THE POLAROGRAPHIC DIFFUSION CURRENT

CURRENT–TIME RELATIONSHIP AT THE DROPPING MERCURY ELECTRODE

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I. INTRODUCTION

A. PURPOSE

The Ilkovic equation was introduced (10) in 1934 to relate the average diffusion-controlled current experienced during polarographic electrolysis at the dropping mercury electrode to the solution concentration and diffusion coefficient of electroactive molecules, the mass rate of flow of mercury from the capillary electrode, and the drop lifetime. A common form of the equation is the following:

$$\bar{i} = 607 n D^{1/2} C m^{2/3} t^{1/6} \tag{1}$$

where $\bar{i}$ is the time-average diffusion current in microamperes, D is the diffusion coefficient of the electroactive substance in square centimeters per second,

C is its concentration in millimoles, m is the mass rate of flow of mercury in milligrams per second, t is the drop lifetime in seconds, and n is the number of Faradays of electricity required per mole of electrode reaction (hence, the number of electrons transferred per active molecule).

In a more general version, which gives the value of the instantaneous current as a function of the same constants and the time measured from the beginning of the formation of a given drop (the maximum instantaneous diffusion current), the numerical term, 607, is replaced by 709.

It has been established over the course of years of polarographic experimentation that the concentration dependence of the current, as expressed by equation 1, is satisfactory. In other respects, however, such as the time dependence of the current, the relationships expressed by equation 1 or its more general forms are inadequate. In response to these inadequacies, progressively deeper and more sophisticated theoretical analyses of the problem have appeared in the literature. At the present time, certain of the discrepancies between theory and experiment have been removed, but the most serious difficulty, the erroneous time dependence of the current as expressed by the Ilkovic equation, remains. At the same time, the mathematical treatment has become increasingly rigorous. The conclusion is almost inescapable that the problem has been incorrectly stated mathematically and that a postulatory revision is necessary.

The purpose of the present study is to examine the theory of the current at a dropping electrode in the most detailed way.

B. THE MATHEMATICAL BASIS OF DIFFUSION THEORY

1. Electrode processes and diffusion

In any chemical problem which involves reaction at a surface, a complete solution requires some consideration of the rate at which reactants reach the surface and/or the rate at which products are withdrawn. This problem is not encountered in homogeneous reactions, where a uniform time-average molecular density is found and where no surface is required to cause reaction to occur. However, in heterogeneous reactions involving a surface at a fixed position with respect to the reactant phase, diffusion gradients are set up, and the mechanism of diffusion becomes important.

Prominent among surface reactions are those occurring at electrodes immersed in solutions. Here, electrons are added to or removed from a chemical species, leaving it changed in nature. If this electron transfer is very rapid, then the rate of reaction depends upon slower steps in the total process, such as the rate of supply of reactive species to the electrode surface. Therefore, when stirring is absent and other chemical reactions in the solution do not interfere, the rate of the electrode reaction will be controlled by diffusion only. In electrode reactions the rate is simply given by the current, since the current represents the number of charges, i.e., electrons, transferred per unit time. This quantity is related to the flux of matter by Faraday's laws of electrolysis. By analysis of the diffusion problem, the flux at the electrode surface and therefore the current can be determined. The current so determined is called the *diffusion* current.

2. The equation of continuity

The flux may be defined as the rate at which matter is transported across a surface S at a point P, per unit area per unit time, and it will be denoted by ϕ. The unit of mass to be chosen is the mole, so that the dimensions of flux are $L^{-2}T^{-1}$.

It will be convenient to define an *isomolar* surface. Consider a solution with a concentration distribution defined by a scalar function of position and time, C. It may be supposed that there is a surface passing through this solution, every point of which at some instant possesses the same value of the concentration function. This surface of constant concentration may be called an isomolar surface. An infinity of such surfaces may be described and no two may cross each other, since this would imply the existence of points in the solution having more than one value of concentration. Such surfaces separate parts of the solution which are more concentrated from parts which are less.

Consider a closed region in the solution bounded by a surface S, not necessarily isomolar, and having a volume V. The rate of flow of matter into this region, dN/dt, in moles per second, may be represented by taking the surface flux, ϕ_S, at every point on the surface, multiplying it by the differential area at that point, and summing these over the entire surface. That is,

$$\frac{dN}{dt} = \int_S \phi_S \, dS \tag{2}$$

But every point P of the surface will be crossed by some isomolar surface, for which the flux vector[2] at P is $\underline{\phi}_n$. Therefore, if the unit normal vector to S at P is $\underline{s}$, the scalar ϕ_s in equation 2 can be written as a vector dot product,

$$\phi_s = \underline{\phi}_n \cdot \underline{s} \tag{3}$$

Using this, equation 2 becomes

$$\frac{dN}{dt} = \int_S \underline{\phi}_n \cdot \underline{s} \, dS \tag{4}$$

Equation 4 may be transformed into a volume integral by applying the divergence theorem of vector analysis:

$$\frac{dN}{dt} = \iint_S \underline{\phi} \cdot \underline{s} \, dS = \iiint_V \operatorname{div} \underline{\phi}_n \, dV \tag{5}$$

Alternatively, the rate of flow of matter into S may be described by considering the rate of change of concentration with time in each differential volume and integrating over V:

$$\frac{dN}{dt} = \iiint_V \frac{\partial C}{\partial t} \, dV \tag{6}$$

In the absence of any sources or sinks of matter within S, the sum of the expressions given by equations 5 and 6 must vanish.

$$\iiint_V \left[\operatorname{div} \underline{\phi}_n + \frac{\partial C}{\partial t} \right] dV = 0 \tag{7}$$

[2] Vector quantities are underscored.

and therefore, for every V,

$$\frac{\partial C}{\partial t} = -\text{div } \phi_n \tag{8}$$

Equation 8 is the form of the equation of continuity applicable to diffusion.

3. Fick's law and the diffusion equation

In the present case, the flux can originate through either diffusion or convection. The fundamental postulate of the general theory of diffusion states that the normal flux at a point P on an isomolar surface is proportional to the concentration gradient at P, i.e.,

$$\phi_n = -D \text{ grad } C = -D \frac{\partial C}{\partial n} \underset{\sim}{n} \tag{9}$$

Equation 9 is a statement of Fick's law in vector form. D is the diffusion coefficient with units of square centimeters per second, $\partial/\partial n$ represents differentiation along a normal to the isomolar surface, and $\underset{\sim}{n}$ is the corresponding unit normal vector.

If, in addition to the diffusion flux, the solution as a whole is subject to convective forces, there will be translation of points on the isomolar surface itself with vector velocity $\underset{\sim}{u}$. This motion will be responsible for a flux of magnitude $\underset{\sim}{u}C$, having the same direction as that of the velocity.

Therefore, in the general case the total flux will be given by the expression

$$\phi_n = -D \text{ grad } C + \underset{\sim}{u}C \tag{10}$$

By introducing this expression for the flux into equation 8, a general equation for diffusion and convection is found:

$$\frac{\partial C}{\partial t} = -\text{div } (-D \text{ grad } C + \underset{\sim}{u}C) = \nabla \cdot (D \nabla C) - \nabla \cdot \underset{\sim}{u}C \tag{11}$$

Equation 11 as it stands is quite general and could serve, for example, to describe the motion of moisture through an inhomogeneous, stratified solid. A liquid, however, is obviously homogeneous and isotropic. This means that for the present case the diffusion coefficient, D, is independent of the coördinates. Accordingly, equation 11 may be written

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \nabla \cdot \underset{\sim}{u}C \tag{12}$$

Equation 12 was first given, without derivation, by MacGillavry and Rideal (21).

Since no coördinate system has thus far been assumed, the Laplacian operator, ∇^2, can be immediately written down in terms of whatever coördinates seem appropriate to a given problem. The form of the divergence term will depend partly upon the nature of the convection velocity, $\underset{\sim}{u}$. For cases in which $\underset{\sim}{u}$ is zero, that is, for pure diffusion, the diffusion equation takes the following forms in rectangular and symmetrical spherical regions, respectively:

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right] \tag{13}$$

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \tag{14}$$

Only one case for which u is not zero will be considered in this work, the case of the symmetrical spherical region. Equation 12 here becomes

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u C) \tag{15}$$

The assumption is made, in finding solutions for equation 12, that the diffusion coefficient, D, is independent of concentration. This assumption is necessary to keep equation 12 within the class of linear differential equations. The alternative would involve mathematics of a much higher order of difficulty. It appears that the discrepancies resulting from this assumption are not too serious provided D is properly chosen.

4. The boundary value problem for electrodes

In attacking a given diffusion problem, solutions of equation 12 which satisfy some specified conditions for given values of the independent variables will be sought. These conditions are the boundary conditions, and the problem thus constructed is a boundary value problem. Theoretically, the number and character of the boundary conditions required would depend on the nature of the differential equation. Actually, a good deal depends on the specification of the physical problem, since, as will be seen, it is difficult to transcribe a physical situation into mathematical terms. In each of the problems to be attacked in this work it will be found that, with one exception, a total of three boundary conditions will be sufficient to produce a physically reasonable solution. Such solutions will be purely formal in that, although they will satisfy the differential equation and the boundary conditions, no attempt will be made to show that they are unique or to define the further conditions under which they will be unique. This mathematical shortcoming should offer no difficulty, since the ultimate criterion for any solution will be comparison with experimental results.

Thus, the mathematical program required to determine the formula for the current is the construction of a boundary value problem, followed by its solution. This solution will be a formula expressing the instantaneous concentration at any point in the investigated region. The flux may now be found through the use of equation 9. The flux is then evaluated at the particular value of the space coördinates which correspond to the electrode surface. The current is the product of the flux at the electrode surface, its area, and the Faraday constant.

C. THE DROPPING MERCURY ELECTRODE

1. Physical description

The dropping mercury electrode is exceedingly simple in construction. A short (5 to 10 cm.) length of capillary tubing with a bore of the order of 0.05 mm. is connected, perhaps by rubber tubing, to a mercury reservoir whose height is adjustable. The tip of the capillary is inserted beneath the surface of the solution to be electrolyzed. The height of the reservoir is adjusted to some position from

25 to 75 cm. higher than the capillary tip. Under these circumstances, mercury falls dropwise from the capillary tip into the solution, the drop lifetime being of the order of 4 sec. A current lead is inserted into the mercury. The rest of the electrical circuit is not essential to this discussion; it consists of a reference electrode, also in contact with the solution, a potentiometer bridge for applying a controlled potential across the electrode system, and voltage- and current-measuring devices.

Thus, current will flow while a given drop is pendant and cease as the drop falls, only to grow once again during the formation and growth of the following drop. It is the detailed analysis of the time dependence of the current during the life of a single drop which is of concern here.

2. Idealizing assumptions

The following idealizing assumptions are usually made for purposes of mathematical analysis:

(1) The potential of the electrode, i.e., the potential impressed on the electrode by the bridge circuit, less the cell iR drop, is considered to be set at a large enough value so that electrolysis of the electroactive material in solution is occurring measurably; for simplicity, it is usually assumed that the potential is large enough to deplete completely the layer of solution next to the electrode surface. Under these circumstances, the limiting diffusion current would be measured. In any case, the potential is considered to be increasing at a slow enough rate so that the potential is essentially constant during the drop lifetime.

(2) The mercury drop is spherical throughout its lifetime; changes in shape at the beginning of drop formation or at the time when the drop begins to separate and fall are to be ignored. High-speed photographs of drop growth (22) have shown this assumption to be essentially correct.

(3) The drop is isolated; no consideration is to be given to the asymmetry of the diffusion region because of the presence of the capillary tube tip above the drop.

(4) The volume rate of drop growth is to be considered constant. This assumption is not accurate and will be given more detailed consideration later. In all the analysis to be considered, however, the mass rate of flow of mercury is defined as the average of the true instantaneous mass rate over the drop lifetime, a quantity which can be measured experimentally. Denoting this quantity by m, it is easily seen that the radius of the mercury drop at any instant is given by the expression

$$r_0^3 = \frac{3mt}{4\pi d} \tag{16}$$

where d is the density of mercury (13.6 g./cm.^{3}) and t is the time. The constant quantity $3m/4\pi d$ will be denoted by the symbol γ.

(5) The drop is motionless with respect to the solution except for growth. Actually, the center of gravity of the pendant drop must move downward with time. This does not appear to have any serious consequences to the analysis.

(6) The solution in which electrolysis is occurring is considered a body of

indefinite extent, with a constant bulk concentration, C_0. At any time, therefore, the concentration around the electrode must approach the value C_0 for sufficiently large values of the space variable. This condition is somewhat loose, and can be made more stringent, as will be seen later.

(7) The diffusion at a single drop is independent of the history of other drops. That is, the initial concentration distribution as the drop begins to form is constant in space and equal to C_0. This implies that the relaxation time of the inhomogeneous concentration distribution around the electrode tip caused by a given drop is small compared with the interval between the falling off of one drop and the beginning of the formation of the next. This assumption is common to all the literature on this subject; it is, however, the least realistic of all, and its replacement by a more convincing initial condition is the basis for a recent attack on the problem (23, 24).

In addition to the assumptions listed, a host of important but self-evident conditions must be tacitly accepted: freedom from stirring motion in the solution, adsorption phenomena at the electrode surface, etc.

II. MATHEMATICAL EVALUATION OF PROPOSED THEORIES

A. INTRODUCTION

In the following section the mathematical formulations and solutions of the problem of the current at a dropping mercury electrode proposed by a number of authors will be given a detailed examination. Any physical or mathematical errors in their respective procedures apparent to the present or other past authors will be pointed out and, where the situation warrants, derivations will be carried through in corrected form, to determine the mathematical consequences of inappropriate or erroneous steps in the formulations or solutions. In all cases, some attempt will be made to evaluate the contributions of each author to the general progress in understanding the current–time relation.

The solutions to be considered fall into several groups. Ilkovic (12), MacGillavry and Rideal (21), Strehlow and von Stackelberg (32), and Kambara and Tachi (15) all used the "differential" approach, consisting of the solution of the diffusion equation with appropriate boundary conditions. Ilkovic (10), von Stackelberg (30), and Matsuda (25) used an "integral" approach, in which the problem is formulated in the form of an integral equation. Finally, the solution of Lingane and Loveridge (19) makes use of an ingenious modification of the original solution of Ilkovic to improve the current equation.

B. THE SOLUTION OF ILKOVIC

The earliest solution of the diffusion problem for the dropping electrode was given by Ilkovic (12), and the resulting equation bears his name. In construction of the boundary value problem, he makes no use of the general diffusion-convection equation (equation 12). Instead, he writes the total differential for C as a function of x and t, where x is the distance from the drop surface to a point in the solution:

$$dC = \left(\frac{\partial C}{\partial x}\right)_t dx + \left(\frac{\partial C}{\partial t}\right)_x dt \qquad (17)$$

Representing by v the velocity of motion of the solution relative to the drop surface, i.e., $dx = -v\, dt$, the total differential expression may be put into the form:

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial t}\right)_x - v\left(\frac{\partial C}{\partial x}\right)_t \tag{18}$$

The ordinary derivative on the left Ilkovic regards as the change of concentration with time at a point which moves with the solution. He reasons that the value of this derivative is unaffected by convection, so that this term can be set equal to $D\frac{\partial^2 C}{\partial x^2}$, after equation 13. Thus,

$$\left(\frac{\partial C}{\partial t}\right)_x = D\frac{\partial^2 C}{\partial x^2} + v\left(\frac{\partial C}{\partial x}\right)_t \tag{19}$$

The partial derivative on the left corresponds to the concentration at a point fixed with respect to the electrode surface.

This formulation, which appears to be a linear approximation to the three-dimensional situation, is inconsistent with the results of the rigorous development given in the previous section. To see the extent of the approximation involved, equation 19 may be compared with the rigorous equation, equation 15. To do this, it is first necessary to perform a transformation of independent variable in the latter, according to the following equations of transformation, in which r is the variable radius and r_0 is the drop radius at time t:

$$x = r - r_0 \tag{20}$$

$$\tau = t \tag{21}$$

The identity transformation, equation 21, is included for generality; τ is an artificial symbol introduced for manipulative convenience and is replaced by t at the end. When the respective derivatives are evaluated and introduced,[3] the form of equation 15 appropriate for comparison is:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{2}{r_0 + x}\frac{\partial C}{\partial x}\right) - \frac{1}{(r_0 + x)^2}\frac{\partial}{\partial x}[(r_0 + x)^2 uC] + \frac{dr_0}{dt}\frac{\partial C}{\partial x} \tag{22}$$

There are essentially two differences between this equation and equation 19. In the latter there is no term of the form

$$\frac{2D}{x}\frac{\partial C}{\partial x}$$

which means, qualitatively, that the effect of the curvature of the spherical region on the diffusion is being ignored.

Secondly, the relationship of the respective terms on the right of each equation

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[3] Derivations and discussion of items indicated by footnote reference 3 will be found in the appendix to reference 23, pages 220–52.

which have to do with convection depend on the choice made for v on the one hand and u on the other. It is evident from equation 16 that

$$\frac{\mathrm{d}r_0}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}(\gamma t)^{1/3} = \frac{1}{3}\frac{\gamma^{1/3}}{t^{2/3}} = \frac{\gamma}{3r_0^2} \tag{23}$$

Further, because the liquid solution is effectively incompressible, each point in it has a velocity with the same proportionality to the inverse of the radial distance squared, i.e., at any point,

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\gamma}{3r^2} \tag{24}$$

With the introduction of these values for the radial convection velocities into equations 19 and 22, the convection terms in the respective equations become identical:

$$\frac{\gamma}{3}\left[\frac{1}{r_0^2} - \frac{1}{(r_0 + x)^2}\right]\frac{\partial C}{\partial x} \tag{25}$$

Thus the discrepancy between Ilkovic's differential equation and the rigorous one lies only in the omission of the curvature term.

However, either because the equation in this form was too difficult to solve or because he did not perceive the relevance of equation 24, Ilkovic used a different method of expressing v in terms of x and t. By restricting the range of x so that at all times its product with the surface area of the drop is a constant, he is led directly to an expression for v in terms of the drop surface area. For, if Ax = constant, then

$$A\frac{\mathrm{d}x}{\mathrm{d}t} = -x\frac{\mathrm{d}A}{\mathrm{d}t} \tag{26}$$

From equation 16, the surface area of the drop is $4\pi(\gamma t)^{2/3}$. Thus $\mathrm{d}A/\mathrm{d}t$ is $8\pi\gamma^{2/3}/3t^{1/3}$ and v is $2x/3t$. Upon introduction of v into equation 19,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \frac{2x}{3t}\frac{\partial C}{\partial x} \tag{27}$$

If substitution is made for u in equation 22, such that $v = 2x/3t$, the convection term assumes a much different form from that in equation 27. It can be concluded that, whereas in equation 19 only the drop curvature is neglected, equation 27, that actually solved by Ilkovic, also expresses the convection effect imperfectly.

These considerations apart, Ilkovic's expression for v is most restrictive. Consider the annular volume between a sphere of radius r_0 and a concentric sphere of radius $r_0 + x$. The volume, V_a, will be given by

$$V_a = \frac{4}{3}\pi[(r_0 + x)^3 - r_0^3] \tag{28}$$

$$= \frac{4}{3}\pi x(3r_0^2 + 3r_0 x + x^2) \tag{29}$$

Thus, for x very small compared with r_0,

$$V_a = 4\pi r_0^2 x = Ax = 4\pi(\gamma t)^{2/3} \tag{30}$$

Therefore equation 27 will hold only for values of x so chosen that the annular volume remains constant in time. Once V_a is chosen, therefore, x becomes a specified function of the time. This would lead to difficulties in satisfying the boundary conditions at $x = 0$ and at $t = 0$, which can be avoided only by making V_a the independent variable.

Ilkovic, in taking account of this situation, does not explain himself very well, so that a certain amount of misunderstanding exists in the literature on the subject (15). He gives the impression that equation 27 is the final equation and that subsequent alterations are part of the solution. Actually, the next step is essential in formulating the boundary value problem. A variable u (unrelated to the symbol u used in the present text) is introduced, having the value $xt^{2/3}$. Since this quantity has the form of the annular volume as given by equation 30, this substitution represents the change of independent variable suggested in the preceding paragraph. The new equation is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial u^2} t^{4/3} \tag{31}$$

The boundary conditions are

$$C(u, 0) = C_0 \tag{32}$$

$$C(0, t) = 0 \tag{33}$$

This formulation neatly sidesteps the difficulty raised by the nature of the convection term introduced earlier. Both conditions are obviously physically sound.

Ilkovic's solution of this problem is available in detail (12) and will not be pursued further here, except to state that it makes use of a variation of the Fourier integral theorem in forming a linear combination of particular integrals and satisfies the boundary conditions in an ingenious fashion. Ilkovic presents the solution

$$C(u, t) = \frac{2C_0}{\pi} \int_0^\infty \frac{\sin \beta u}{\beta} \exp[-\tfrac{3}{7}\beta^2 D t^{7/3}] \, d\beta \tag{34}$$

but points out that it is unnecessary to perform the integration, since the flux at the drop surface is the quantity desired. Differentiation of equation 34 with respect to x and evaluation of the result at $x = 0$ yields

$$\left(\frac{\partial C}{\partial x}\right)_0 = \frac{C_0}{\sqrt{\tfrac{3}{7}\pi D t}} \tag{35}$$

If the scalar flux from equation 9 is written out, it is immediately seen that the flux at the electrode surface, that is, the origin of x, is given by

$$\phi_0 = -D \left(\frac{\partial C}{\partial x}\right)_0 \tag{36}$$

Further, the total amount of material reaching the electrode surface per unit time must be given by the product of the flux and the electrode area. The unit of

mass here is the mole; consequently, the current will be the product of the number of moles reaching the electrode surface per unit time and the number of coulombs per mole. The latter is simply nF, where n is the number of equivalents per mole and F is Faraday's constant (96,500 coulombs per equivalent). Thus the current is

$$i = nFC_0 \cdot 4\pi r_0^2 \cdot (3 \tfrac{7}{7} \pi Dt)^{-1/2} \cdot D \tag{37}$$

By introducing the value of r_0 from equation 16 and lumping the numerical constants, it is found that

$$i = 0.732 nFC_0 m^{2/3} D^{1/2} t^{1/6} \tag{38}$$

In this equation, concentration is in units of moles per cubic centimeter and the mass flow rate of mercury, m, is in grams per second, giving the current in amperes. In order to have the equation in more convenient laboratory units, the concentration should be expressed in millimoles per liter, m in milligrams per second, and the current in microamperes. When the necessary dimensional constants are introduced and the value of F included, equation 38 becomes

$$i = 709 n C_0 D^{1/2} m^{2/3} t^{1/6} \tag{39}$$

This equation gives the instantaneous value of the current, which evidently has the form of a sixth-order parabola in the time. It is sometimes convenient to know the time-average current, which can be found by integrating equation 39 over the time and dividing by the drop lifetime, τ:

$$\bar{\imath} = 709 \frac{i}{t^{1/6}} \cdot \frac{1}{\tau} \int_0^\tau t^{1/6} \, dt = \frac{6}{7} \cdot 709 \frac{i}{t^{1/6}} \tau^{1/6} = 607 n C_0 \, D^{1/2} m^{2/3} \tau^{1/6} \tag{1}$$

Equations 1 and 39 are the best-known forms of the Ilkovic equation. As has been stated earlier, the time dependence predicted by equation 39 is not experimentally correct.

C. THE SOLUTION OF MACGILLAVRY AND RIDEAL

Though Ilkovic gave the first solution for the problem of the dropping mercury electrode, the best-known treatment was given by MacGillavry and Rideal (21). Their analysis is reproduced with some simplification in the most widely used monograph on polarography (16), and the treatment has been characterized as "rather rigorous" in a recent monograph on electrochemical methods (9). It is generally felt that the shortcomings in the result are caused by excessive idealization rather than by mathematical defects. It will be shown that this is not the case.

MacGillavry and Rideal begin the formulation of the boundary value problem with equation 15 for diffusion and convection in a symmetrical spherical region. When the convection velocity, u, given by equation 24, is introduced into the convection term, equation 15 becomes

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - \frac{\gamma}{3r^2} \frac{\partial C}{\partial r} \tag{40}$$

A new coördinate system is introduced at this point, the equations of transformation being

$$\rho^3 = r^3 - r_0^3 = r^3 - \gamma t \tag{41}$$

$$\tau = t \tag{42}$$

The new independent variable, ρ, can be visualized as the radius of a hypothetical sphere whose volume is equal to that enclosed between concentric spheres of radii r_0 and r. The transformed equation[3] is

$$\frac{\partial C}{\partial t} = D \frac{(\rho^3 + \gamma t)^{4/3}}{\rho^5} \left[\rho \frac{\partial^2 C}{\partial \rho^2} + 2 \left(\frac{\rho^3 - \gamma t}{\rho^3 + \gamma t} \right) \frac{\partial C}{\partial \rho} \right] \tag{43}$$

This transformation may be verified by beginning with equation 12 and introducing ρ as an independent variable at the beginning, observing that in the (ρ, t) system the radial velocity, u, is zero. This vanishing of the convection term is the chief value of the change.

The next step is critical. The authors seek to put equation 43 into a more readily integrable form. They reason that, since the region of interest is that volume of solution which is very close to the drop, the quantity ρ^3 can be assumed to be very small in comparison with γt, the drop radius. Thus, equation 43 can be simplified to

$$\frac{\partial C}{\partial t} = D \frac{(\gamma t)^{4/3}}{\rho^5} \left[\rho \frac{\partial^2 C}{\partial \rho^2} - 2 \frac{\partial C}{\partial \rho} \right] \tag{44}$$

This assumption has been correctly criticized (32) on the ground that the thickness of the diffusion layer is much larger than this estimate acknowledges. A related defect lies in the ambiguous nature of the functional dependence expressed by equation 44. It is clear that the transformation which carried equation 40 into equation 43 is perfectly appropriate. C becomes a function of two variables, ρ and t, the former of which is exactly specified for any given values of r and t. With the simplification leading to equation 44, quite a difference obtains. C is now a function of two variables, ρ and t, the former of which is confined to a certain region depending on t; t becomes the only really independent variable. This results from the specification that $\rho^3 \ll \gamma t$. Thus, if equation 44 is to be treated formally as a partial differential equation, the special character of the independent variables must be kept in mind.

A further change of independent variable is made at this point, given by

$$x = \rho^3 \tag{45}$$

$$y = t^{7/3} \tag{46}$$

With these changes, and the introduction of a constant,

$$M = \frac{27}{7} \gamma^{4/3} D \tag{47}$$

the differential equation becomes

$$\frac{\partial C}{\partial y} = M \frac{\partial^2 C}{\partial x^2} \tag{48}$$

The boundary conditions are formulated from the requirements that the concentration be uniform and equal to a constant, C_0, throughout the solution at the start, and that it vanish at the electrode surface afterwards. Thus, in terms of r and t, ρ and t, and x and y, respectively,

$$C(r, 0) = C_0 \tag{49}$$

$$C(0, t) = 0 \tag{50}$$

$$C(\rho, 0) = C_0 \tag{51}$$

$$C(0, t) = 0 \tag{52}$$

$$C(x, 0) = C_0 \tag{53}$$

$$C(0, y) = 0 \tag{54}$$

These are the only conditions explicitly stated by MacGillavry and Rideal. Equation 48 and conditions 53 and 54 thus constitute the boundary value problem to be solved. As shown later, the problem thus stated is incomplete.

No procedure for the solution of this problem is given by MacGillavry and Rideal. They simply introduce, as "the customary solution of interest in diffusion problems," the following expression involving the error function, symbolized erf:[3]

$$C = A + B \operatorname{erf}\left(\frac{x}{2\sqrt{My}}\right) \tag{55}$$

MacGillavry and Rideal introduce boundary conditions 53 and 54; after transformation to the (ρ, t) coördinate system, the expression for the concentration is

$$C = C_0 \operatorname{erf}\left\{\frac{1}{6}\left(\frac{7\gamma}{3D}\right)^{1/2}\frac{\rho^3}{(\gamma t)^{7/6}}\right\} \tag{56}$$

It is not necessary to introduce the reciprocal of transformations 41 and 42, since it is only the flux that is desired. Differentiation of equation 56 with respect to ρ and the subsequent mechanical operations necessary to find the current are presented in the original paper. The resulting expressions for the instantaneous and average current are identical with those derived by Ilkovic, equations 1 and 39; however, the concentration function obtained as a solution of this problem (equation 56) is not identical with that of Ilkovic, equation 34.

The following consideration will show that equation 56 is an erroneous solution under the conditions imposed on the problem. A solution for equation 48 is sought. Let the operational method be formally applied to equation 48. In the notation of Churchill (8), let

$$L\left\{C(x, y)\right\} = \bar{c}(x, s)$$

Then the Laplace transform of equation 48, using condition 53, is

$$s\bar{c} - C_0 = M\frac{\mathrm{d}^2\bar{c}}{\mathrm{d}x^2} \tag{57}$$

This ordinary differential equation is to be solved, subject to the transform of the remaining boundary condition (equation 54):

$$\bar{c}(0, s) = 0 \tag{58}$$

The solution of the homogeneous part of equation 57 is

$$\bar{c} = k_1 \exp\left(-\sqrt{\frac{s}{M}}\, x\right) + k_2 \exp\left(\sqrt{\frac{s}{M}}\, x\right) \tag{59}$$

where k_1 and k_2 are arbitrary constants. In addition, equation 57 has a particular integral, C_0/s. The general solution is therefore

$$\bar{c} = k_1 \exp\left(-\sqrt{\frac{s}{M}}\, x\right) + k_2 \exp\left(\sqrt{\frac{s}{M}}\, x\right) + \frac{C_0}{s} \tag{60}$$

Since there are two arbitrary constants in equation 60, two boundary conditions are required for their evaluation. It will be recalled that MacGillavry and Rideal provided only two. Of these, one has been used in equation 57; consequently, only one is still available for use with equation 60. For MacGillavry and Rideal to have achieved solution in the form of equation 55, one other boundary condition was needed; by investigating the effect of various boundary conditions on the form of the solution, the nature of the unstated, but essential, missing condition can be determined. Let it be assumed that this condition is a restriction on C as x approaches some boundary point other than zero. Immediately, a difficulty arises. MacGillavry and Rideal have specified in their simplification of equation 43 to equation 44 that ρ is to remain small in comparison with γt, i.e., the equations are applicable only to a region close to the drop surface. Let this important restriction be ignored, however, and allow the introduction of the following (improper) boundary condition:

$$\lim_{x \to \infty} \bar{c}(x, s) = \frac{C_0}{s} \tag{61}$$

Equation 61 is the transform of

$$\lim_{x \to \infty} C(x, t) = C_0 \tag{62}$$

which would itself be derived from a condition of the same form in terms of the original variables, r and t. This condition is accurate, physically, but, as has been shown, its use is mathematically erroneous.

Inspection of equation 60 shows that condition 61 requires k_2 to be zero; otherwise, the second term on the right would increase without bound as x passed to the limit. The remaining arbitrary constant, k_1, is evaluated using condition 58. The solution of the transformed boundary value problem follows:

$$\bar{c} = -\frac{C_0}{s} e^{-\sqrt{\frac{s}{M}}\, x} + \frac{C_0}{s} \tag{63}$$

The inverse transform of equation 63, when appropriately rearranged and the ρ coördinate reintroduced through equations 45 and 46, is identically the result

of MacGillavry and Rideal (equation 56). Thus it has been shown that the inclusion of a mathematically inconsistent and therefore proscribed boundary condition (condition 61) is essential in order to achieve the solution presented by these authors. Consequently, equation 56 is an erroneous solution of the boundary value problem as stated.

It is of some interest to find the solution to the problem of MacGillavry and Rideal subject to conditions which actually do reflect the restrictions implicit in their differential equation. Let δ be a constant equal to the maximum permissible value of ρ^3, and therefore the maximum permissible value of x under the condition that $\rho^3 \gg \gamma t$. Then, if it were true, as MacGillavry and Rideal believe, that outside of the region limited by δ the concentration is unaffected by the electrolysis, a solution of the diffusion problem would have to satisfy the expression:

$$\lim_{x \to \delta} C(x, y) = C_0 \tag{64}$$

The solution for the boundary value problem consisting of MacGillavry and Rideal's simplified equation (equation 48), together with the appropriate boundary conditions 53, 54, and 64, is[3]:

$$C(x, y) = C_0 \left[1 + \sum_{j=0}^{\infty} \left\{ \operatorname{erf} \frac{2j\delta + x}{2\sqrt{My}} - \operatorname{erf} \frac{(2j + 2)\delta - x}{2\sqrt{My}} \right\} \right] \tag{65}$$

The series in equation 65 is rapidly convergent for small y, which is the case here. This solution satisfies the differential equation as well as the boundary conditions. As δ becomes larger, convergence is more and more rapid, until, as $\delta \to \infty$, the solution retains only the first term of the series:

$$C(x, y) = C_0 \left[1 + \operatorname{erf} \left(\frac{x}{2\sqrt{My}} \right) - 1 \right] = C_0 \operatorname{erf} \left(\frac{x}{2\sqrt{My}} \right) \tag{66}$$

This rapid convergence is a consequence of the fact that erf $\infty = 1$. Note that equation 66 is identically the concentration function of MacGillavry and Rideal (equation 55).

The current corresponding to the concentration distribution of equation 65 can be calculated by a procedure exactly analogous to the one given in the discussion of Ilkovic's work. The result[3] is

$$i = 709nC_0 D^{1/2} m^{2/3} t^{1/6} \left\{ 1 + 2 \sum_{j=1}^{\infty} \exp(-j\alpha)^2 \right\} \tag{67}$$

where α is defined by

$$\alpha = 100 \, \delta m^{-2/3} t^{-7/6} D^{-1/2} \tag{68}$$

The units are those which are conventional in experimental work, as presented earlier.

The first term of equation 67 is identical with the equation derived by Ilkovic and by MacGillavry and Rideal. If the value of α^2 is very large, e.g., 10, the terms in the summation would be negligible. On the other hand, if the exponent is small, the series terms would be large and the series would converge slowly.

To decide this point, it is necessary to have some estimate of the size of δ. This quantity has the dimensions of a volume; it can be interpreted as the annular shell about the drop within which, at any instant, the concentration is different from (and less than) that in the bulk of the solution.

It will be recalled that MacGillavry and Rideal assumed that the quantity ρ^3 is much smaller than γt, the drop volume, i.e., that

$$\frac{\rho^3 - \gamma t}{\rho^3 + \gamma t} \cong -1 \tag{69}$$

Now a trial substitution will reveal that if the quotient $\rho^3/\gamma t$ remains less than 0.01, this approximation will not be in error by more than 2 per cent. δ represents the maximum possible value of ρ^3; consequently, the value $0.01\ \gamma t$ can be assigned to δ. It is true that this assignment is arbitrary and tells nothing about the possible functional nature of δ. However, for an order-of-magnitude computation, it is perfectly satisfactory.

Introduction of the value $0.01\ \gamma t$ for δ leads to the following expression for α^2:

$$\alpha^2 = 3.10 \times 10^{-10} m^{2/3} t^{-1/3} D^{-1} \tag{70}$$

Now even the slowest moving of solutes have diffusion coefficients larger than 10^{-7} cm.²/sec. Thus for a moderate value of the time, e.g., 3 sec., and a usual value of m, e.g., 1–2 mg./sec., it is evident that the order of magnitude of α^2 is at most 10^{-3} (α is, of course, dimensionless). Therefore, the exponent is small, the series of equation 67 converges slowly (the terms decreasing from 1), and the series factor must have an appreciable magnitude.

Fortunately, a more rapidly converging series may be utilized to compute i by taking advantage of the following identity (2):

$$1 + 2\sum_{n=0}^{\infty} \exp{-(nx)^2} = \frac{\sqrt{\pi}}{x}\left\{1 + 2\sum_{n=1}^{\infty} \exp{-\left(\frac{n\pi}{x}\right)^2}\right\} \tag{71}$$

Using this to evaluate the second factor of equation 67, the current becomes

$$i = 709 n C_0 D^{1/2} m^{2/3} t^{1/6} \left\{\frac{\sqrt{\pi}}{\alpha} + \frac{2\sqrt{\pi}}{\alpha}\sum_{j=1}^{\infty} \exp{-\left(\frac{j\pi}{\alpha}\right)^2}\right\} \tag{72}$$

where α^2 has the value given in equation 70.

With a value of α^2 of the order of 10^{-3} or smaller, as estimated, the exponential terms of equation 72 vanish, and the second factor is well approximated by $\sqrt{\pi}/\alpha$. The magnitude of this factor varies from about 500 for the faster moving ions at relatively large values of the time (10^{-5} cm.²/sec., 10 sec.) to about 10 for experimental values at the other extreme (10^{-7} cm.²/sec., 0.01 sec.). The Ilkovic equation effectively represents the experimental current to a first approximation; consequently equation 72, which is the Ilkovic equation multiplied by the factor under consideration, must be grossly in error. It follows that the assumption made by MacGillavry and Rideal about the thickness of the diffusion layer is completely invalid.

D. THE SOLUTION OF STREHLOW AND VON STACKELBERG

The fact that the current calculated from equation 72 is too high by orders of magnitude indicates that the estimate of the size of the diffusion layer (i.e., $\delta = 0.01 \, \gamma t$) is too small. A small diffusion layer implies a steep gradient and therefore a high current. This discrepancy cannot be corrected merely by introducing a larger estimate of δ into α; this estimate is an integral part of MacGillavry and Rideal's formulation of the problem. No change in the estimate can be made without deriving a new solution in which the form of the concentration function might be completely different.

Such a second-order solution is available. It was first given by Strehlow and von Stackelberg (32), and, while it is far from rigorous, it represents a better approximation than that of Rideal and MacGillavry. It suffers from the same inconsistency as the analysis of the latter revealed, however, and the same kind of revision of the solution is necessary.

Strehlow and von Stackelberg begin with equation 43, as derived by MacGillavry and Rideal, but feel that it is unrealistic to suppose, as do the latter authors, that ρ^3 is negligible compared with γt. They point out that such an assumption represents the expansion of $(\rho^3 + \gamma t)^{-1/2}$ and $(\rho^3 - \gamma t)^{4/3}$ in Taylor's series, only the first term being retained. Thus

$$\frac{\rho^3 - \gamma t}{\rho^3 + \gamma t} = 1 - \frac{2\rho^3}{\gamma t} + 2\left(\frac{\rho^3}{\gamma t}\right)^2 + \cdots \tag{73}$$

$$D\frac{(\rho^3 + \gamma t)^{4/3}}{\rho^5} = D(\gamma t)^{4/3}\rho^{-5}\left[1 + \frac{4\rho^3}{3\gamma t} + \frac{2}{9}\left(\frac{\rho^3}{\gamma t}\right)^2 + \cdots\right] \tag{74}$$

Strehlow and von Stackelberg proceed with their analysis by retaining the first two terms of these expansions. Thus, they are required to solve:

$$\frac{\partial C}{\partial t} = \frac{D}{\rho^5}(\gamma t)^{4/3}\left(1 + \frac{4}{3}\frac{\rho^3}{\gamma t}\right)\left[\rho\frac{\partial^2 C}{\partial \rho^2} - 2\left(1 - 2\frac{\rho^3}{\gamma t}\right)\frac{\partial C}{\partial \rho}\right] \tag{75}$$

The balance of the analysis closely parallels that of MacGillavry and Rideal, so that the boundary conditions used by Strehlow and von Stackelberg do not take account of the severe restriction of the region of applicability of equation 75 caused by the approximation made. In addition, certain quantities arising during the analysis, which are actually time-dependent, are dealt with by making use of their constant time-average values; this ordinarily dubious procedure need cause no concern in view of the more general difficulties encountered.

The current expression ultimately derived by their procedure is

$$i = 709nC_0D^{1/2}m^{2/3}t^{1/6}(1 + AD^{1/2}m^{-1/3}t^{1/6}) \tag{76}$$

This expression is derived from a concentration distribution function which must be considered erroneous. A detailed solution[3] which takes into account the limited range of the differential equation shows that the current is given by

$$i = 709nC_0\,D^{1/2}m^{2/3}t^{1/6}\left\{\frac{\sqrt{\pi}}{\beta} + \frac{2\sqrt{\pi}}{\beta}\sum_{j=1}^{\infty}\exp-\left(\frac{j\pi}{\alpha}\right)^2\right\} \tag{77}$$

where β is defined by

$$10^4 \delta^2 m^{-4/3} t^{-7/3} D^{-1} (1 + \tfrac{4}{3}e) = \beta^2 (1 + \tfrac{4}{3}e) \tag{78}$$

and where e, a constant introduced by Strehlow and von Stackelberg, is defined as the time average of $\rho^3/\gamma t$.

Because of the assumptions made in formulating equation 75, equation 77 will hold only to the extent that

$$\frac{\rho^3 - \gamma t}{\rho^3 + \gamma t} \cong - \left(1 - 2\frac{\rho^3}{\gamma t}\right) \tag{79}$$

is satisfied. By trial, if the value of ρ^3 is no greater than 0.1 γt, equation 79 will be in error by no more than 2 per cent. Introducing $\rho^3 = 0.1 \gamma t$ into equation 77, the exponential terms become, for reasonable values of the experimental quantities, vanishingly small, and the bracketted factor takes on values ranging from 50 for fast moving ions and relatively large values of t (10 sec.) down to about 1 for slow moving ions and very small (0.01 sec.) values of the time. Again, the conclusion must be drawn that the size of the diffusion layer has been considerably underestimated.

E. THE SOLUTION OF KAMBARA AND TACHI

Kambara and Tachi (15) have presented a solution which resembles that of Strehlow and von Stackelberg, but it need not be considered in very great detail because of an error they make in deriving their differential equation. Briefly, they introduce a new dependent variable,

$$\varphi = rC = \varphi(r, t) \tag{80}$$

and transform to the independent variables used by Ilkovic, x, the distance from the drop surface, and t. They write the total differential of φ as:

$$d\varphi = \frac{\partial \varphi}{\partial t} dt + \frac{\partial \varphi}{\partial x} dx \tag{81}$$

They then convert the diffusion equation for a stationary spherical surface into the same system of variables, finding

$$\frac{d\varphi}{dt} = D \frac{\partial^2 \varphi}{\partial x^2} \tag{82}$$

Proceeding much as Ilkovic did, and with the same reasoning, Kambara and Tachi introduce equation 82 into equation 81. Their resulting differential equation is

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{\gamma}{3} \left(\frac{1}{r_0^2} - \frac{1}{r^2}\right)\frac{\partial \varphi}{\partial x} \tag{83}$$

which is erroneous. Direct transformation of equation 40 shows[3] that the correct result is:

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{\gamma}{3} \left(\frac{1}{r_0^2} - \frac{1}{r^2}\right) \frac{\partial \varphi}{\partial x} + \frac{\gamma}{3r^3} \varphi \tag{84}$$

It is sufficient to observe of their subsequent procedure that they, like MacGillavry and Rideal, and Strehlow and von Stackelberg before them, are forced to restrict the range of their differential equation by an approximation which is essential to the achievement of a simple solution. Later, in evaluating boundary conditions, the restriction is ignored. Consequently, their result would have been questionable in any case.

F. VON STACKELBERG'S INTEGRAL METHOD

It appears that in all four analyses of the diffusion problem which have been discussed, the concept of "diffusion layer thickness" must be introduced at one point or another, generally with the aim of simplifying the differential equation. There exists another approach to this problem, which might be called the "integral" method, as opposed to the "differential" methods which have been discussed, in which the diffusion layer thickness is introduced at the start and is central to the solution of the problem. This method appears to be superior, in general, to the differential method, and, as utilized by Matsuda (25) (cf. next section), the integral method provides the most nearly definitive solution to the Ilkovic problem which has yet been achieved.

The integral method as used by von Stackelberg (30) will be described first. He defines two different "diffusion layer thicknesses", an "integral" thickness, Δ, and a "differential" thickness, δ, as follows:

$$\Delta = \frac{2}{C_0} \int_{r_0}^{\infty} (C - C_0) \, dr \tag{85}$$

$$\delta = \frac{C_0}{(\partial C / \partial r)_{r=r_0}} \tag{86}$$

The former quantity corresponds to the thickness of a hypothetical region of the solution immediately around the electrode, having a volume sufficient to contain the total number of molecules actually reduced up to that time at a concentration equal to the bulk solution concentration of active molecules. The differential thickness represents the space coördinate of the intercept of a line tangent to the concentration gradient at the electrode surface with the line $C = C_0$. The designation "diffusion layer thickness" for these quantities is misleading, for they are not to be understood as measuring the extent of the region in which the concentration is inhomogeneous. They are simply numbers which happen to have the dimensions of length. This is of no importance, however, in the development to follow.

From the earlier discusssions of the relation of current to flux, it is easily seen that

$$i = \frac{nFC_0 \cdot 4\pi r_0^2 \, D}{\delta} \tag{87}$$

Further, since the time integral of the current must be the total amount of charge transferred, an equivalent definition for Δ is

$$\Delta = \frac{2}{4\pi r_0^2 \cdot nFC_0} \int_0^t i \, dt \tag{88}$$

Combining these equations produces von Stackelberg's integral equation:

$$\Delta = \frac{2D}{r_0^2} \int_0^t r_0^2 \, \delta^{-1} \, dt \tag{89}$$

von Stackelberg's integral equation cannot be solved without more information about the relationship between δ and Δ. Such a relationship can be found, for example, by using the equivalent relationship between the corresponding functions for a plane electrode or a stationary spherical electrode, functions which can be calculated from solutions to the problem of diffusion at such electrodes.

The solutions for the diffusion problems at stationary electrodes are relatively simple, and the results for the boundary conditions necessary in the present case are well known (7). Therefore, the procedure involves the determination of δ and Δ from the available solutions by the use of the defining equations (equations 85 and 86). Some relationship between δ and Δ can thereby be established. Introduction of the relationship into equation 89 produces an integral equation which can, in principle, be solved for δ. δ being known, the current can be evaluated with the use of equation 87.

Though straightforward in principle, this procedure involves certain difficulties. For one thing, there is no theoretical basis for the assumption that δ and Δ will have the same relationship at a stationary electrode as they will at a moving one. Secondly, it turns out that the form of the relationship between δ and Δ usually renders the integral equation too difficult to solve. Therefore, recourse is usually made by those using the integral approach (13, 14, 15, 30, 32) to approximations, the deleterious effect of which it is difficult to evaluate. The most serious objection involves the use of an integration interval which extends to infinity, inasmuch as the greater part of this interval is generally excluded by the nature of the approximations made during the simplification. This is related to the difficulties of the differential approach.

The actual procedures are straightforwardly presented in the literature (13, 14, 15, 30, 32) and need not be discussed here. The nature of the solutions obtained is of interest.

If the relationship between δ and Δ is based on the solution for the stationary plane electrode, the Ilkovic equation (equation 1) results. If the relationship is based on the solution for the stationary spherical electrode, a form of equation 76, derived originally by Strehlow and von Stackelberg (32), results. The only difference among the several versions of the formula for the current derived from the stationary spherical electrode solution appears in the value assigned to the numerical constant which occurs in the second term of equation 76. The values assigned range from 17 to 39. This second term amounts in general to a few per cent of the magnitude of the first term, and so may be considered a second-order correction.

G. THE SOLUTION OF MATSUDA

The work of Matsuda (25) represents a nearly definitive solution to the problem whose solution was originally undertaken by Ilkovic. In the opinion of the

present authors, Matsuda's approach is the best-formulated attack on the problem yet made.

Matsuda begins with the general equation for diffusion and convection, as introduced earlier:

$$\frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) - \frac{\gamma}{3r^2} \frac{\partial C}{\partial r} \tag{40}$$

with initial and boundary conditions "clearly given" by

$$C = C_0' \qquad (t = 0, r > r_0) \tag{90}$$

$$C = 0 \qquad (t > 0, r = r_0) \tag{91}$$

$$C = C_0 \qquad (t > 0, r \rightarrow \infty) \tag{92}$$

$$r^2 \frac{\partial C}{\partial r} = 0 \qquad (t > 0, r \rightarrow \infty) \tag{93}$$

Matsuda multiplies both sides of equation 40 by r^2 and integrates both sides with respect to r from r_0, the drop radius, to infinity. He writes as his result:

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} (C_0 - C) r^2 \, dr = D r_0^2 \left(\frac{\partial C}{\partial r} \right)_{r=r_0} \tag{94}$$

This is not immediately obvious and Matsuda does not elaborate. The intervening steps appear to be somewhat as follows:

When equation 40 is integrated, it becomes

$$\int_{r_0}^{\infty} \left(\frac{\partial C}{\partial t} \right) r^2 \, dr = D r^2 \left(\frac{\partial C}{\partial r} \right) \Big]_{r_0}^{\infty} - \frac{\gamma}{3} C \Big]_{C(r_0)}^{C(\infty)} \tag{95}$$

which, upon application of the appropriate boundary conditions, becomes

$$\int_{r_0}^{\infty} \left(\frac{\partial C}{\partial t} \right) r^2 \, dr = -D r_0^2 \left(\frac{\partial C}{\partial t} \right)_{r_0} - \frac{\gamma}{3} C_0 \tag{96}$$

The function on the left may be expanded according to the rules for differentiating under the integral sign, giving

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C \, dr + (r^2 C)_{r_0} \frac{\partial r_0}{\partial t} \tag{97}$$

Since $C(r_0, t) = 0$, the second term is zero. Now if the function

$$\frac{\partial}{\partial t} \int_{r_0}^{\infty} r^2 C_0 \, dr = -(r^2 C_0)_{r_0} \frac{\partial r_0}{\partial t} = -\frac{C_0}{3} \frac{\partial r_0^3}{\partial t} = -\frac{C_0}{3} \frac{\partial (\gamma t)}{\partial t} = -\frac{C_0 \gamma}{3} \tag{98}$$

is introduced, Matsuda's result, equation 94, follows at once.

At this point Matsuda introduces a new upper limit for the integral in equation 94. He reasons that since the inhomogeneity of the concentration extends only a short way into the solution, it may be considered to be confined within a radius $r_0 + \theta(t)$, where θ is a function of time and he chooses $r_0 + \theta(t)$ as his

new upper limit (the erroneous upper limit printed in the original paper is obviously a typographical error). Now a change of variable is made, given by

$$r = r_0 + x \tag{99}$$

and in terms of the new variable, x, equation 94 becomes

$$\frac{\partial}{\partial t} \int_0^\theta (C_0 - C)(r_0 + x)^2 \, dx = Dr_0^2 \left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{100}$$

which ought to be called Matsuda's integro-differential equation.

In considering this portion of Matsuda's work it appears, first of all, that Matsuda's final boundary condition, equation 93, is in error. It will be recalled that, while in most cases of diffusion the flux is simply given by $-D\partial C/\partial r$, in the present problem of interacting diffusion and convection, the flux is given by

$$-D \frac{\partial C}{\partial r} + \frac{\gamma}{3r^2} C$$

Thus at infinity $\partial C/\partial r$ is undoubtedly zero; it is also necessary that the flux be zero. Therefore, the product $\left(r^2 \dfrac{\partial C}{\partial r}\right)_\infty$ cannot be zero, but must be equal to $\gamma C/3D$. Upon carrying the analysis through using this condition, it turns out that the quantity $\gamma C_0/3$ must be subtracted from the right side of equation 94.

Actually, this matter can be adjusted, since, if one derives equation 94 by integrating equation 40 immediately from r_0 to $r_0 + \theta$ rather than from r_0 to ∞, one finds directly

$$\frac{\partial}{\partial t} \int_{r_0}^{r_0+\theta} r^2(C_0 - C) \, dr = Dr_0^2 \left(\frac{\partial C}{\partial r}\right)_{r=r_0} \tag{101}$$

provided that the following boundary conditions are substituted for those given by Matsuda:

$$C = C_0 \qquad r = \theta, t > 0 \tag{92b}$$

$$r^2 \frac{\partial C}{\partial r} = 0 \qquad r = \theta, t > 0 \tag{93b}$$

This correction is important in revealing the true nature of the assumptions necessary to achieve Matsuda's solution. Both conditions 92b and 93b are innovations in the theory, though it will be recalled that the present authors used a condition much like 92b in demonstrating the magnitude of the error involved in some of the treatments discussed earlier. It was pointed out in the discussion of the "integral" methods that the diffusion layer "thicknesses" defined there were only nominal, having only the dimensions, not the quality, of length. Matsuda, however, intends that there be assumed a real, numerically definite length, which separates the solution into two regions, one in which the concentration is homogeneous and one in which it is not. Condition 93b defines the continuity between the regions; it states that there is a flux, to be sure, but only convection is responsible for it. No flow of matter passes between the regions by virtue of diffusion.

The only other feature of the derivation of equation 100 which is technically unsatisfactory involves Matsuda's method for the transformation of coördinates from (r, t) to (x, t). It can be shown, however, that by making this transformation in equation 40 and then integrating, the same result is achieved.

The method of solution of equation 100 which is used by Matsuda is very ingenious. The unknown function $C_0 - C$ is first expanded as a polynomial in x/θ:

$$C_0 - C = C_0 \frac{r_0}{r_0 + x} \left(1 + \sum_{j=0}^{\nu} A_j \left(\frac{x}{\theta} \right)^j \right) \tag{102}$$

The ν unknown coefficients are to be determined by suitable boundary conditions. Note that equation 102 satisfies boundary condition 91 in its present form. In his paper Matsuda carries out two calculations: in one he sets ν equal to 6, and in the other, ν equal to 10. The first calculation will be described.

In order to find the values of the coefficients A_j, Matsuda makes use of the following additional conditions:

$$C(\theta, t) = C_0 \qquad \left(\frac{\partial C}{\partial x} \right)_{\theta = x} = 0 \qquad \left(\frac{\partial^2 C}{\partial x^2} \right)_{\theta = x} = 0$$

$$\left(\frac{\partial^3 C}{\partial x^3} \right)_{\theta = x} = 0 \qquad \left(\frac{\partial^4 C}{\partial x^4} \right)_{\theta = x} = 0 \qquad \left(\frac{\partial^2 [(r_0 + x)C]}{\partial x^2} \right)_{x = 0} = 0 \tag{103}$$

Of these, the first and second follow from conditions 92b and 93b. The last results from the introduction of the (x, t) coördinates into equation 40, followed by setting x equal to zero. The remaining relationships are new. They are logical extensions of Matsuda's assumption about the diffusion layer and constitute further continuity conditions at the interface between inhomogeneous and homogeneous regions of the solution.

The calculation involved in finding the coefficients is essentially that of solving six simultaneous equations in six unknowns. The calculation is not difficult and the result is

$$C_0 - C =$$

$$C_0 \frac{r_0}{r_0 + x} \cdot \left[1 - 3 \left(\frac{x}{\theta} \right) + 10 \left(\frac{x}{\theta} \right)^3 - 15 \left(\frac{x}{\theta} \right)^4 + 9 \left(\frac{x}{\theta} \right)^5 - 2 \left(\frac{x}{\theta} \right)^6 \right] \tag{104}$$

Inspection shows that all the boundary conditions (equation 103) are completely satisfied by equation 104; for instance, the sum of the coefficients is zero, so that $C_0 - C$ is zero when $x = \theta$. The others follow similarly. The only difficulty with equation 104 enters when r_0, and therefore t, is allowed to approach zero. It turns out that θ is a series in ascending positive powers of t; consequently, the ratios x/θ increase without bound as t becomes small. Thus $C_0 - C$ is indeterminate under these conditions. This ambiguity surrounding the requirements of equation 90 is the most serious mathematical defect in Matsuda's work.

Matsuda now introduces equation 104 into equation 102 and carries out the

integration. No difficulties arise, and after simplification, the result is a non-linear differential equation of first order:

$$\frac{d}{dt}\left(\tfrac{3}{14}r_0^2\theta + \tfrac{1}{28}r_0\theta^2\right) = Dr_0^2\left(\frac{1}{r_0} + \frac{3}{\theta}\right) \tag{105}$$

The solution of equation 105 is difficult. Matsuda writes

$$\theta = \sqrt{Dt}\sum_{j=0}^{\infty}\alpha_j(\gamma^{-1/3}D^{1/2}t^{1/6})^j \tag{106}$$

intending, presumably, to determine the α_j by direct substitution and subsequent equating of the coefficients of equal powers of t. He does not attempt to justify his use of function 106 and discusses none of its mathematical properties such as convergence. Dimensional analysis of the physical situation reveals that the form of the terms of equation 106 is only one among a number of reasonable possibilities. There seems to be no *a priori* reason for Matsuda's use of this particular functional form.

Matsuda gives no exact procedure for the solution, but the present authors carried out the calculations in the following manner: $r_0 = (\gamma t)^{1/3}$ was introduced in equation 105, and both sides were multiplied by θ. The first four terms of θ from equation 106 were substituted into equation 105. To evaluate θ^2, the Cauchy product $\theta \times \theta$ was formed in the form of an array, retaining four terms. After simplification, the first derivative of the quantity in the parentheses of equation 105 was found, and arranged in the order of ascending powers of t. A new Cauchy product was now formed between this quantity and θ. Coefficients of like powers of t (the powers are all fractional, of the form $n/6$, where n is an integer) were collected and set equal to zero. The set of equations so formed could be solved for the coefficients α_j. Matsuda's result is

$$\theta = \sqrt{Dt}[2\sqrt{3} + \tfrac{4}{5}(\gamma^{-1/3}D^{1/2}t^{1/6}) - \tfrac{19}{75}\sqrt{3}(\gamma^{-1/3}D^{1/2}t^{1/6})^2$$
$$+ \tfrac{856}{6375}(\gamma^{-1/3}D^{1/2}t^{1/6})^3 - \cdots] \tag{107}$$

Since the current is given by the product of Faraday's constant, the electrode area, and the flux at the electrode surface, it follows from equation 104 that:

$$i = 4\pi r_0^2 nFDC_0\left(\frac{1}{r_0} + \frac{3}{\theta}\right) \tag{108}$$

The quantity in parentheses can be evaluated by using equation 105. Matsuda's final result, after adjusting the dimensions to experimental quantities in the usual way, is

$$i = 709nC_0D^{1/2}m^{2/3}t^{1/6}[1 + 35.5(D^{1/2}m^{-1/3}t^{1/6}) + 266(D^{1/2}m^{-1/3}t^{1/6})^2 - \cdots] \tag{109}$$

A second calculation carried out by Matsuda for ν of equation 102 equal to 10 yields the same equation with respective constants in the series, 1, 36.3, and 343. In actual magnitudes the first three terms, using reasonable experimental values for D, m, etc., have the approximate ratio $100:3:0.3$.

Matsuda executed the same calculation once again under somewhat different assumptions to determine the magnitude of the shielding effect of the capillary tube. The upper part of the depleted shell of solution surrounding the drop is cut by the plane tip of the capillary. Actually, therefore, the integration in equation 100 should be carried out over an unsymmetrical spherical region, bounded partly by a plane. The result of this calculation is to show that the values of the respective constants in equation 109 should become 1, 23.9, and 62.9.

The special virtues of Matsuda's work are two: It is capable of indefinite extension to greater and greater precision simply by increasing the value of ν in equation 102. Of course the labor of the calculation is increased thereby. Secondly, there is no question about any approximation of the extent of the diffusion layer thickness. θ is developed, by this method, in such a way as to make a solution, previously chosen only to satisfy the boundary conditions, satisfy the differential equation as well. This is in complete contrast to the usual method, which is to find a solution for the differential equation, and then to modify this solution to suit the boundary conditions. No doubt the concentration function derived by Matsuda's procedure is an approximation; nevertheless, the expression for the flux, which depends only on the thickness of the diffusion layer, ought to be reliable.

H. THE SOLUTION OF LINGANE AND LOVERIDGE

The contribution of Lingane and Loveridge (19), which appeared simultaneously with that of Strehlow and von Stackelberg (32), is actually not so much a formal solution as an ingenious and simple pragmatic correction to the Ilkovic equation (1) which brings it into the form of equation 76, the two-term equation of Strehlow and von Stackelberg, while at the same time going far toward making the differences between equation 1 and equation 76 more explicable physically. Lingane and Loveridge noticed that the constant $(3 \mathstrut/7)^{1/2}$, which appears in the expression for the surface concentration gradient derived by Ilkovic (equation 35), is the only factor which distinguishes equation 35 from the corresponding expression for diffusion at a stationary plane electrode:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C_0}{\sqrt{\pi D t}} \tag{110}$$

They hypothesized that the factor $(3\mathstrut/7)^{1/2}$ takes account of the effect of the convection due to drop growth on the magnitude of the flux; they considered, therefore, that the Ilkovic approach correctly accounts for the growth factor but not for the drop curvature. To overcome the latter defect, Lingane and Loveridge introduced the factor $(3\mathstrut/7)^{1/2}$ into the expression for the surface concentration gradient at a stationary spherical electrode, as a multiplier of the factor $(Dt)^{1/2}$, wherever the latter occurs. They derived the equation for the current from this modified flux expression; their result, after simplification, is identical with equation 76 except for the numerical value of the constant A, for which they find 39. It will be recalled that the solution of Strehlow and von Stackelberg takes account of both drop curvature and drop growth; thus the remarkable result of

Lingane and Loveridge appears to confirm their supposition that the drop-growth convection effect is reflected by the constant $(\tfrac{3}{7})^{1/2}$.

I. SUMMARY

The theory of the current at the dropping mercury electrode has passed through a series of developments, each more sophisticated than the last, culminating in the work of Matsuda (25), who has carried the mathematical part of the theory to a point of great rigor and whose method is capable of extension (at the cost of computational labor) to any degree of accuracy. It now remains to be seen to what extent the results of the theory fit the experimental description of the current–time relation.

A striking feature of the theoretical work which has been done on this problem lies in the close similarity of the equations for the current as derived by different authors by diverse approaches, some of them, as has been shown, seriously in error. At the same time, the concentration functions derived by the various authors, from which the surface flux and current are calculated, have differed greatly. For example, equation 1 was derived by both Ilkovic (12) and MacGillavry and Rideal (21) by different methods; the corresponding concentration functions, given by equations 34 and 56, differ greatly. It appears that while the concentration functions are quite sensitive to the means of analysis, their slopes at the electrode surface are not.

III. EXPERIMENTAL EVALUATION OF PROPOSED THEORIES

A. THE EXPERIMENTAL CURRENT–TIME VARIATION

A thorough discussion of each of the factors which affect the diffusion current will be found in Chapter IV of the well-known monograph by Kolthoff and Lingane (16). The prevailing evidence indicates that the Ilkovic equation and its modifications can account more or less satisfactorily, at the practical level, for the influence of each of the many factors which affect the diffusion current. In detail, however, there are discrepancies between theory and experiment; in particular, the time dependence expressed by the Ilkovic equation is inadequate. The time dependence is the concern of this study, and the following discussion will relate only to this factor, whose primary importance to the physical theory of polarography is self-evident; if the current–time relation predicted by theory is experimentally not realized, the theory itself becomes suspect.

The earliest experimental evaluations of the Ilkovic equation seemed to bear out the one-sixth power law predicted (11). More recent work (3, 13, 18, 20, 27, 28, 29, 31, 33), however, using more refined experimental methods, has tended to contradict the early results. The discrepancies which have come to light are of two sorts: first, it has been shown in many cases that the experimental average currents are appreciably lower than those predicted experimentally; secondly, careful studies of the current as a function of time have shown that the one-sixth power time relation indicated by the Ilkovic equation is not obeyed at all during the first third of the drop life and is obeyed only approximately during the final two-thirds. Only slight improvement is realized by using the time law predicted by one of the modified forms of the Ilkovic equations.

Of the data which are available on the current–time relationship, those of Taylor, Smith, and Cooter (33) are the most detailed, particularly at small values of the time. They investigated this relationship for a rather restricted situation; they give detailed data for two drops, obtained under fairly typical and nearly identical experimental conditions. Their data include specification of neither the head of mercury used nor the physical dimensions of the capillary used; this is unfortunate since, as will be shown, it makes the calculation of initial and final m-values impossible.

MacDonald and Wetmore (20) present data on the reduction of copper(II) ion, for which they are able to evaluate the diffusion coefficient with much greater accuracy than is usually the case. Their data cover a range of concentrations and a range of drop times, in contrast to those of Taylor, Smith, and Cooter, but are less detailed at small values of the time.

Lingane (18) presents a variety of curves for two different capillaries, at different values of the drop time. Unfortunately, no tabulation of the data is given.
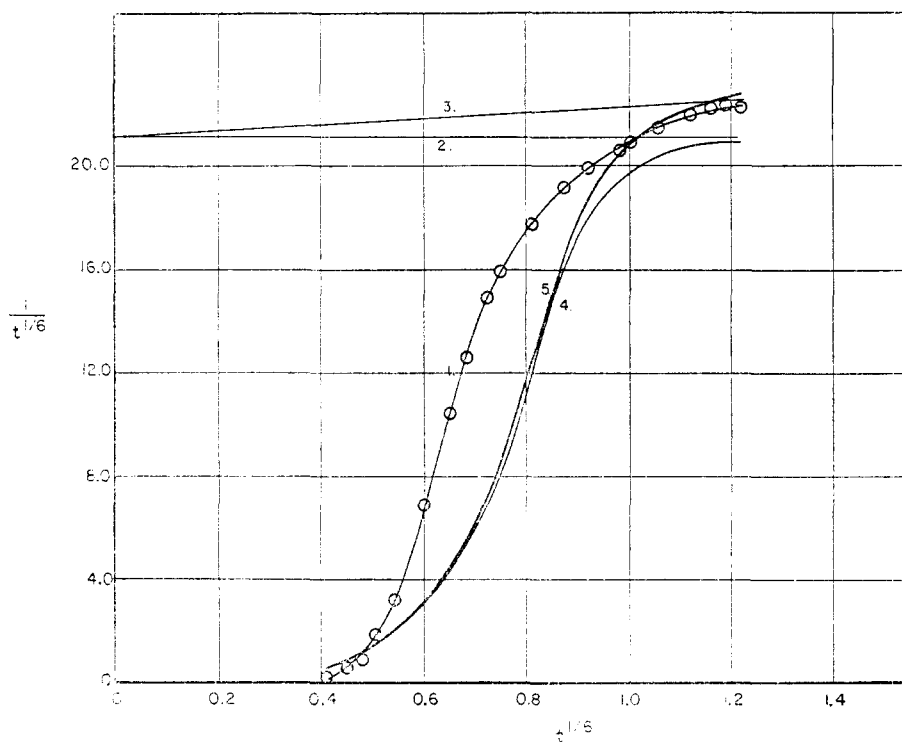

FIG. 1. The current–time dependence at the dropping mercury electrode, theoretical and experimental. Curve 1, experimental data of Taylor, Smith, and Cooter (33). Curve 2, theoretical curve based on simple Ilkovic equation 39. Curve 3, theoretical curve based on Matsuda equation 109. Curve 4, theoretical curve based on Markowitz–Elving equation 115; plane approximation, parabolic initial gradient. Curve 5, theoretical curve based on Markowitz–Elving equation; spherical approximation, parabolic initial gradient.

The experimental procedures used in gathering the three sets of data just cited all involved the use of electronic equipment for measuring the current. However, the method of recording the current used by Taylor, Smith, and Cooter involved the use of a rotating drum camera to record the deflection of the beam of a cathode ray oscillograph. The photographic record was analyzed with what appears to be great accuracy by means of a special comparator. This entire technique seems superior to those used by the other authors cited, who photographed the trace on the face of a cathode ray oscilloscope; methods of analyzing such photographs were not described.

The actual behavior of the current with time is exhibited by curve 1 of figure 1, which represents the data of Taylor, Smith, and Cooter (Drop No. 1). This is typical of the behavior encountered by all investigators. The data are plotted as $i/t^{1/6}$ vs. $t^{1/6}$. The Ilkovic equation, so plotted, appears as a straight line, parallel to the $t^{1/6}$ axis. The Matsuda version, equation 109, appears as shown by curve 3 of figure 1 (the curvature resulting from the third-order term is so slight as to be indistinguishable). The data appear as an S-shaped curve, which approaches neither equation except as a limit near the end of the drop life. In considering such curves, it is well to remember that the diffusion coefficient is not known very accurately; this means that the actual vertical position of the theoretical curves is in some doubt, though this inaccuracy does not affect their shape.

B. HYPOTHESES ON THE DISCREPANCY BETWEEN EXPERIMENT AND THEORY

Two suggestions have been advanced to account for the wide discrepancy between the experimental results and the theoretical prediction. Lingane (18) relates the discrepancy to the variation in mercury flow rate during the drop lifetime, while Markowitz and Elving (23, 24), following a suggestion of Airey and Smales (3), have mathematically developed the idea that the freshly forming drop begins its life in a region partially depleted by the electrolysis at the preceding drop.

Lingane (18) suggests that the low value of the current early in the drop life may be accounted for by the neglect in the theoretical analysis of the time dependence of m, the rate of flow of mercury. The current is directly proportional to the drop area, which is taken to be directly proportional to $m^{2/3}$. Thus, were the initial value of m lower than the assumed average value, the drop area, and consequently the current, would be smaller than theory predicts at small values of t.

To evaluate this suggestion, it is necessary to have some idea of the time dependence of m. A discussion of this is found in the monograph by Kolthoff and Lingane (16) (where, incidentally, the authors state that the observed discrepancy between observed and theoretical current is too large to be accounted for by the variability of m). When the Poiseuille equation, which relates the volume of a liquid flowing through a capillary to the capillary dimensions, the viscosity of the liquid, η, the differential head, ΔP, and the time, is combined with the definition of m, there results

$$m = \frac{Vd}{t} = \frac{\pi r_c^4 d}{8L\eta} \Delta P \tag{111}$$

where r_c, L, and d are, respectively, the radius and length of the capillary and the density of mercury. This equation is strictly true only for liquids which wet glass, unlike mercury, for circumstances under which the kinetic energy of the discharged liquid is negligible, and for steady state conditions, i.e., constant ΔP. The dropping electrode would seem to meet none of these requirements for small t.

Kolthoff and Lingane cite Kucera (17) to show that, for a pendant drop at the tip of a small capillary, the back pressure, which diminishes the nominal hydrostatic head, can be expressed as

$$p_{\text{back}} = \frac{2\sigma}{r_d} \tag{112}$$

where σ is the interfacial tension at the drop surface in dynes per centimeter and r_d is the radius of the drop. Combining equation 111 and equation 112:

$$m = \frac{\pi r_c^4 d}{8L\eta} \left(p - \frac{2\sigma}{r_d} \right) \tag{113}$$

Since m, according to equation 113, depends on the drop radius, while, from equation 16, the drop radius depends on m, it is seen that m is given only implicitly by equation 113. Combining equations 16 and 113 leads to a complicated equation in fractional powers of m, intractable to formal methods of solution. Trial calculation might be made for m for specific values of the time, but the results would not be general. Furthermore, the general validity of equation 113 has not been established, either experimentally or theoretically, for the dynamic case under consideration.

First of all, the citation of the paper by Kucera and the absence of any further references to substantiate equation 112 is rather strange, since this equation has such a central place in Lingane's interpretation. Kucera's paper deals mainly with the effect of polarization on the interfacial tension of water and mercury. In the few paragraphs devoted to a discussion of the back pressure, equation 112 is introduced, but no justification is given. No mention of any treatment of the rate of growth of mercury drops is to be found in several authoritative treatises and compendia dealing with capillarity and other surface effects (1, 5, 6). Bouasse (6) and Bikerman (5) both characterize the usual methods of the determination of surface tension, to certain of which the dropping electrode has similarities, as static rather than dynamic methods. Bouasse indicates that mathematical difficulties would be anticipated in any treatment of drops which are falling (tombante) as opposed to those which are static (pendant). It appears that in any complete treatment, some account would have to be taken of the contact angle in the system mercury–water–glass (4), at least for the very early stages of drop formation. The contact angle would vary from case to case, depending on the nature of the solution and the kind of glass of which the capillary tube is made. Other factors, such as the adsorption on the drop surface of surface-active

material from the solution, would generally operate to diminish σ. Equation 112 cannot be regarded as more than an approximation. Nevertheless, the probability is good that m is time-dependent, and that its time dependence is superficially described in parametric form by equations 16 and 113.

Lingane's suggestion that this time dependence is responsible for the current–time behavior of his data cannot, however, be accepted as the complete explanation. For one thing, such a suggestion is inadequate to explain Lingane's own data. In one case, under conditions almost identical to those governing the data of figure 1, a calculation shows that the ratio of the m-value expected from equation 112 at the beginning of drop formation to that at the end of the drop life is about 0.6. m occurs to the two-thirds power in the Ilkovic equation; thus, were a time-dependent m introduced, the current–time curve for this equation, corresponding to curve 2 in figure 1, should start somewhat lower and end somewhat higher than curve 2, the ratio of initial to final current being $0.6^{2/3}$ or 0.7. (It will be recalled that the time-average value of m is ordinarily used in the Ilkovic equation.) The situation is similar for the modified version of the Ilkovic equation, where the slope, as well as the ordinates, should be somewhat lower at small values of time than at large. It can be seen from figure 1 that such differences could not nearly account for the discrepancies between theory and experiment.

It must be admitted, as Lingane points out, that were a time-dependent m introduced into the differential equation at the outset of the analysis, the theoretical outcome would be different and the current derived might have an entirely different form. On the other hand, it is certain that the initial value of the drop area is finite, and for a short period of time, as mercury begins to emerge from the capillary without much change in nominal radius, the area ought to be relatively constant. The "mathematical" drop, however, as used in the derivations, starts from zero area. It follows that, for a short period of time, the physical drop is larger than the corresponding mathematical drop, so that, initially, the true current should actually be greater than the mathematically derived current, rather than the reverse. In fact, if the time dependence of the m-value were the only effect causing the discrepancy between theory and experiment, and the finite initial drop area were taken into consideration, the initial current ought to be infinite, as shown, for instance, by equation 108:

$$ i = AnFDC_0 \left(\frac{1}{r_0} + \frac{3}{\theta} \right) \tag{108} $$

Since θ has $t^{1/2}$ as a factor, $3/\theta$ increases without bound as t goes to zero.

It appears from these considerations that the question of the exact influence of a time-dependent m on the theoretical situation must remain open for the present. However, it also seems unlikely that such a hypothesis can completely account for the disparity between theory and experiment, although the time dependence of m should certainly be taken into account in any complete theory. The neglect of this factor in the past is probably due to the mathematical complications which would be consequent to its inclusion. Since, as this review shows,

these difficulties are very severe even without a time-dependent m, neglect of the time dependence of m on these grounds is understandable.

Airey and Smales (3) have suggested that the freshly forming drop begins its growth in a region of solution where the concentration is less than that in the bulk solution as a result of depletion by electrolysis at the immediately preceding drop. Markowitz and Elving (23, 24) incorporated this postulate into current–time theory by discarding the usual boundary condition of constant initial concentration in favor of a new one:

$$C(r, 0) = C_0 F(r) \tag{114}$$

$F(r)$ is an arbitrary initial distribution function having values between 0 and 1, chosen so as best to represent the assumed physical situation. To avoid mathematical difficulties, the model of Lingane and Loveridge (19), in which the factor $\tfrac{3}{7}$ is used to account for the effect of drop growth, was adopted. Solutions were sought for the problems of diffusion to stationary plane and spherical electrodes with inhomogeneous initial concentration distributions. By the use of the Laplace transform calculus, the electrode surface flux was determined in a form in which the trial functions, $F(r)$, occurred in integrals whose evaluation could be deferred to the final stages of the calculation.

To describe the initial concentration distribution the most useful form of $F(r)$ was found to be the quadrant of a parabola, with the value zero at the origin and with no discontinuity at the depleted region boundary. The time-dependent coördinate of this boundary was determined by using the Ilkovic equation 1 as a first approximation in calculating the volume of solution necessary to contain all of the electroactive material consumed during the lifetime of a drop. The chosen $F(r)$ was introduced into the equation for the flux, and the integrals were evaluated. Following the procedure of Lingane and Loveridge, the quantity $\tfrac{3}{7}$ was associated with the product Dt wherever the latter occurred, and the equivalent spherical area was introduced. For the plane electrode model, the final equation for the current is

$$i = kt^{1/6} \left\{ \frac{2\sqrt{3\pi Dt/7}}{\mu} \operatorname{erf} \frac{\mu}{2\sqrt{3Dt/7}} + \frac{12Dt}{7\mu^2} \left[e^{-7\mu^2/12Dt} - 1 \right] \right\} \tag{115}$$

The Ilkovic constant, k, represents the product, $709 \, nD^{1/2}Cm^{2/3}$, and μ is the coördinate of the depleted region boundary; the form of μ is complex. It can be shown that the bracketed factor of equation 115 reduces to 1 when μ approaches zero, corresponding to the classical derivations of the Ilkovic equation with constant initial concentration. Thus, in the limit of vanishing depleted region, equation 115 approaches the Ilkovic equation.

The current–time behavior of equation 115 was compared with the experimental data of Taylor, Smith, and Cooter (33). The experimental constants of these investigators were introduced and the current calculated as a function of time. The results, plotted in figure 1, show excellent agreement with the experimental curve. Even better agreement can be achieved by the use of the corresponding spherical electrode solution; the latter solution is analogous to those

of the classical derivations which result in a two-constant equation for the current, as, for example, the solution of Lingane and Loveridge. Introduction of an empirical constant by trial to account for the portion of depleted solution swept away by the fall of the preceding drop improves the agreement of experimental and theoretical results for values of the constant which reflect partial attrition of the depleted region from this cause.

The good agreement of equation 115 and its spherical counterpart with the experimental results indicates that the introduction of the depleted-region concept is a very satisfactory way of bridging the disparity between theory and experiment. A thorough discussion of the various assumptions and approximations made in the mathematical development has been given by Markowitz (23), who concluded that the validity of the result is not seriously affected by them.

IV. CONCLUSIONS

A detailed and critical study of the theoretical and mathematical contributions of various authors to the theory of the growth of the current at the dropping mercury electrode has been carried out, and the results compared with the best experimental work available. It appears that none of the theoretical equations can predict the experimental current–time relationship accurately, especially during the early stages of drop growth.

Two suggestions have been advanced to resolve the discrepancy between theory and experiment. One suggestion attributes the discrepancy to the neglect in all of the theoretical analyses of the variation in the rate of flow of mercury during the drop lifetime. The other suggestion uses the hypothesis that a drop begins its life in a region of solution partially depleted of electroactive material as a result of electrolysis at the preceding drop. Mathematical development of the latter idea results in a theoretical current–time relationship which is substantially in agreement with the experimental data. It appears that the combination of the two suggestions outlined would result in even better agreement.

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[4] No attempt has been made to list all of the papers which deal with the current–time relation at the dropping mercury electrode. Only the important theoretical studies and a few illustrative papers have been cited. In particular, several recent papers (e.g., reference 26) which have dealt with the effect of changing potential on the time dependence of the current have been omitted from consideration. Other pertinent references can be located via references 9 and 16, and the *Bibliography of Polarographic Literature, 1922–1955*, E. H. Sargent and Co., Chicago, Illinois (1956).

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