the diffusion coefficient given in the literature.

Solving Equation (29) for $\underline{C}_0 - \underline{C}$ yields

$$\underline{C}_0 - \underline{C} = \underline{C}_0 \frac{r_0}{r} \operatorname{erfc}\left(\frac{r - r_0}{\sqrt{4D_0 f(t)}}\right) \quad (30)$$

Differentiating Equation (29) partially with respect to \underline{r} , and evaluating the resulting expression at $\underline{r} = \underline{r}_0$ gives the value of the concentration gradient at the surface of the mercury drop:

$$\left(\frac{\partial \underline{C}}{\partial \underline{r}}\right)_{r_0} = \underline{C}_0 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right]. \quad (31)$$

Substitution of Equations (30) and (31) into Equation (26) yields

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r_0 r \operatorname{erfc}\left(\frac{r - r_0}{\sqrt{4D_0 f(t)}}\right) dr = D_0 r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right]. \quad (32)$$

The integration is simplified somewhat by letting

$$x = \frac{r - r_0}{\sqrt{4D_0 f(t)}} \quad (33)$$

or

$$r = r_0 + \sqrt{4D_0 f(t)} x$$

and

$$dr = \sqrt{4D_0 f(t)} \, dx.$$

The limits of integration, $r = r_0$, $r = \infty$ become $x = 0$, $x = \infty$. Equation (32) is written

$$\begin{aligned} \frac{\partial}{\partial t} \int_0^{\infty} r_0 \left[r_0 + \sqrt{4D_0 f(t)} \, x \right] \sqrt{4D_0 f(t)} \operatorname{erfc}(x) \, dx \\ = D r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right]. \end{aligned} \quad (34)$$

Rearranging, Equation (34) becomes

$$\begin{aligned} \frac{\partial}{\partial t} \left[\sqrt{4D_0 f(t)} \, r_0^2 \right] \int_0^{\infty} \operatorname{erfc}(x) \, dx + \frac{\partial}{\partial t} \left[4D_0 f(t) r_0 \right] \int_0^{\infty} x \operatorname{erfc}(x) \, dx \\ = D_0 r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right]. \end{aligned} \quad (35)$$

The integrals in the first and second terms of the left side are easily evaluated with the aid of the following relation:

$$\int \operatorname{erfc}(x) \, dx = x \operatorname{erfc}(x) - \frac{1}{\sqrt{\pi}} e^{-x^2} + k,$$

where k is a constant of integration. The first integral is computed directly:

$$\int_0^{\infty} \operatorname{erfc}(x) \, dx = x \operatorname{erfc}(x) \Big|_0^{\infty} - \frac{1}{\sqrt{\pi}} e^{-x^2} \Big|_0^{\infty}$$

or

$$\int_0^{\infty} \operatorname{erfc}(x) dx = \frac{1}{\sqrt{\pi}} \quad (36)$$

Integration by parts is used to calculate the second integral:

$$\int_0^{\infty} x \operatorname{erfc}(x) dx = x^2 \operatorname{erfc}(x) \Big|_0^{\infty} - \int_0^{\infty} x \operatorname{erfc}(x) dx + \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx$$

or

$$2 \int_0^{\infty} x \operatorname{erfc}(x) dx = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx$$

or

$$\int_0^{\infty} x \operatorname{erfc}(x) dx = \frac{1}{4} \left[\frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx \right] = \frac{1}{4}, \quad (37)$$

where

$$\frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx = \operatorname{erf}(\infty) = 1.$$

With Equations (36) and (37) and multiplying through by π , Equation (35) reduces to

$$\frac{\partial}{\partial t} \left[2\sqrt{\pi D_0 f(t)} r_0^2 + \pi D_0 f(t) r_0 \right] = \pi D_0 r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right].$$

Since \underline{r} has been integrated out of the expression, the partial time derivative can be replaced by a total time derivative. The final expression is

$$\frac{d}{dt} \left[2r_0^2 \sqrt{\pi D_0 f(t)} + r_0 \pi D_0 f(t) \right] = \pi D_0 r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f(t)}} \right]. \quad (38)$$

Equation (30) is a first order, nonlinear ordinary differential equation with $\underline{f}(t)$ taken as the dependent variable. The equation does not lend itself to be easily solved. A series solution can be readily obtained but it is only one of many solutions.

SOLUTION OF THE NONLINEAR EQUATION

Solutions for the nonlinear equation will now be obtained. The radius of the mercury drop will be treated as it is in the literature,²

Dimensionless Equation

Equation (38) is put into dimensionless form by the substitutions

$$\bar{t} = \frac{D_0^3}{\gamma_0^2} t \quad (39)$$

and

$$\bar{r}(\bar{t}) = \frac{D_0^3}{\gamma_0^2} f(t), \quad (40)$$

where \bar{t} represents reduced time. Equation (38) then becomes

$$\frac{d}{d\bar{t}} \left[2\bar{t}^{2/3} \bar{\theta} + \bar{t}^{1/3} \bar{\theta}^2 \right] = \pi \bar{t}^{2/3} \left[\frac{1}{\bar{t}^{1/3}} + \frac{1}{\bar{\theta}} \right], \quad (41)$$

where $\bar{\theta} = \bar{r}(\bar{t})$ and $r_0^3 = \frac{\gamma_0 t}{D_0^3}$.

Numerical Integration

Many numerical methods can be applied to Equation (41). The method to be used here is the fourth-order Runge-Kutta process.¹⁰

¹⁰ Stanton, R. G., Numerical Methods for Science and Engineering, Prentice-Hall, 151 (1964).

Equation (41) is put into the form

$$\frac{d\bar{\theta}}{d\bar{t}} = F(\bar{t}, \bar{\theta}).$$

The equations to be used in the Runge-Kutta integration are:

$$\begin{aligned} k_1 &= hF(\bar{t}, \bar{\theta}), \\ k_2 &= hF(\bar{t} + \frac{h}{2}, \bar{\theta} + \frac{k_1}{2}), \\ k_3 &= hF(\bar{t} + \frac{h}{2}, \bar{\theta} + \frac{k_2}{2}), \\ k_4 &= hF(\bar{t} + h, \bar{\theta} + k_3) \end{aligned} \quad (42)$$

and

$$\Delta\bar{\theta} = \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4)$$

where h is the increment in \bar{t} in each calculation. The k 's are determined by starting with a value for \bar{t} and $\bar{\theta}$; then $\Delta\bar{\theta}$ is calculated. A new \bar{t} and $\bar{\theta}$ are inserted into each of the k 's and a second $\bar{\theta}$ is calculated. The process is repeated as often as desired. Ten integrations were carried out. The results are plotted in Figure 3. The quantities plotted are $\bar{\theta}^2/\pi = \bar{f}(\bar{t})$ and \bar{t} . Table 1 gives representative values for each integration. Calculations were made on an IBM 1620 digital computer. The program is given in Appendix 1.

A series solution of Equation (41) can be obtained in the following way: Let $\bar{\theta}$ be represented by the series

$$\bar{\theta} = \sqrt{\pi \bar{r}} \sum_{j=0}^{\infty} a_j \bar{r}^{j/6}. \quad (43)$$

Multiply Equation (41) through by $\bar{\theta}$, carry out the indicated operations and equate all like powers of \bar{r} . The procedure gives

$$\bar{\theta} = \sqrt{\pi \bar{r}} \left[\frac{3}{7} + \frac{3}{35} \bar{r}^{1/6} - \frac{171}{29,400} \sqrt{\pi 21} \bar{r}^{2/6} + \dots \right]. \quad (44)$$

Squaring Equation (44) and dividing through by yields

$$\frac{\bar{\theta}^2}{\pi} = \bar{r}(\bar{r}) = \frac{3}{7} \bar{r} + \frac{6}{245} \sqrt{\pi 21} \bar{r}^{7/6} - \frac{135\pi}{4900} \bar{r}^{8/6} + \dots \quad (45)$$

Equation (45) is a particular solution of Equation (41); it is also a limiting solution for all other solutions to Equation (41). Notice that the coefficient of the linear term in \bar{r} is the same as that introduced by Lingane and Loveridge.

Matsuda's Equation

Matsuda's concentration gradient at $\underline{r} = \underline{r}_0$ is

$$\left(\frac{\partial C}{\partial r} \right)_{r_0} = C_0 \left[\frac{1}{r_0} + \frac{3}{\theta_m} \right], \quad (46)$$

where the subscript, \underline{m} , denotes Matsuda. Equation (46) is comparable to Equation (31) if

$$\frac{\theta_m}{3} = \phi, \quad (47)$$

where ϕ compares with $\underline{\theta}$.

The nonlinear equation derived in Matsuda's theory is

$$\frac{d}{dt} \left[\frac{3}{14} r_o^2 \theta_m + \frac{1}{28} r_o \theta_m^2 \right] = D_o r_o^2 \left[\frac{1}{r_o} + \frac{3}{\theta_m} \right]. \quad (48)$$

Inserting Equation (47) into Equation (48) and multiplying through by 28/9 gives

$$\frac{d}{dt} \left[2r_o^2 \phi + r_o \phi^2 \right] = \frac{28}{9} D_o r_o^2 \left[\frac{1}{r_o} + \frac{1}{\phi} \right]. \quad (49)$$

Substitutions (39) and (40) reduce Equation (49) to

$$\frac{d}{dt} \left[2\bar{t}^{2/3} \bar{\phi} + \bar{t}^{1/3} \bar{\phi}^2 \right] = \frac{28}{9} \bar{t}^{2/3} \left[\frac{1}{\bar{t}^{1/3}} + \frac{1}{\bar{\phi}} \right]. \quad (50)$$

Solutions for Equation (50) are obtained in the same manner as before. Only one integration, of Equation (50) was performed. The calculations are listed in Table 2 with Run 4.

A series solution to Equation (50) can be obtained in the same manner as Equation (45); it is

$$\frac{\bar{\phi}^2}{\pi} = \frac{4\bar{t}}{3\pi} + \frac{16\sqrt{3}}{45\pi} \bar{t}^{7/6} - \frac{56}{225\pi} \bar{t}^{8/6} + \dots \quad (51)$$

Equation (51) is a limiting solution for all other solutions of Equation (50).

Discussion of Solutions

Matsuda gave $\frac{\theta}{m}$ physical significance by stating that it is the depleted layer thickness. If θ in the present theory has similar significance, then the solutions represented in Figure 3 imply various initial conditions.¹¹ Those solutions below the series solution indicate that the solute is concentrated around the electrode. The diffusion occurs for a time t before the solution becomes homogeneous. Then depletion proceeds. The series solution implies that the concentration distribution is homogeneous everywhere initially. Those solutions above the series solution imply that the concentration is low about the mercury drop; for small time θ is very large meaning that the concentration must be small around the drop.

¹¹Duffey, G. H., (submitted for publication).

Table I. Variation of $\frac{\bar{\theta}^2}{\pi}$ with \bar{t} for Various Starting Values.

Reduced Time \bar{t}	Run 1	Run 2	Run 3	Run 4	Run 5
1.000×10^{-9}	3.590×10^{-6}	2.160×10^{-6}	1.169×10^{-6}	5.380×10^{-7}	7.910×10^{-8}
2.000×10^{-9}	2.360×10^{-6}	1.368×10^{-6}	7.040×10^{-7}	3.030×10^{-7}	3.870×10^{-8}
4.000×10^{-9}	1.455×10^{-6}	8.040×10^{-7}	3.910×10^{-7}	1.572×10^{-7}	1.874×10^{-8}
8.000×10^{-9}	8.260×10^{-7}	4.340×10^{-7}	2.000×10^{-7}	7.720×10^{-8}	1.083×10^{-8}
1.600×10^{-8}	4.330×10^{-7}	2.190×10^{-7}	9.910×10^{-8}	3.990×10^{-8}	1.012×10^{-8}
2.160×10^{-8}	3.220×10^{-7}	1.621×10^{-7}	7.450×10^{-8}	3.240×10^{-8}	1.162×10^{-8}
3.200×10^{-8}	2.180×10^{-7}	1.115×10^{-7}	5.490×10^{-8}	2.830×10^{-8}	1.539×10^{-8}
4.240×10^{-8}	1.667×10^{-7}	8.870×10^{-8}	4.780×10^{-8}	2.870×10^{-8}	1.961×10^{-8}
6.400×10^{-8}	1.198×10^{-7}	7.110×10^{-8}	4.590×10^{-8}	3.430×10^{-8}	2.880×10^{-8}
8.640×10^{-8}	1.023×10^{07}	6.790×10^{-8}	5.040×10^{-8}	4.240×10^{-8}	3.860×10^{-8}
1.280×10^{-7}	9.670×10^{-8}	7.510×10^{-8}	6.420×10^{-8}	5.930×10^{-8}	5.700×10^{-8}
2.560×10^{-7}	1.310×10^{-7}	1.217×10^{-7}	1.170×10^{-7}	1.149×10^{-7}	1.139×10^{-7}
5.120×10^{-7}	2.360×10^{-7}	2.320×10^{-7}	2.300×10^{-7}	2.290×10^{-7}	2.290×10^{-7}
1.024×10^{-6}	4.620×10^{-7}	4.610×10^{-7}	4.600×10^{-7}	4.590×10^{-7}	4.590×10^{-7}

Table I. (continued)

Reduced Time \bar{t}	Run 6	Run 7	Run 8	Run 9	Run 10
3.200×10^{-8}	1.036×10^{-8}				
4.240×10^{-8}	1.607×10^{-8}				
6.400×10^{-8}	2.670×10^{-8}	6.010×10^{-9}			
8.640×10^{-8}	3.710×10^{-8}	2.300×10^{-8}			
1.280×10^{-7}	5.610×10^{-8}	4.740×10^{-8}	1.191×10^{-8}		
1.696×10^{-7}	7.480×10^{-8}	6.870×10^{-8}	4.370×10^{-8}		
2.560×10^{-7}	1.135×10^{-7}	1.098×10^{-7}	9.470×10^{-8}	6.660×10^{-8}	2.390×10^{-8}
3.456×10^{-7}	1.538×10^{-7}	1.512×10^{-7}	1.408×10^{-7}	1.214×10^{-7}	9.220×10^{-8}
5.120×10^{-7}	2.290×10^{-7}	2.270×10^{-7}	2.200×10^{-7}	2.080×10^{-7}	1.904×10^{-7}
1.024×10^{-6}	4.590×10^{-7}	4.580×10^{-7}	4.550×10^{-7}	4.500×10^{-7}	4.420×10^{-7}

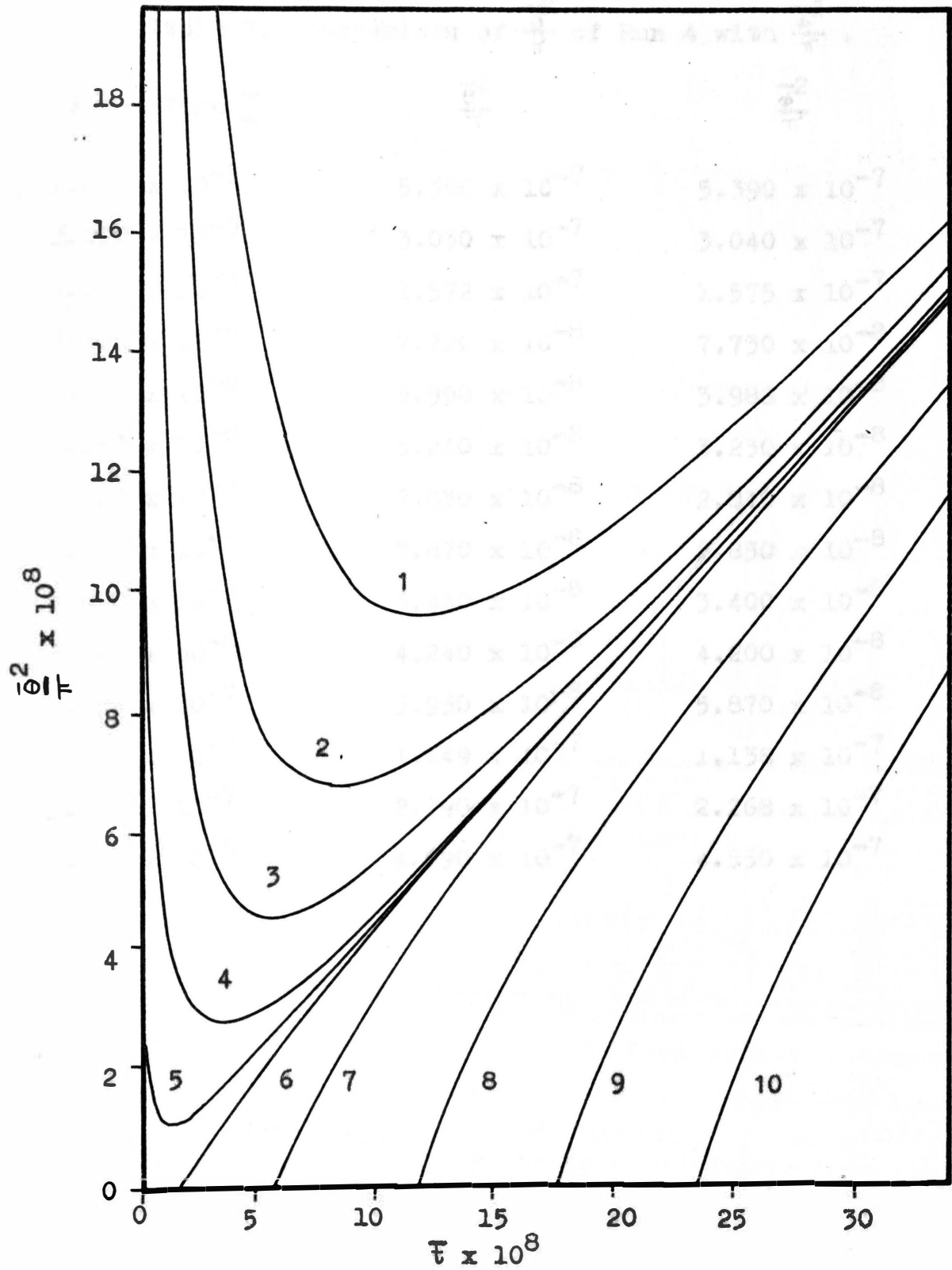


Figure 3. Variation of $\bar{\theta}^2/\pi$ with $\bar{\tau}$

Table 2. Comparison of $\frac{\bar{\theta}^2}{\pi}$ of Run 4 with $\frac{\bar{\phi}^2}{\pi}$.

Reduced Time \bar{t}	$\frac{\bar{\theta}^2}{\pi}$	$\frac{\bar{\phi}^2}{\pi}$
1.000×10^{-9}	5.380×10^{-7}	5.390×10^{-7}
2.000×10^{-9}	3.030×10^{-7}	3.040×10^{-7}
4.000×10^{-9}	1.572×10^{-7}	1.575×10^{-7}
8.000×10^{-9}	7.720×10^{-8}	7.730×10^{-8}
1.600×10^{-8}	3.990×10^{-8}	3.988×10^{-8}
2.160×10^{-8}	3.240×10^{-8}	3.230×10^{-8}
3.200×10^{-8}	2.830×10^{-8}	2.810×10^{-8}
4.240×10^{-8}	2.870×10^{-8}	2.850×10^{-8}
6.400×10^{-8}	3.430×10^{-8}	3.400×10^{-8}
8.640×10^{-8}	4.240×10^{-8}	4.200×10^{-8}
1.280×10^{-7}	5.930×10^{-8}	5.870×10^{-8}
2.560×10^{-7}	1.149×10^{-7}	1.138×10^{-7}
5.120×10^{-7}	2.290×10^{-7}	2.268×10^{-7}
1.024×10^{-6}	4.590×10^{-7}	4.550×10^{-7}

COMPARISON OF THEORY WITH EXPERIMENT

Experimental Curve

The expression for instantaneous current to a spherical electrode is given by

$$i = nFD_0 4\pi r_0^2 \left(\frac{\partial C}{\partial r} \right)_{r_0}, \quad (52)$$

where n is the number of electrons transferred in the reduction, F the Faraday constant, D_0 the diffusion coefficient, $4\pi r_0^2$ the area of the mercury drop and $\left(\frac{\partial C}{\partial r} \right)_{r_0}$ the gradient of the concentration at the drop surface.

Inserting Equation (31) into Equation (52) gives

$$i = 4 nFD_0 C_0 r_0^2 \left[\frac{1}{r_0} + \frac{1}{\sqrt{\pi D_0 f_E(t)}} \right], \quad (53)$$

where the subscript, E , denotes experiment.

Solving for $f_E(t)$ yields

$$f_E(t) = \frac{1}{\pi D_0} \left[\frac{i}{4\pi nFD_0 C_0 r_0^2} - \frac{1}{r_0} \right]^{-2}. \quad (54)$$

Equation (54) is multiplied by D_0^3/γ_0^2 to give

$$\bar{F}_E(\bar{t}) = \frac{D_0^2}{\pi \gamma_0^2} \left[\frac{i}{4\pi nFD_0 C_0 r_0^2} - \frac{1}{r_0} \right]^{-2}. \quad (55)$$

Putting experimental values of \underline{i} and \underline{t}^{12} into Equation (55) gives a relationship between $\underline{I}_E(\bar{t})$ and \bar{t} as shown with points in Figure 4. Table 3 gives values of $\underline{I}_E(\bar{t})$ and \bar{t} for the corresponding \underline{t} and \underline{t} . The behavior of the experimental $\underline{I}_E(\bar{t})$ is quite similar to the theoretical curves in Figure 3.

Comparison of Curves

Figure 4 shows the comparison of Run 4 with experiment. The starting value for Run 4 is used for Equation (50) and the resulting calculations are listed in Table 2. This solution of Equation (54) is not plotted in Figure 4 because of the closeness of values with Run 4.

The agreement between experiment and theory is very close for small times. For large times, the experimental curve becomes linear with a slope of approximately .388. The theoretical curve becomes linear also but with a slope of .444. Matsuda's curve, if plotted, yields a slope of .442 for large times.

Equations (41) and (50) differ by the factors and 28/9. These factors account for the close agreement between Matsuda's theory and the present theory.

¹²Taylor, J. K., Smith, R. E., and Cooter, T. L., J. Research Natl. Bur. Standards, 42, 387 (1949).

Table 3. Variation of $\bar{F}_E(\bar{t})$ with \bar{t} .

i (μa)	t (sec)	\bar{t}	$\bar{F}_E(\bar{t})$
4.20	0.049	1.110×10^{-8}	5.559×10^{-8}
6.74	0.076	1.720×10^{-8}	3.500×10^{-8}
8.67	0.104	2.350×10^{-8}	3.100×10^{-8}
12.48	0.204	4.620×10^{-8}	3.598×10^{-8}
14.42	0.296	6.700×10^{-8}	4.383×10^{-8}
16.81	0.461	1.043×10^{-7}	5.817×10^{-8}
18.47	0.635	1.437×10^{-7}	7.400×10^{-8}
20.05	0.863	1.953×10^{-7}	9.491×10^{-8}
20.99	1.038	2.349×10^{-7}	1.111×10^{-7}
22.92	1.451	3.283×10^{-7}	1.463×10^{-7}
24.83	2.005	4.538×10^{-7}	1.929×10^{-7}
25.94	2.446	5.536×10^{-7}	2.315×10^{-7}
26.81	2.932	6.635×10^{-7}	2.776×10^{-7}
27.38	3.392	7.676×10^{-7}	3.251×10^{-7}

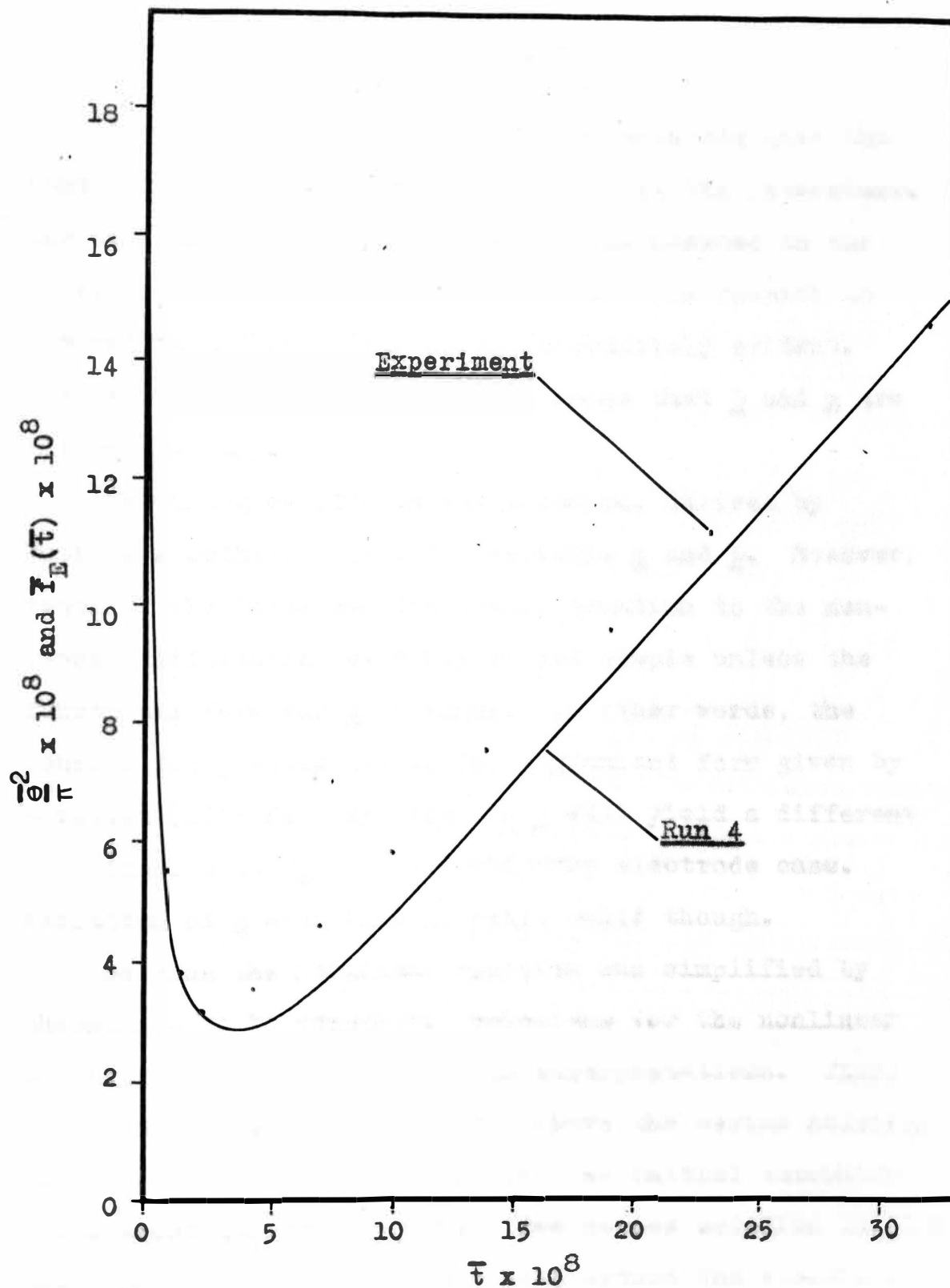


Figure 4. Comparison of $I_E(\bar{\tau})$ with Run 4

SUMMARY AND CONCLUSIONS

The derivation of the diffusion equation gave the same partial differential equation as in the literature. The way that the convection term is introduced in the literature does account for diffusion with respect to the medium although this is not immediately evident. The derivation is general in the sense that \underline{D} and \underline{m} are allowed to vary.

The integro-differential equation, derived by Matsuda's method, allows for variable \underline{m} and \underline{D} . However, reducing the integro-differential equation to the nonlinear differential equation is not simple unless the functional form for \underline{D} is known. In other words, the choice for \underline{C} would not be the convenient form given by Equation (27); for variation in \underline{D} will yield a different relationship for \underline{C} in the stationary electrode case. Variation of \underline{m} with time is still valid though.

Solving the nonlinear equation was simplified by choosing \underline{m} to be constant. Solutions for the nonlinear equation imply certain physical interpretations. Those solutions represented by curves above the series solution (Curves 1, 2, 3, 4 and 5) are for low initial concentrations about the mercury drop. The series solution implies that the concentration is the same around the electrode initially, as it is throughout the electrolyte. Solutions

below the series solution (Curves 6, 7, 8, 9 and 10) are for high initial concentrations about the drop.

The results show that the concentration function describing the diffusion does not need to be broken up into two parts. The choice for \underline{C} given in this paper avoids any questionable boundary conditions such as those employed by Matsuda.¹ The form for $\underline{F}(\bar{t})$ derived from this theory does have the same form as $\underline{F}_E(\bar{t})$. The similarity in the behavior of $\underline{F}(\bar{t})$ and $\underline{F}_E(\bar{t})$ indicates that the choice for \underline{C} is nearly correct. Perhaps if $\underline{f}(t)$ in Equation (29) is allowed to vary with r also, then the solutions for $\underline{f}(r_0, t)$ may agree with $\underline{f}(t)$ even better.

It is obvious that the present theory does not describe the experimental results completely. More work has to be done. This paper does indicate that a new choice for \underline{C} , where $\underline{f}(t)$ is replaced by $\underline{f}(r, t)$, may lead to the desired agreement between theory and experiment. Choosing the desired form for $\underline{f}(r, t)$ and assigning physical meaning to it is the problem to be solved next.

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APPENDIX I

Solutions of Equations (41) and (50) can be obtained by the following program:¹³

```

C
C   PROGRAM TO SOLVE A NONLINEAR DIFFERENTIAL EQUATION
C   USING FOURTH ORDER RUNGE KUTTA
C
G=(3.*.002305)/(4.*3.14159265*13.55)
G=G**.33333333
GG=G*G
GGG=G*GG
PUNCH 500,GGG
500 FORMAT(E20.8)
C=8.*GG
D=2.*G
E=C/4
F=0
1000 READ 1100,TS,YS,DT,N,DC
1100 FORMAT(3F10.0,15,5XE20.8)
A=6.*DC*G
A=A*3.14159265
B=G*A
RS=TS**(.16666667)
R2=RS*RS
R3=RS*R2
R4=R2*R2
R8=R2*TS
Y2=YS*YS
Y3=YS*Y2
IF(YS) 1150,1150,1175
1150 YP=0.
GO TO 1190
1175 YP=(A*TS*YS+B*R8-C*R2*Y2-D*Y3-F*R4*YS)/(E*R3*YS+
D*Y2*RS)
1190 YTP=6.*R2*R3*YP
YSQ=YS*YS
YSQ=YSQ/(3.14159265*DC)
PUNCH 1200,TS,YS,YSQ,YTP

```

¹³ Germain, B., Programming The IBM 1620, Prentice-Hall, Inc., Englewood, New Jersey, 1962, p. 102.

```

1200 FORMAT(3F10.7,E16.8)
    RSS=RS
    DO 2000 I=1,N
    TS=TS+DT
    RS=TS**(.16666667)
    DR=RS-RSS
    XM1=DR*YP
    ADD=XM1/2.
    DRH=DR/2.
    JUMP=-1
1300 ARS=RSS/DRH
    AR2=ARS*ARS
    AR3=ARS*AR2
    AR4=AR2*AR2
    AR6=AR3*AR3
    AR8=AR6*AR2
1400 AYS=YS+ADD
1450 AY2=AYS*AYS
    AY3=AYS*AY2
    YP=(A*AR6*AYS+B*AR8-C*AR2*AY2-D*AY3-F*AR4*AYS)
    YP=YP/(E*AR3*AYS+D*AY2*ARS)
    IF(JUMP) 1500,1600,1700
1500 JUMP=0
    XM2=DR*YP
    ADD=XM2/2.
    GO TO 1400
1600 JUMP=1
    XM3=DR*YP
    ARS=RS
    AR2=RS*RS
    AR3=RS*AR2
    AR4=AR2*AR2
    AR6=TS
    AR8=TS*AR2
    GO TO 1400
1700 IF(JUMP-1) 1800,1800,1900
1800 JUMP=2
    XM4=DR*YP
    YS=YS+(XM1+2.*XM2+2.*XM3+XM4)/6.
    AYS=YS
    GO TO 1450
1900 YTP=6.*RS**5*YP
    YSQ=YS*YS
    YSQ=YSQ/(3.14159265*DC)
    PUNCH 1200,TS,YS,YSQ,YTP
2000 RSS=RS
    GO TO 1000
    END

```

For Equation (41), the thirteenth card should read $A=A*3.14159265$ and for Equation (50) the thirteenth card should read $A=A*3.11111111$.