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A New Partial Differential Equation and a New Instantaneous Current-time Curve for Polarography

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A NEW PARTIAL DIFFERENTIAL EQUATION AND A NEW INSTANTANEOUS
CURRENT-TIME CURVE FOR POLAROGRAPHY

BY

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

1965

A NEW PARTIAL DIFFERENTIAL EQUATION AND A NEW INSTANTANEOUS
CURRENT-TIME CURVE 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 Advised Aug 3 1964
Date

_____ Head, Physics Department 8/3/64
Date

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RBK

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INTRODUCTION

Present theories describing polarographic processes are inadequate; for, they do not correctly predict experimental results. Investigations which center on this variance are actually too few even though polarographic analysis is widely employed. Most probably, this lack of inquiry stems from researchers being content with equations which satisfactorily predict the average diffusion current. However, this use of the average conceals how poorly the instantaneous time-dependence of the diffusion current is represented.

Accordingly, this paper attempts to illuminate the situation and do what it can to remedy the problem.

Some authors have sought to make theory agree with experiment by improving the approximate solution of the accepted partial differential equation (p.d.e.). Such attempts have met with little success¹ in predicting the instantaneous current. Consequently, a revision of the basic postulates is suggested.

The present paper points out a flaw inherent in the accepted p.d.e. A corrected p.d.e. is then derived which, however, seems to be intractable. Nevertheless, not being able to solve the p.d.e. does not detract from its implications.

A few workers have adopted a nonrigorous approach to the problem and have obtained better results. Since a solution to the new

¹J. M. Markowitz and P. J. Elving, Chem. Revs., 58, 1047 (1959).

p.d.e. was not found, the present study also engages in a nonrigorous research which proves fruitful, yielding better results than have hitherto been obtained.

This paper begins with a compendium of polarography for the purpose of familiarization. It then explains the nature of the problem that confronts polarography. This is followed by a derivation of a new p.d.e. and a derivation of a function that fits the instantaneous current-time data.

POLAROGRAPHY

Around 1920, Jaroslav Heyrovsky invented a method of analysis based on the concentration polarization which occurs at a small electrode in a solution.² He called it polarography, probably to emphasize this dependence on polarization.

Thus, one may define polarography as the method of analysis based on electrolyzing a minute fraction of a solution in a cell consisting of one small, easily polarizable, and one large non-polarizable electrode.³ Subsequent examination of the current-voltage curve obtained from the electrolysis reveals the nature and concentration of the reacting material.

Originally, the current-voltage curves were plotted manually at the expense of much labor and time. This circumstance was relieved, and exploitation of polarography was made possible, when in 1925, Heyrovsky developed the polarograph. This instrument automatically records the current-voltage curves, now termed polarograms.

Apparatus

Figure 1 is a diagram of a simplified arrangement used in polarographic analysis.

The apparatus consists of a reservoir D that supplies mercury to a fine glass capillary E via a flexible rubber tube. The capillary,

²J. Heyrovsky, Chem. Listy, 16, 256 (1922).

³O. H. Muller, The Polarographic Method of Analysis, 2nd Ed., Chemical Education Publishing Co.: Easton, Pa., 1956, p. 64.

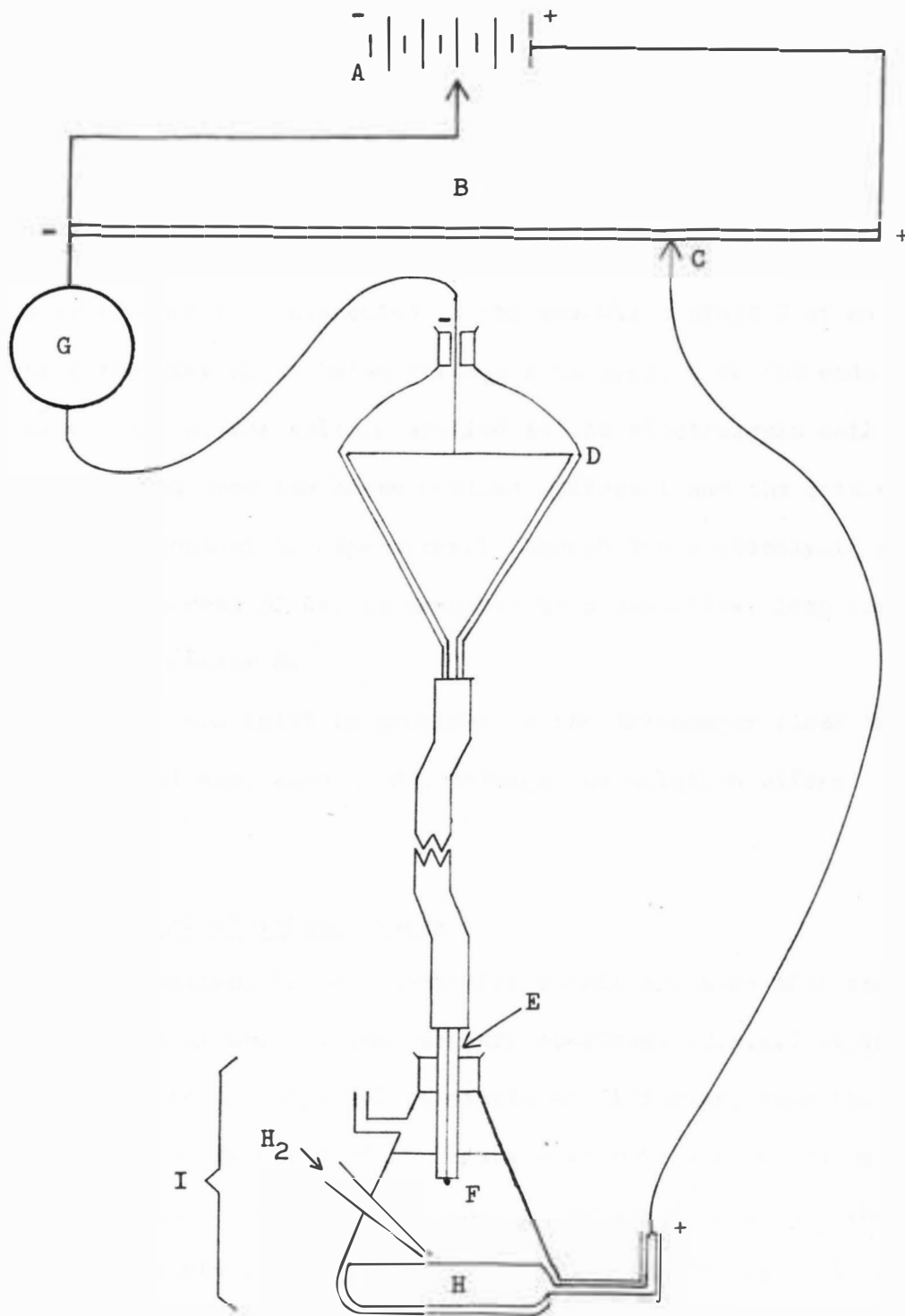


Figure 1. Schematic Drawing of Dropping Mercury Electrode Apparatus

which is between 5 and 10 cm long, has a diameter of about 0.05 mm, so that by properly adjusting the height of the reservoir, mercury will issue dropwise from the capillary at F, at about the rate of 3 sec per drop. The drops, which form small polarizable electrodes, fall into a pool of mercury H, which forms a large non-polarizable electrode. The latter electrode is connected to the movable contact C of an accurate slide wire B. A known voltage A is applied to the ends of the slide wire. Hence, the voltage applied to the electrolysis cell I can be calculated from the known applied voltage A and the setting of the slide wire contact C. The current through the electrolysis cell, which does not exceed 50 μ a, is measured by a sensitive, long period, ballistic galvanometer G.

A small glass inlet is provided on the Erlenmeyer flask for bubbling an inert gas, such as H_2 , through the solution before electrolysis.

Operation and Current-Voltage Curve

When conditions in the electrolysis cell are such that the rate of reaction at the dropping mercury electrode (d.m.e.) depends solely on the rate of supply of reactants by diffusion, then the current-voltage curve pictured in Figure 2 is obtained in the following manner: The applied voltage is gradually increased by moving the contact C, in Figure 1, from left to right across the slide wire. At each setting of the contact, the current is measured by the maximum deflection of the galvanometer G.

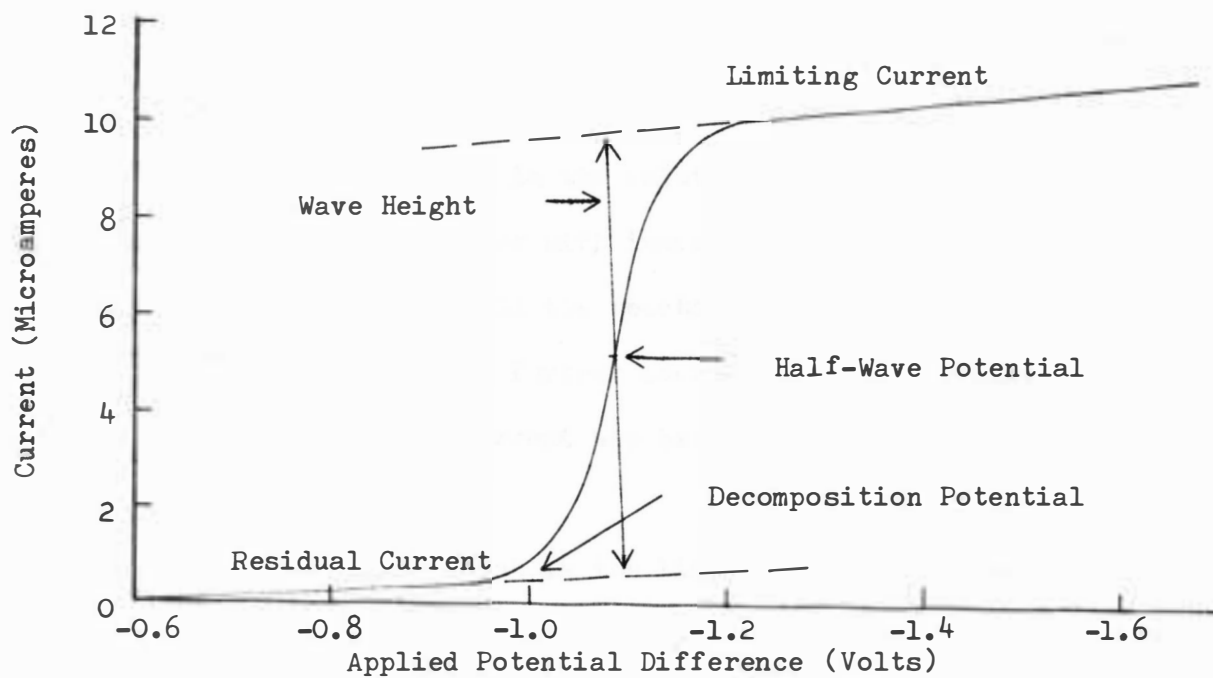


Figure 2. Current-Voltage Curve Obtained Manually

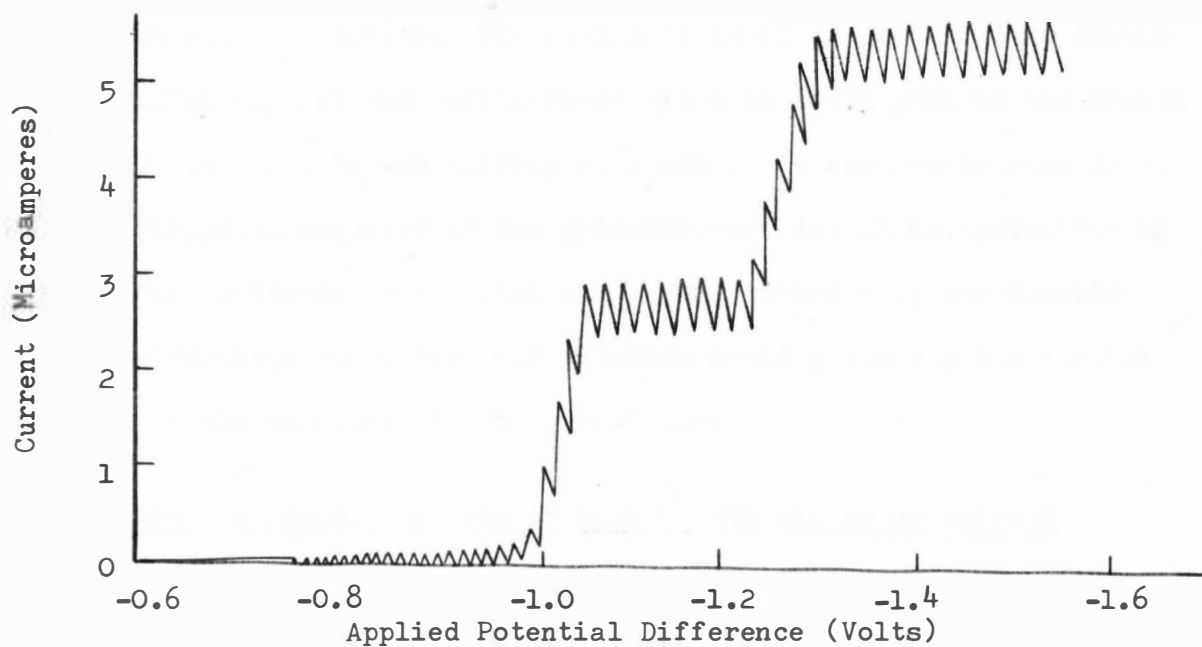


Figure 3. Current-Voltage Curve (Polarogram) Obtained With Polarograph

The small linear increase of current constitutes the residual current. A large increase in current occurs when the decomposition potential of some substance in the solution is reached. This large increase in current continues with increasing voltage until the voltage attains a value such that all the reacting material reaching the electrode is electrolyzed. Further increase in voltage will produce no increase in diffusion current and hence the limiting current is established.

The wave-height, which is the limiting current minus the extrapolated residual current, is the diffusion current and is a function of the concentration of the reacting material. The half-wave potential is characteristic of the nature of the reacting material.

Figure 3 is a current-voltage curve (polarogram) recorded by the polarograph. The case here represents two reacting substances present in the solution. The oscillations of the broken line follow the deflections of the galvanometer and each small peak in the broken line corresponds to the falling of a drop. It can now be seen why a long period is required of the galvanometer, for it is convenient to have the oscillations somewhat localized. A manually constructed current-voltage curve for this solution would produce a curve which would be the envelope of the broken line.

Conditions Necessary for Observation of the Diffusion Current

A polarized electrode assumes a potential appreciably different from that at a point in the body of the solution, while a nonpolarized

electrode does not, regardless of the half-cell reactions occurring at its surface. Now in a polarographic cell, the polarized electrode is the mercury drop and the nonpolarized electrode is the pool of mercury. Hence, any electromotive force applied to the cell becomes the potential of the d.m.e. and this potential determines whether a given half-cell reaction can occur.

At the d.m.e. it is assumed that electron transfer to the reducible ion occurs immeasurably fast. The rate of the half-cell reaction then depends on how fast the ion can be supplied from the body of the solution by virtue of diffusion. For a fixed drop the diffusion rate is proportional to the concentration in the bulk of the solution. Then the current to the d.m.e. would be constant and one would say that a steady state concentration polarization existed. For a drop growing under given conditions, a related proportionality is found.

Ions of the reacting material can reach the d.m.e. via diffusion and electrical migration (migration of charged particles in an electrical field⁴). The current must be controlled by diffusion, so, electrical migration is eliminated by adding a relatively large concentration of an indifferent salt (substance that will migrate but will not react with the ions being studied nor with the electrode in the potential range being used⁵). The ions of the salt effectively limit

⁴Muller, op. cit., p. 60.

⁵Ibid., p. 62.

the potential gradient to a diminutive region next to the electrode so that it no longer affects movement of the ions being investigated.

When the drops fall, they stir the solution to some extent. If the drop rate is faster than 3 sec per drop, the stirring becomes severe, bringing undepleted solution into contact with the d.m.e. Then, incompatible maxima appear in the resulting current-voltage curves. Any stirring with a drop rate slower than 3 sec per drop is effectively eliminated by adding gelatin to the solution.

Oxygen is reduced at small applied emf's, and the resulting current masks the currents of other materials in the solution. Therefore, oxygen is removed by bubbling inert gas through the solution. (Its relatively high concentration in the solution forces oxygen to diffuse into the bubbles, whereupon the bubble removes it from the solution.)

The residual current⁶ is the result of a small charging or "condenser" current. That is, the drop and pool of mercury act as a small capacitor in the electrical circuit, and after each drop falls there is a new capacitor to be charged. As the emf. is increased, more charge can be stored on the capacitor, resulting in a linear increase of the residual current.

When there is more than one material present in the solution, it may happen that their current-voltage curves overlap. The curves

⁶I. M. Kolthoff and J. J. Lingane, Polarography, 2nd Ed., Interscience Publishers, Inc.: New York, 1952, p. 6.

can often be separated by changing the pH of the solution or by forming suitable complexes.⁷

In practice, polarographic analysis is carried out by first comparing the half-wave potential with those that are tabulated for different substances. With the material identified, one determines the unknown concentration by comparing the diffusion current with a calibration curve previously obtained with known solutions.

Advantages and Applications of Polarography

Advantages⁸ of the d.m.e. and of polarography are these: (1) The surface is reproducible, smooth, and continually renewed. (2) Mercury amalgamates with most metals lowering their decomposition potential. (3) The voltage needed to reduce hydrogen is highest on mercury so much work can be done in acid solutions without interference from evolution of hydrogen. (4) Simultaneous quantitative and qualitative analysis of several components of a solution is possible. (5) Only small quantities of solution are needed. Indeed, a cell designed by Majer needs only 0.005 ml. of solution. (6) The detecting range is between 0.01 and 10^{-6} M giving the method high sensitivity. (7) The polarograph makes rapid analysis possible and provides a permanent record of the current-voltage curve.

⁷Muller, op. cit., p. 153.

⁸Ibid., pp. 29 and 147.

With these potent advantages in mind, Otto H. Muller suggests that polarography be ranked along with calorimetry, spectroscopy, potentiometry, and other specialized methods of analytical chemistry.⁹

Applications of polarography are wide and numerous and growing. In inorganic analysis practically all elements as well as many alloys have been subjected to the method. Many organic compounds react at the d.m.e. and polarography therefore finds uses in biology, biochemistry, and medicine. Polarographic analysis can be carried out in solutions using nonaqueous solvents, making many water-insoluble substances subject to the method. In research polarography is well suited for the study of oxidation-reduction phenomenon and rates of reaction in kinetic studies.¹⁰

⁹Ibid.

¹⁰Kolthoff and Lingane, op. cit., p. 14.

DIFFICULTIES IN THE ACCEPTED THEORY

Knowing how the diffusion current is established, one can now turn to the problem of formulating mathematical equations which explain and predict this phenomenon.

Accepted Partial Differential Equation

Reducible ions reach the d.m.e. by virtue of differences in concentration in various parts of the medium. The direction of movement is from high to low concentration regions. The amount of material reaching, or the instantaneous current to, the electrode is therefore given by

$$i = nFAD \left(\frac{\partial C}{\partial r} \right)_{r=r_0} \quad (1)$$

where n is the number of faradays of electricity required per mole of electrode reaction, F is the faraday (96500 coulombs), A is the instantaneous area of the electrode in cm^2 , D is the diffusion coefficient peculiar to the reacting substance and is numerically equal to the number of moles diffusing across unit area in unit time per unit concentration gradient perpendicular to the area (cm^2/sec), and $\left(\frac{\partial C}{\partial r} \right)_{r=r_0}$ is the concentration gradient (the rate of change of concentration with respect to distance r measured normal to area) evaluated at the electrode surface r_0 (moles/ cm^4).

Evaluation of the partial derivative in Eq. (1) requires knowledge of the concentration C as a function of the distance r and the time t . This function is determined by the partial differential

equation describing diffusion to the electrode and the proper boundary conditions. The accepted¹¹ form is

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] - \frac{\gamma}{3r^2} \frac{\partial C}{\partial r} \quad (2)$$

$$C(r_0, t) = 0, \quad \lim_{r \rightarrow \infty} C(r, t) = C_0 \quad t > 0 \quad (3)$$

where r is the distance from the center of the electrode, γ is a constant relating the cubed radius of the drop to its age, and C_0 is the concentration in the bulk of the solution.

Equation (2) is developed in the same manner as the p.d.e. for a stationary spherical electrode, except that the movement of the diffusing material by the moving medium is accounted for by the last term on the right.

Ilkovic and Modified Ilkovic Equations

An approximate solution to the boundary value problem was first obtained by Ilkovic. From this he obtained the diffusion current equation

$$i = 706nD^{1/2}C_m^{2/3}t^{1/6} \mu a \quad (4)$$

in which 706 is a combination of numerical constants and m is the mass rate of flow of mercury (mg/sec). When all quantities are measured in the units hitherto indicated, and when the concentration is expressed in millimoles per liter, the current (Eq. (4)) is in microamperes (μa).

¹¹Markowitz and Elving, op. cit.

Since the galvanometer measures the average current, Eq. (4) is integrated over the life of the drop and then divided by the drop time, t_{\max} , to obtain the theoretical average current:

$$i = 607nD^{1/2}C_m^{2/3}t_{\max}^{1/6} \mu a. \quad (5)$$

Either Eq. (4) or (5) is referred to as the Ilkovic equation.¹²

Lingane and Loveridge¹³ have noted that the concentration gradient used by Ilkovic in Eq. (1) differs from the concentration gradient at a plane electrode by a numerical multiplying factor of $(3/7)^{1/2}$. They then argue that the Ilkovic equation has neglected the curvature of the electrode and that a more nearly correct equation should be obtained by introducing the constant into the concentration gradient at the stationary spherical electrode and using this result in Eq. (1). Thus, they get the following equations, which are analogous to Eqs. (4) and (5):

$$i = 706nD^{1/2}C_m^{2/3}t^{1/6} + 31560nDC_m^{1/3}t^{1/3} \quad (6)$$

$$\bar{i} = 607nD^{1/2}C_m^{2/3}t^{1/6} \left[1 + \frac{39D^{1/2}t^{1/6}}{m^{1/3}} \right] \quad (7)$$

Either Eq. (6) or (7) is referred to as the modified Ilkovic equation.

It is of interest to note that the modified Ilkovic equation has also been derived by Kambara and Tachi using the same procedure

¹²I. M. Kolthoff and J. J. Lingane, op. cit., pp. 41-43.

¹³J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc., 72, 438 (1950).

as Ilkovic but with a higher order approximation in the intervening mathematics.¹⁴

Comparison With Experiment

Equations (4) and (6) will now be checked against experiment. In this way, one will be able to judge the validity of the equations for himself.

A search of the literature provides only one article by Taylor, Smith, and Cooter, which has sufficiently accurate results and enough tabulated data so that it is possible to construct a valid current-time curve.

Taylor, Smith, and Cooter¹⁵ performed their measurements on an aqueous solution of the Cd^{++} ion whose concentration was 3.018 mmoles/liter. The solution also contained a 0.1 molar concentration of KCl (indifferent salt) to stop electrical migration and a .01% concentration of gelatin to suppress current maxima. The rate of flow of mercury was 2.305 mg/sec, and the drop time was 3.392 sec. Finally, the diffusion coefficient for the Cd^{++} ion can be theoretically calculated¹⁶ and is found to be 7.2×10^{-6} cm²/sec. This information is now substituted into Eq.'s (4) and (6), thus preparing them for plotting

¹⁴T. Kambara and I. Tachi, Proceedings International Polarographic Congress, Prague, 1951, Part I, p. 126.

¹⁵J. K. Taylor, R. E. Smith and T. L. Cooter, J. Research Natl. Bur. Standards, 42, 387 (1949).

¹⁶Kolthoff and Lingane, op. cit., p. 94.

Equation (4) becomes

$$\begin{aligned}
 i &= 706nD^{1/2}C_m^{2/3}t^{1/6} \mu a \\
 &= 706(2)(7.2 \times 10^{-6})^{1/2}(3.018)(2.305)^{2/3}t^{1/6} \mu a \\
 &= 19.94t^{1/6} \mu a.
 \end{aligned} \tag{8}$$

Equation (6) becomes

$$\begin{aligned}
 i &= 706nD^{1/2}C_m^{2/3}t^{1/6} + 31560nDC_m^{1/3}t^{1/3} \mu a \\
 &= 19.94t^{1/6} + (31560)(2)(7.2 \times 10^{-6})(3.018)(2.305)^{1/3}t^{1/3} \mu a \\
 &= 19.94t^{1/6} + 1.81t^{1/3} \mu a.
 \end{aligned} \tag{9}$$

Table I contains the data of Taylor, Smith, and Cooter for the experimental current-time plot and also a tabulation of calculated quantities used in plotting Eqs. (8) and (9).

Figure 4 contains the resulting comparison plots. The first particular that attracts attention is that neither of the equations fits the real current-time curve very closely at all. The modified Ilkovic equation seems to be an improvement over the Ilkovic equation; for it approaches the real curve during the latter part of the drop life.

Throughout the polarographic literature, it is common practice to compare the results of experiments with the average currents, Eqs. (5) and (7). It generally happens that the Ilkovic equation (5) yields average currents that are lower than the experimental values. The modified Ilkovic equation (7) yields average currents that are

Table I. Tabulation of data needed to construct comparison plots

Experimental data		Theoretical data for Ilkovic and modified Ilkovic equations					
Time t	Current i	Time t	$t^{1/6}$	$t^{1/3}$	$19.94t^{1/6}$	$1.81t^{1/3}$	$19.94t^{1/6} + 1.81t^{1/3}$
(sec)	(μ a)	(sec)	(sec) ^{1/6}	(sec) ^{1/3}	(μ a)	(μ a)	(μ a)
0.000	0.00	0.0	0.0000	0.0000	0.00	0.000	0.00
0.049	4.20	0.1	0.6813	0.4642	13.58	0.840	14.42
0.104	8.67	0.2	0.7647	0.5848	15.23	1.058	16.29
0.153	10.91	0.3	0.8182	0.6694	16.32	1.211	17.53
0.204	12.48	0.4	0.8584	0.7362	17.11	1.332	18.44
0.296	14.42	0.5	0.8909	0.7937	17.77	1.447	19.22
0.461	16.81	0.6	0.9248	0.8435	18.42	1.526	19.95
0.635	18.47	0.7	0.9423	0.8879	18.78	1.607	20.39
0.863	20.05	0.8	0.9635	0.9285	19.20	1.680	20.88
1.038	20.99	0.9	0.9825	0.9655	19.60	1.748	21.35
1.451	22.92	1.0	1.0000	1.0000	19.94	1.810	21.75
2.005	24.83	1.5	1.0699	1.1447	21.35	2.037	23.39
2.446	25.94	2.0	1.1225	1.2599	22.40	2.280	24.68
2.937	26.81	2.5	1.1650	1.3570	23.25	2.455	25.71
3.392	27.38	3.0	1.2010	1.4420	24.00	2.610	26.61

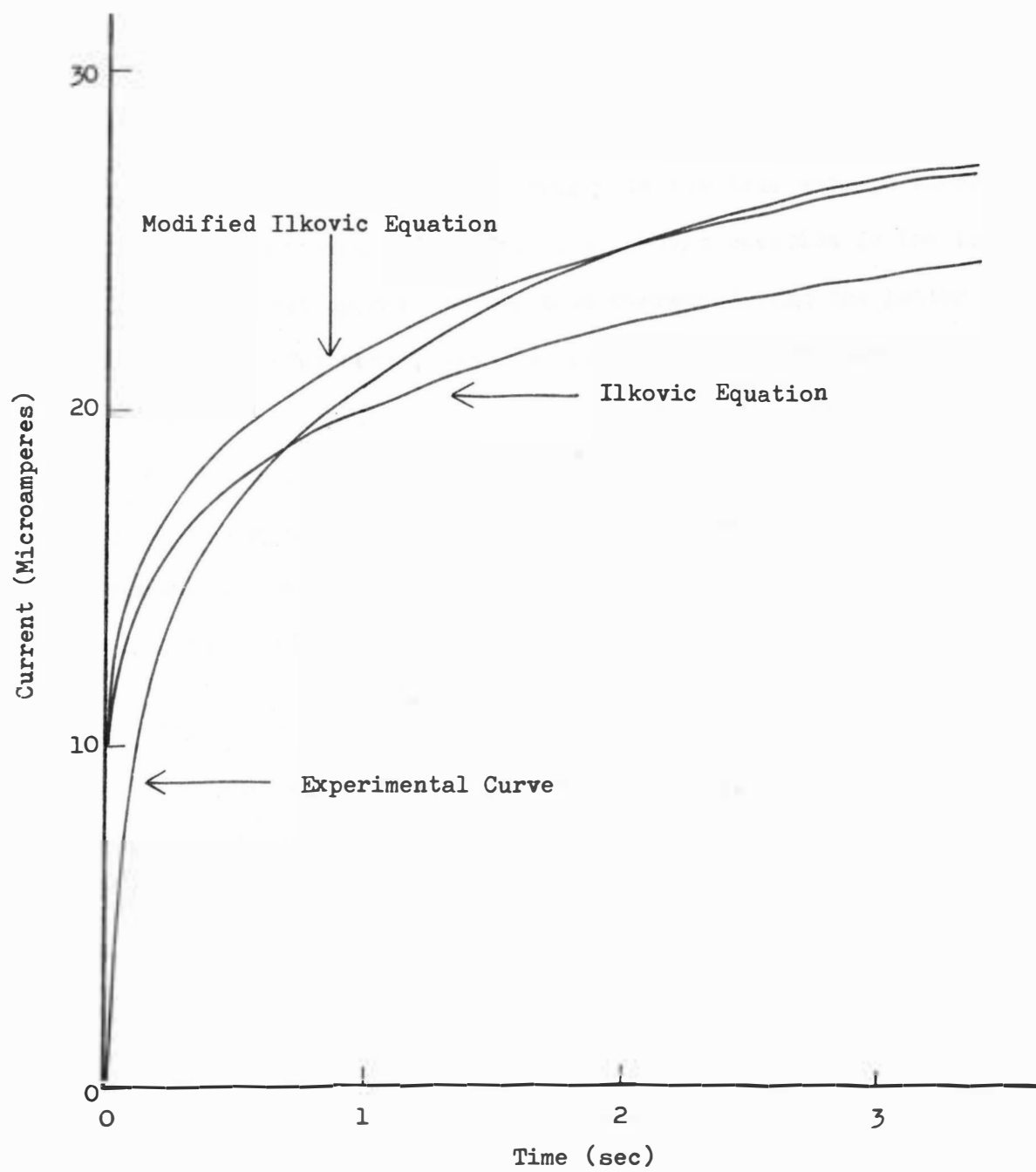


Figure 4. Comparison Plots

larger than experimental values.¹⁷ Such results are easily explained with the help of Figure 4. In this figure one observes that the current corresponding to the Ilkovic equation is too large at the beginning and too small at the end, two compensating errors that make its average current compare more favorably to the true average current. The current corresponding to the modified Ilkovic equation is too large at the beginning, but approaches the true current during the latter part of the drop life; hence, its average current will be larger than the true average current.

The preceding considerations invariably lead one to realize that any valid comparison between theory and experiment should involve instantaneous current-time curves rather than average currents. The latter procedure hides the real discrepancy.

Origin of the Trouble

The trouble may be that the existing equations have not properly formulated or accounted for the phenomena as they were assumed to have done. Or, the trouble may be that effects neglected in the idealizations are in fact asserting themselves noticeably in the physical situation, so that the existing equations do not account for all effects. Or, the trouble with the existing equations may be that they contain both of the above shortcomings.

¹⁷Kolthoff and Lingane, op. cit., p. 95.

Markowitz and Elving¹⁸ have shown that different approximations and procedures used in solving the accepted p.d.e. have yielded poor results. Indeed, their work supports the first suggestion above indicating that the given p.d.e. must be in error. In pursuing this idea, it was found that the accepted p.d.e. does not properly contain the concept that diffusion occurs with respect to the medium. That is, in the derivation of the accepted p.d.e., the concentration gradient is applied in terms of a space variable rather than in terms of a variable that is fixed with respect to the medium. This fact can be recognized in Eq. (2); for, here the terms depending on diffusion are identical for the case of diffusion up to a stationary spherical electrode. The next section contains a derivation of a p.d.e. that properly accounts for this concept.

The last suggestion given above is the most realistic and forms the basis of the calculations carried out in the section following the next.

¹⁸Markowitz and Elving, op. cit.

A NEW PARTIAL DIFFERENTIAL EQUATION

Assumptions

The idealizing assumptions made for mathematical expediency are listed and discussed below:

1. The potential of the d.m.e. is large enough to completely deplete the layer of solution next to the electrode surface. Since electron transfer occurs immeasurably fast, this is a realistic assumption and it assures that the rate of reaction is dependent on the rate of supply of the reducible ions. This assumption provides one of the boundary conditions, expression (3), of the preceding section.

2. The mercury drop is spherical. This assumption can be considered a fact because MacNevin and Balis¹⁹ have used a high-speed motion picture camera to verify that the drops are not only perfect spheres but that they also make a clean break from the capillary tip.

3. The volume rate of growth is constant. This assumption has not been subjected to verification. Lingane²⁰ argues that use of a nonconstant volume rate of growth would significantly change pertinent equations and go a long way in closing the gap between theoretical and experimental current-time curves. It is here advanced that the moving column of mercury will have a relatively large momentum which

¹⁹W. M. MacNevin and E. W. Balis, J. Am. Chem. Soc., 65, 660 (1943).

²⁰J. J. Lingane, J. Am. Chem. Soc., 75, 788 (1953).

would persist in keeping the rate of flow constant by counteracting any back pressure caused by the interfacial tension of the mercury drop.

4. The drop is motionless except for its growth. Actually, the center of mass moves downward as the drop grows, but this motion is neglected.

5. The solution is considered a body of infinite extent. Antweiler²¹ has utilized an ingenious optical method that photographically reveals depleted regions in the solution. Pictures of the d.m.e. in operation show that the effective diffusion layer is about 0.005 cm thick.

6. The mercury drop is isolated. This assumption is at best an approximation. The pictures by Antweiler definitely show that the capillary tip obstructs the diffusion field. However, this effect is neglected, for its inclusion would eliminate the possibility of deriving a p.d.e.

7. There is no depleted solution left at the capillary tip by the preceding drop. This assumption has not been verified. Whether or not there is depleted solution left by the preceding drop is a moot point. Perhaps this question could have been answered in the experiments by Antweiler if he had taken pictures of the beginning of drop

²¹Von H. J. Antweiler, Ztschr. Elektrochem., 44, 888 (1938).

formation. Indeed, Markowitz and Elving²² use the idea of depleted solution left behind to develop a theoretical current-time curve substantially in agreement with the experimental current-time curve. However, assumption 7 is used because the contrary approach presents a formidable problem.

Effects to be Considered

It is now possible to recognize the following three effects which the pending derivation will fully take account of:

- 1) Diffusion occurs with respect to the medium.
- 2) The area of diffusion increases with time.
- 3) The solution originally occupying the volume of the mercury drop will be present as a layer of solution around the drop.

Another "distinct" effect is that the outward velocity of the drop surface counteracts the decay of the concentration gradient at the surface of the drop. However, the solution allows for this as long as movement of the medium and the boundary are properly introduced.

Derivation of the Partial Differential Equation

First, consider an infinitesimal spherical shell of the solution at some particular instant when it is out a given distance from the d.m.e. as in Figure 5. The radius of the growing electrode is denoted by r_0 . Taking the volume rate of growth constant yields

²²J. M. Markowitz and P. J. Elving, J. Am. Chem. Soc., **81**, 3518 (1959).

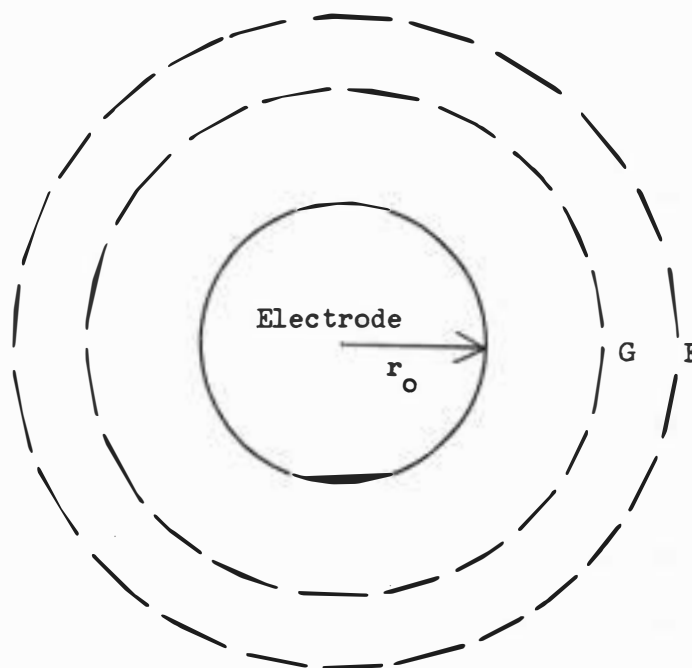


Figure 5. Position of Spherical Shell

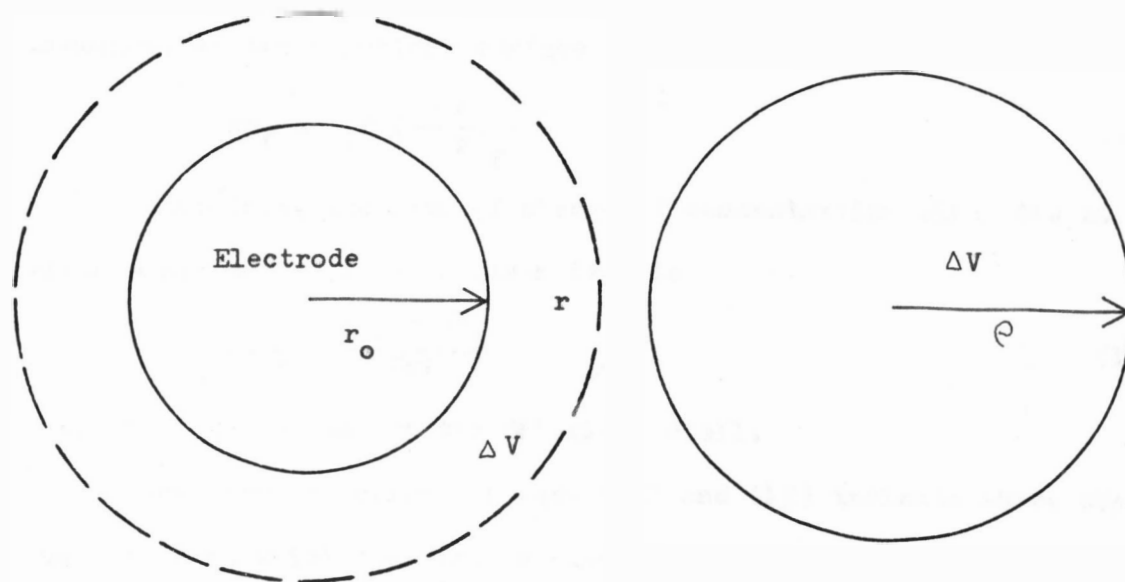


Figure 6. Definition of ρ

$$\frac{4}{3} \pi r_0^3 = \frac{m t}{d} = \alpha t \quad (10)$$

where \underline{m} is the mass rate of flow of mercury, \underline{d} the density of mercury, and $\underline{\alpha}$ the volume rate of flow of mercury, which is constant. Equation (10) is solved for r_0^3 to get

$$r_0^3 = \frac{3 \alpha}{4 \pi} t = \gamma t \quad (11)$$

Equation (11) states that the cubed radius is directly proportional to the age of the drop.

Since the surface G moves with the fluid, electroreducible material crosses this surface because of diffusion forces only. If the area of surface G is denoted by \underline{A}_g , then the number of moles \underline{dN}_g that diffuse across this surface in the time \underline{dt} is given by the expression

$$dN_g = A_g D \left(\frac{\partial C}{\partial r} \right)_g dt \quad (12)$$

Likewise, at the spherical surface F one has the equation

$$dN_f = A_f D \left(\frac{\partial C}{\partial r} \right)_f dt \quad (13)$$

Therefore, the rate of change of concentration with time in the given spherical shell at a given time is

$$\frac{\partial C}{\partial t} = \frac{dN_f - dN_g}{V dt} \quad (14)$$

where \underline{V} is the volume of the spherical shell.

Now, the subscripts in Eqs. (12) and (13) indicate where the quantities to which they are applied are to be evaluated. If the

concentration gradient $\partial C / \partial r$ is to be used, it will have to be evaluated at some point which is a function of time. That is, one cannot have the evaluation $(\partial C / \partial r)_{r_g}$, because this freezes the position of surface G . Rather, the evaluation would have to be $(\partial C / \partial r)_{g(t)}$, which would allow surface G to move.

Instead of carrying out such a procedure, the concentration gradient with respect to the space variable r will be replaced by a concentration gradient with respect to a variable ρ that is fixed with respect to the fluid. The variable ρ is defined as the radius of a hypothetical sphere whose volume is the same as the volume enclosed between the surface of the growing drop and a spherical surface of radius larger than the radius of the drop. This is pictured in Figure 6. By the definition one can write

$$4/3 \pi r^3 - 4/3 \pi r_0^3 = 4/3 \pi \rho^3$$

$$\rho^3 = r^3 - r_0^3 = r^3 - \gamma t \quad (15)$$

where the last equality holds by virtue of Eq. (11).

The new variable ρ is truly fixed with respect to the medium; for, it can be argued that each particle of the medium which is at a different distance from the origin of the mercury drop will have a different value of ρ , and each particle will always retain its value of ρ .

The rule for differentiating function of functions gives

$$\frac{\partial c}{\partial r} = \frac{\partial c}{\partial \rho} \frac{\partial \rho}{\partial r}$$

Now, differentiating Eq. (15) implicitly with respect to \underline{r} yields

$$3 \rho^2 \frac{\partial \rho}{\partial r} = 3r^2$$

Substituting this in the previous equation will give the desired relation between the concentration gradients:

$$\frac{\partial c}{\partial r} = \frac{r^2}{\rho^2} \frac{\partial c}{\partial \rho} = \frac{(\rho^3 - r_0^3)^{2/3}}{\rho^2} \frac{\partial c}{\partial \rho} \quad (16)$$

In Figure 5, the spherical surface G has the space radius \underline{r}_g , so $\underline{\rho}$ for this surface is

$$\rho_g^3 = r_g^3 - r_0^3 \quad (17)$$

The surface F has the space radius $\underline{r}_g + \underline{dr}$, so $\underline{\rho}$ for this surface is

$$\rho_f^3 = (\rho_g + d\rho)^3 = (r_g + dr)^3 - r_0^3 \quad (18)$$

Therefore, the volume \underline{V} of the spherical shell is given by

$$V = \frac{4\pi}{3} (r_g + dr)^3 - \frac{4\pi}{3} r_g^3 = \frac{4\pi}{3} (\rho_g + d\rho)^3 - \frac{4\pi}{3} r_0^3 -$$

$$\frac{4\pi}{3} \rho_g^3 - \frac{4\pi}{3} r_0^3$$

Expanding this result and neglecting infinitesimals of second and higher order yields

$$V = 4\pi r_g^2 dr = 4\pi \rho_g^2 d\rho \quad (19)$$

The area of surface G is (using Eq. (17))

$$A_g = 4\pi r_g^2 = 4\pi (\rho_g^3 + r_0^3)^{2/3} \quad (20)$$

while that of F is (using Eq. (18))

$$A_f = 4 \pi (r_g + dr)^2 = 4 \pi \left[(e_g + de)^3 + r_o^3 \right]^{2/3} \quad (21)$$

Finally, substituting Eqs. (16), (20), and (21) into Eqs. (12) and (13) they become

$$dN_g = 4 \pi (e_g^3 + r_o^3)^{2/3} D \frac{(e_g^3 + r_o^3)^{2/3}}{e_g^2} \left(\frac{\partial c}{\partial e_g} \right) dt \quad (22)$$

$$dN_f = 4 \pi \left[(e_g + de)^3 + r_o^3 \right]^{2/3} D \frac{\left[(e_g + de)^3 + r_o^3 \right]^{2/3}}{(e_g + de)^2} \times \left(\frac{\partial c}{\partial e_f} \right) dt \quad (23)$$

The new concentration gradients are still bearing a general subscript. However, one can now give them a specific evaluation:

$$\left(\frac{\partial c}{\partial e} \right)_g = \left(\frac{\partial c}{\partial e} \right)_{e_g} \quad (24)$$

$$\left(\frac{\partial c}{\partial e} \right)_f = \left(\frac{\partial c}{\partial e} \right)_{e_g + de} = \left(\frac{\partial c}{\partial e} \right)_{e_g} + \left(\frac{\partial^2 c}{\partial e^2} \right)_{e_g} de \quad (25)$$

Then Eqs. (22) and (23) become

$$dN_g = 4 \pi (e_g^3 + r_o^3)^{4/3} \frac{D}{e_g^2} \left(\frac{\partial c}{\partial e} \right)_{e_g} dt \quad (26)$$

$$dN_f = 4 \pi \left[(e_g + de)^3 + r_o^3 \right]^{4/3} \frac{D}{(e_g + de)^2} \left[\left(\frac{\partial c}{\partial e} \right)_{e_g} + \left(\frac{\partial^2 c}{\partial e^2} \right)_{e_g} de \right] dt \quad (27)$$

The infinitesimal in the denominator of Eq. (27) is neglected. Then Eqs. (26), (27), and (19) are substituted into Eq. (14) to give the following:

$$\frac{\partial c}{\partial t} = \frac{4 \pi \left[(r_g + dr)^3 + r_o^3 \right]^{4/3} D \left[\left(\frac{\partial c}{\partial r} \right) r_g + \left(\frac{\partial^2 c}{\partial r^2} \right) r_g dr \right] dt}{4 \pi r^4 dr dt} - \frac{4 \pi (r_g^3 + r_o^3)^{4/3} D \left(\frac{\partial c}{\partial r} \right) r_g dt}{4 \pi r^4 dr dt} \quad (28)$$

This equation is true for any spherical surface G, so the subscript g can be dropped.

Note that

$$\begin{aligned} \left[(r + dr)^3 + r_o^3 \right]^{4/3} &= \left[(r^3 + r_o^3) + 3r^2 dr + 3r(dr)^2 + (dr)^3 \right]^{4/3} \\ &= \left[(r^3 + r_o^3) + 3r^2 dr \right]^{4/3} \\ &= (r^3 + r_o^3)^{4/3} + 4(r^3 + r_o^3)^{1/3} r^2 dr + \dots \end{aligned}$$

By using Eq. (29) but dropping the terms of second and higher order, Eq. (28) becomes

$$\frac{\partial c}{\partial t} = \frac{4 \pi \left[(r^3 + r_o^3)^{4/3} + 4(r^3 + r_o^3)^{1/3} r^2 dr \right] D \left[\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} dr \right] dt}{4 r^4 dr dt} - \frac{4 \pi (r^3 + r_o^3)^{4/3} D \frac{\partial c}{\partial r} dt}{4 \pi r^4 dr dt} \quad (30)$$

The numerator is now expanded and proper terms are cancelled. Also, terms containing second and higher order infinitesimals are

neglected to give the following expression

$$\frac{\partial C}{\partial t} = \frac{4\pi(\rho^3 + r_0^3)^{4/3} D \frac{\partial^2 C}{\partial \rho^2} d \rho dt + 16\pi(\rho^3 + r_0^3)^{1/3} \rho^2 D \frac{\partial C}{\partial \rho} d \rho dt}{4\pi \rho^4 d \rho dt} \quad (31)$$

Finally, by cancelling common factors and substituting Eq. (11), the desired p.d.e. is obtained

$$\frac{\partial C}{\partial t} = \frac{(\rho^3 + \gamma t)^{4/3}}{\rho^4} D \frac{\partial^2 C}{\partial \rho^2} + \frac{4(\rho^3 + \gamma t)^{1/3}}{\rho^2} D \frac{\partial C}{\partial \rho} \quad (32)$$

The boundary conditions are

$$C(0, t) = 0, \quad \lim_{\rho \rightarrow \infty} C(\rho, t) = C_0, \quad t > 0 \quad (33)$$

In the derivation, effects (1) and (2) have been explicitly introduced. Now to show that effect (3) has been implicitly accounted for, the following transformation of coordinates is employed.

$$\begin{aligned} C(\rho, t) &\longrightarrow C(r, \tau) \\ r^3 &= \rho^3 + \gamma t, \quad \tau = t \end{aligned} \quad (34)$$

Again using the rules for differentiating functions of functions and employing Eqs. (34), one gets the relations,

$$\frac{\partial C(r, \tau)}{\partial \rho} = \frac{\partial C}{\partial r} \frac{\partial r}{\partial \rho} + \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial \rho} = \frac{\rho^2}{r^2} \frac{\partial C}{\partial r} \quad (35)$$

$$\frac{\partial^2 C(r, \tau)}{\partial \rho^2} = \frac{\partial C}{\partial r} \frac{\partial^2 r}{\partial \rho^2} + \frac{\partial^2 C}{\partial r^2} \left(\frac{\partial r}{\partial \rho} \right)^2 = \left(\frac{2\rho}{r^2} - \frac{2\rho^4}{r^5} \right) \frac{\partial C}{\partial r} + \frac{\rho^4}{r^4} \frac{\partial^2 C}{\partial r^2} \quad (36)$$

$$\frac{\partial C(r, \tau)}{\partial t} = \frac{\partial C}{\partial r} \frac{\partial r}{\partial t} + \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial t} = \frac{\gamma}{3r^2} \frac{\partial C}{\partial r} + \frac{\partial C}{\partial \tau} \quad (37)$$

Substituting Eqs. (34), (35), (36), and (37) into Eq. (32)

gives,

$$\frac{\gamma}{3r^2} \frac{\partial C}{\partial r} + \frac{\partial C}{\partial \tau} = \frac{r^4}{\rho^4} D \left[\left(\frac{2\rho}{r^2} - \frac{2\rho^4}{r^5} \right) \frac{\partial C}{\partial r} + \frac{\rho^4}{r^4} \frac{\partial^2 C}{\partial r^2} \right] + \frac{4r}{\rho^2} D \frac{\rho^2}{r^2} \frac{\partial C}{\partial r}$$

$$\frac{\partial C}{\partial \tau} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \left(1 + \frac{r^3}{\rho^3} \right) \frac{\partial C}{\partial r} \right] - \frac{\gamma}{3r^2} \frac{\partial C}{\partial r} \quad (38)$$

Equation (38) should not be compared with the accepted p.d.e. (keeping in mind that $\underline{\gamma}$ and \underline{t} are the same). The accepted p.d.e. was explicitly set up to produce the convective term; hence, one must conclude that since Eq. (38) also contains the convective term, Eq. (32) implicitly accounts for effect (3).

Neither Eq. (32) nor (38) could be solved. Indeed, applying the same approximation to Eq. (38) as Ilkovic did to the accepted p.d.e. was ineffective, the trouble being that the approximation did not separate the independent variables as it did in the accepted p.d.e.

A NEW CURRENT-TIME RELATIONSHIP

A solution to the new p.d.e. would have proved very interesting and conceivably it might have gone a long way in diminishing the discrepancy between the theoretical and experimental current-time curves. In any event, however, it is certain that the unrealistic assumptions, (6) and (7), of the preceding section would ultimately have to be accounted for.

What follows, then, is a nonrigorous attempt to incorporate all features that are actually at work in the physical situation. Such nonrigorous approaches are not new in polarographic literature. Nevertheless, the approximations seem more reasonable than those made by other workers and better results are obtained.

Formulation of a Soluble Problem

The process can be broken down into a series of stages, each stage of which is diffusion up to a stationary spherical electrode.

The concentration function for the stationary spherical electrode of radius r_0 is

$$C(r,t) = C\left(1 - \frac{r_0}{r}\right) + \frac{2Cr_0}{r\sqrt{\pi}} \int_0^{\frac{r-r_0}{2\sqrt{Dt}}} e^{-y^2} dy \quad (39)$$

from which the concentration gradient at the surface of the electrode is found to be

$$\left(\frac{\partial C}{\partial r}\right)_{r_0} = C\left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt}}\right) \quad (40)$$

Since Eq. (40) governs the instantaneous current to the electrode, the problem reduces to determining how Eq. (40) must be modified before it can be used to calculate the instantaneous concentration gradient at the d.m.e.

The modification needs to take into account the following effects: (1) The velocity of the drop surface enhances the concentration gradient. (2) Depleted solution left from the previous drop hinders diffusion. (3) The capillary obstructs the diffusion field. A consideration of these effects at a given stage of the process will tell how Eq. (40) should be modified.

Solution

Consider the d.m.e. when its radius is r_0 . If there were a stationary spherical electrode of radius r_0 that had been in operation for the length of time that it took for the d.m.e. to form a drop of this size, its concentration-distance curve would look like Figure 7. But the result of effect (1) is to displace lower parts of the curve to the right with respect to higher parts. This change is pictured in Figure 8, where the dotted lines represent the supposed real situation for the d.m.e.

From Figure 8 one observed that the concentration gradient (represented by the tangent line) at the drop surface is larger than it would have been if the drop had been stationary from its inception.

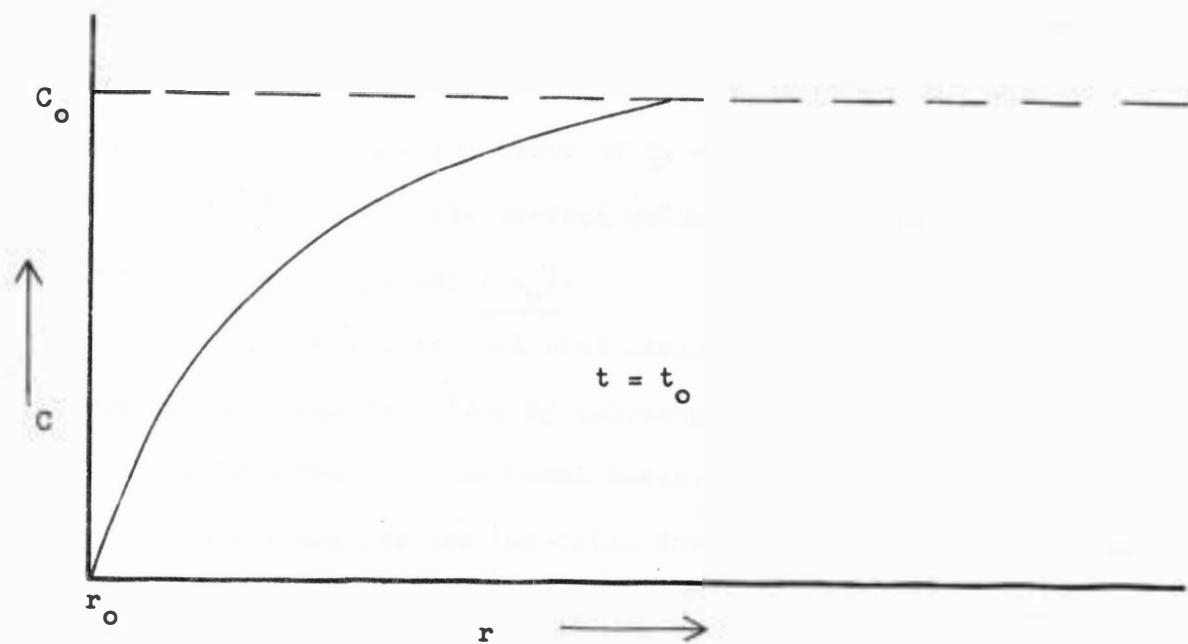


Figure 7. Concentration-Distance Curve for Solid Spherical Electrode

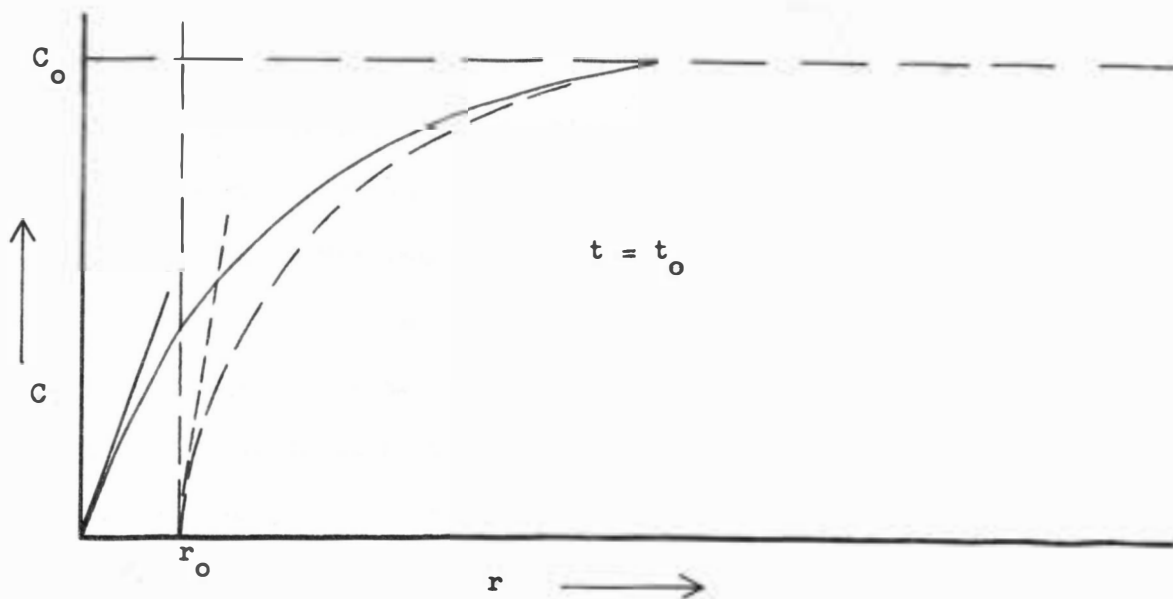


Figure 8. Concentration-Distance Curve for D.M.E.

Now, one can see that Eq. (39) does not give the right variation of concentration with distance. However, the true picture would be approximated if some earlier value of \underline{t} , rather than \underline{t}_0 , were substituted into Eq. (39). The correct value of \underline{t} must be representable by some function of \underline{t}_0 , say $f(\underline{t}_0)$.

It should be pointed out that Lingane and Loveridge's modified Ilkovic equation can be gotten by choosing $f(t) = (3/7)t$. This choice makes sense from the above argument because $(3/7)\underline{t}$ is an earlier time than \underline{t} . The way Lingane and Loveridge derived their equation is poor. They got the factor $3/7$ from a comparison with the Ilkovic equation which is known to be in error. One should note, however, that the modified Ilkovic equation does fit physical data fairly well for the latter life of the drop.

This discussion, then, suggests that a part of $f(t)$ should be of the form at , where a is some constant to be evaluated in a reasonable manner. Furthermore, effects (2) and (3) have not yet been treated. This begins to give one an indication of the shortcomings of the modified Ilkovic equation.

Now, assume the young drop grows in depleted solution. This would correspond to having diffusion proceed for a while before one begins to count the time. That is, there will already exist for the new drop a concentration gradient comparable to the gradient that would have been produced by the drop at a later time if it had started in undepleted solution. Therefore, effect (2) will be reflected in

$f(t)$ as an additive (later time) constant, say b . Thus far then,

$$f(t) = at + b \quad (41)$$

Effect (3) is interesting because other authors are not at all concerned about it. By studying pictures made by Antweiler of the d.m.e., it was decided that effect (3) would be accounted for by subtracting out a constant area from the area of the diffusion field. A calculation was carried through with this idea, using the modified Ilkovic equation. The results were surprisingly good. This effect will be reflected in $f(t)$ via some additive constant. For, the effect is constant and consequently cannot be reflected in $f(t)$ as a function of time. Of course, the constant is absorbed in b so Eq. (41) stays the same.

With Eq. (41) substituted in Eq. (40), the concentration gradient at the surface of the d.m.e. is

$$\left(\frac{\partial c}{\partial r}\right)_{r=r_0} = c\left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Df(t)}}\right) \quad (42)$$

where r_0 is now the radius of the d.m.e. Substitution of Eq. (42) into Eq. (1) yields the instantaneous current to the d.m.e.

$$i = nFADc\left(\frac{1}{r} + \frac{1}{\sqrt{\pi Df(t)}}\right) \quad (43)$$

The subscript on r has been dropped. Since the instantaneous area A of the mercury drop is known, Eq. (43) can be rewritten to give

$$i = nFDC4\pi\left(r + \frac{r^2}{\sqrt{\pi Df(t)}}\right) \quad (44)$$

Finally, one is concerned with the evaluation of a and b.

First, solve Eq. (44) for f(t):

$$f(t) = at + b = \frac{1}{\pi D} \left[\frac{nFDC4\pi r^2}{i - nFDC4\pi r} \right]^2 \quad (45)$$

Equation (45) predicts that a plot of the quantity on the right against time would yield a straight line. In testing this result, the data of Taylor, Smith, and Cooter are used to rewrite Eq. (45). From Eqs. (10) and (11), and from the data on page 16 one obtains

$$r = \left(\frac{3m}{4\pi d} t \right)^{1/3} = \left[\frac{(3)(2.305)}{(4\pi)(13600)} t \right]^{1/3} = 0.0344t^{1/3} \text{ cm} \quad (46)$$

Using Eq. (46) and the information on page 16, Eq. (45) becomes

$$\begin{aligned} at + b &= \frac{1}{(\pi)(7.2 \times 10^{-6})} \left[\frac{(2)(96500)(7.2 \times 10^{-6})(3.018)(4\pi)(0.0344)^2 t^{2/3}}{i - (2)(96500)(7.2 \times 10^{-6})(3.018)(4\pi)(0.344)t^{1/3}} \right]^2 \\ &= \left[\frac{13.05t^{2/3}}{i - 1.81t^{1/3}} \right]^2 \text{ sec} \quad (47) \end{aligned}$$

where i is given in microamperes.

When Eq. (47) is plotted with the experimental values for i, (all experimental data and calculated quantities needed for this plot are tabulated in Table II), one gets the curve pictured in Figure 9. This verifies the prediction except for values of time less than 0.1 sec. This is not surprising for during this short interval of time the velocity of the drop surface is relatively great and therefore one does not expect diffusion to be occurring normally.

Table II. Tabulation of data needed to plot Equation (47)

Experimental Data		Theoretical Calculations			
Time	Current	$1.81t^{1/3}$	$i-1.81t^{1/3}$	$13.05t^{2/3}$	$\frac{13.05^{2/3}}{i-1.81t^{1/3}}$ ²
t (sec)	i (μ a)	(μ a)	(μ a)	(μ a)	(sec)
0.049	4.20	0.66	3.54	1.75	.245
0.076	6.74	0.77	5.97	2.34	.154
0.104	8.67	0.85	7.82	2.89	.137
0.204	12.48	1.07	11.41	4.52	.156
0.296	14.42	1.21	13.21	5.82	.194
0.461	16.81	1.40	15.41	7.81	.257
0.635	18.47	1.56	16.91	9.66	.326
0.863	20.05	1.73	18.32	11.87	.419
1.038	20.99	1.83	19.16	13.38	.487
1.451	22.92	2.06	20.87	16.75	.643
2.005	24.83	2.28	22.55	20.75	.846
2.446	25.94	2.44	23.50	23.61	1.015
2.932	26.81	2.60	24.22	26.70	1.215
3.392	27.38	2.72	24.66	29.45	1.430

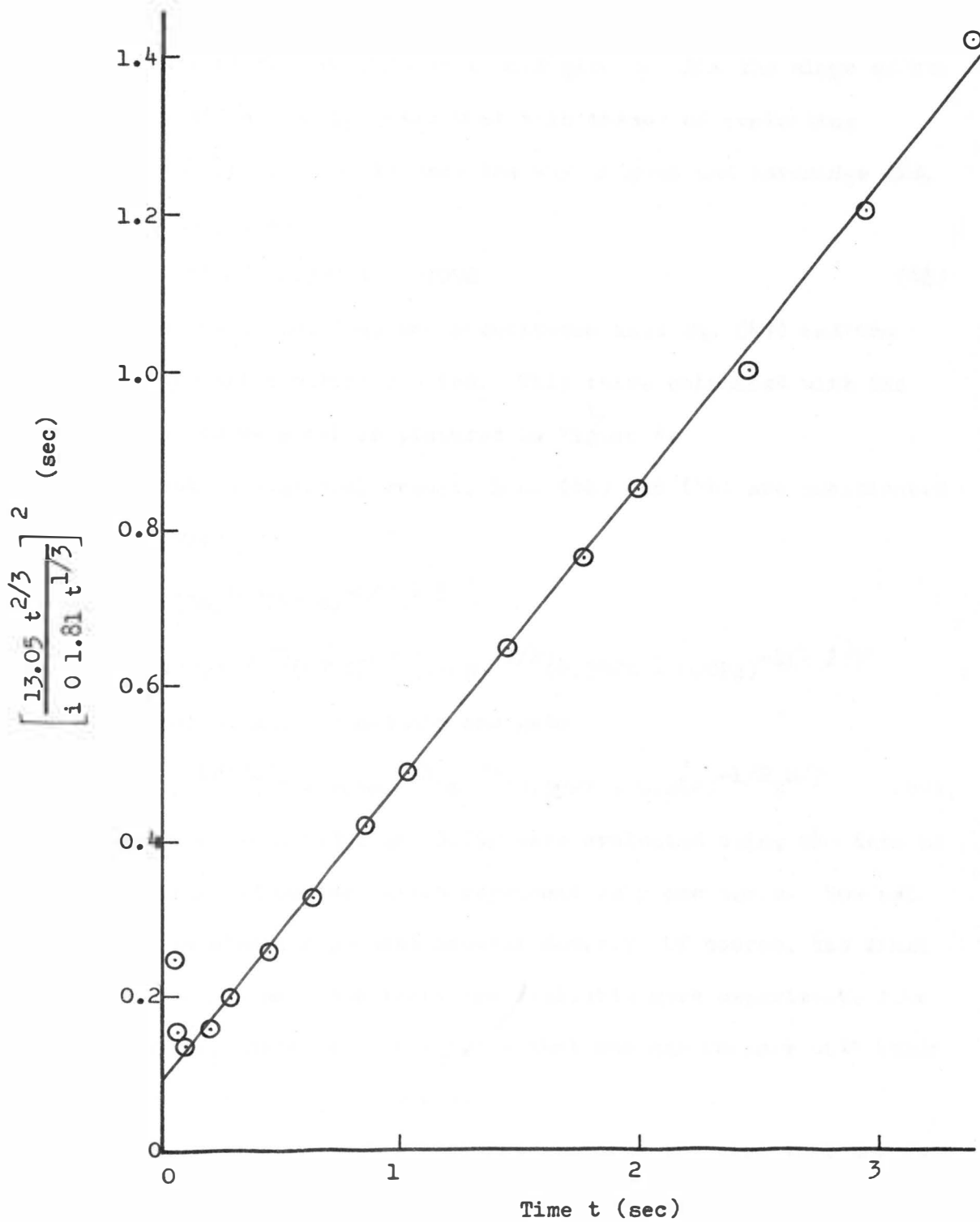


Figure 9. Experimental Verification of Prediction

One can evaluate a and b using this straight line. That is, the intercept of the ordinate axis will give b while the slope of the line will yield a . It is clear that this manner of evaluating constants is more reasonable than the way Lingane and Loveridge did. The evaluation gives

$$f(t) = 0.392 t + 0.092 \quad (48)$$

As a check, Eq. (48) was substituted into Eq. (47) and the resulting current function plotted. This curve coincided with the experimental curve which is pictured in Figure 4.

To obtain a general result, Eqs. (46) and (48) are substituted into Eq. (44):

$$i = nFDC4\pi(zm)^{1/3}(4\pi d)^{-1/3}t^{1/3} + nFDC4\pi(zm)^{2/3}(4\pi d)^{-2/3}(\pi D)^{-1/2}(0.392t + 0.092)^{-1/2}t^{2/3}$$

or, combining physical constants one gets

$$i = 31560nDCm^{1/3}t^{1/3} + 464nD^{1/2}Cm^{2/3}(0.392t + 0.092)^{-1/2}t^{2/3} \quad (49)$$

The constants 0.392 and 0.092 were evaluated using the data of Taylor, Smith, and Cooter, which represent only one d.m.e. How well will these constants represent another d.m.e.? Of course, the final answer will only come when there are available more experiments like that of Taylor, Smith, and Cooter, so that one can compare with other instantaneous current-time curves.

However, the following argument supports the view that Eq. (49) will ably predict the instantaneous current to any d.m.e. now in use.

The general success of the modified Ilkovic equation which makes use of the constant $3/7$, suggests that in the present equation the comparable constant 0.392 will also represent most d.m.e.'s.

Pictures made by Antweiler show that the diameter of the drop and its diffusion layer is between $1/3$ and $1/2$ the diameter of the capillary at the moment of pending drop fall. Hence, the shielding effect of the capillary used in any d.m.e. apparatus will be the same. Therefore, in going from one d.m.e. to another, the constant 0.092 will not change as a result of any "change" in the shielding effect.

The amount of depleted solution left behind depends on the size of the falling drop and on the relation of the capillary to the drop. Now, even if there are small variations in the drop time and the mass rate of flow of mercury, the change in size of the falling drop will be very small - negligibly small in regard to the amount of depleted solution that will be left behind. As argued above, the relation of the capillary to the drop is essentially the same for all d.m.e.'s. Therefore, the constant 0.092 will not change as a result of any "change" in the amount of depleted solution left behind.

SUMMARY AND CONCLUSIONS

It has been shown that the accepted p.d.e. (2) neglects the fact that diffusion occurs with respect to the medium. This concept is correctly accounted for in the new p.d.e. (42). For this reason, the new p.d.e. is theoretically superior to the accepted p.d.e. However, the new p.d.e. has not yet been solved and the approximations made with the accepted p.d.e. get one nowhere with the new p.d.e.

Consequences of the hypotheses that diffusion occurs with respect to the medium, that the drop grows in partially depleted solution, and that the capillary obstructs diffusion have been quantitatively developed in a nonrigorous manner. Agreement of the resulting current-time curve with the experimental curve suggests that the above effects are an essential part of the physical situation.

The success of Eq. (49) also suggests that the mass rate of flow of mercury is truly constant as assumed. Of course this is not positive proof and the assumption needs to be experimentally verified.

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