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DROP OF POTENTIAL IN THE METALLIC ELECTRODES OF CERTAIN ELECTROLYTIC CELLS

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ABSTRACT

In certain precise measurements of electrolytic resistance of solutions, the platinum electrodes are necessarily very thin so that one cannot neglect the drop of potential in them. Formulas are obtained for this drop in the case of two types of cylindrical cells, one in which the current is axial, the other partly axial and partly radial. The potential admits of accurate evaluation in the first case and the results obtained confirm the method outlined for the treatment of a general shape of cell.

CONTENTS

I. INTRODUCTION

In work during 1915–16 in connection with the examination of various sources of error in the equipment and technique then in use for measuring the conductivity of solutions and to develop precision methods and apparatus therefor, Taylor, Bennett, and Acree [1] studied a number of important electrical and chemical factors. One of these subjects was the proper design of the metal electrodes and the glass containing vessels.

In connection with this last item the above authors noted small deviations in the apparent resistance of solutions surrounding closely spaced disk electrodes 0.1 mm thick and 5 cm in diameter, depending on whether the current entered the disk through a post welded at the center or through this post and three others 120° apart at the edge of the disk. Because of possible corresponding variations in the distribution of the current through the electrodes and solution, and of the electrode phenomena and capacitance over the electrode surface, the above authors desired equations set up for the resistance of typical disk and cylindrical cup electrodes used in their work. With the magnitude of this small factor known accurately for stated conditions it is possible to determine separately the resistance of the solution

[1] J. Am. Chem. Soc. 38, 2396, 2403, 2415 (1916).

and the effects of the series capacitance at the electrode surfaces. With this object in view, the following treatment of the resistance of the metal electrodes themselves is presented.

The total current I (t) sent through an electrolytic cell when an emf E (t) is applied to it by means of electrodes is, in general, given to a first approximation by assuming that the current distribution throughout the electrodes and solution at every instant t is that which would be produced (ultimately) by a constant emf having this instantaneous value E (t), that is, the quasi-stationary state. Let V^0 be the potential of this first approximation in the electrodes or solution. The vector current density $i^0 = -\lambda \nabla V^0$ where the conductivity λ has the value λ_e in the electrodes and λ_s in the solution. At the contact surfaces S_1 and S_2 of electrodes with the solution this potential V^0 is continuous and the normal component $i_n{}^0$ of the current density is continuous. The constant contact potential difference between solution and metal is here ignored since it cancels out of the equations connecting current and applied emf when the electrodes are both of the same material and possess the same surface characteristics. Since the current density is solenoidal, the potential V^0 satisfies Laplace's equation, and for given shape of the solution volume T_s and electrode volumes T_1 and T_2 is determined by the above boundary conditions at the internal boundaries S_1 and S_2, together with the vanishing of the normal current at the external boundaries and the assignment of V^0 or the normal current densities at the entrance section S_{01} and exit section S_{02}, where the current is led into or out of the electrodes by the lead-wires. This first approximation is never sufficiently accurate to represent the results of experiments, but if the applied emf is sufficiently small these may be generally very accurately represented by assuming the existence of a polarization film of very small thickness Δ near the contact surfaces S_1 and S_2. This electrical double-layer, which is equivalent to a capacitance per unit area $k = \frac{\epsilon}{4\pi\Delta}$ (ϵ being the dielectric constant in the film), seems to be the predominant electrostatic effect, so that any simple distribution of charge on S_1 or S_2, or on the external boundaries, is negligible compared to it. This constitutes a condenser K_1 at S_1, K_2 at S_2, and the two being in series amount to a condenser K where

$$K_1 = kS_1,\ K_2 = kS_2,\ \text{and}\ \frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} = \frac{1}{k}\left(\frac{1}{S_1} + \frac{1}{S_2}\right),\ \text{where}\ k = \frac{\epsilon}{4\pi\Delta} \tag{1}$$

If λ_0 is the conductivity of the film, the first condenser has an internal resistance R_{01} which amounts to a shunt on it and the second R_{02}, their resistance in series being R_0, where

$$R_{01} = \frac{\Delta}{\lambda_0 S_1},\ R_{02} = \frac{\Delta}{\lambda_0 S_2},\ \text{and}\ R_0 = R_{01} + R_{02} = \frac{\Delta}{\lambda_0}\left(\frac{1}{S_1} + \frac{1}{S_2}\right) \tag{2}$$

so that

$$\gamma \equiv \frac{4\pi\lambda_0}{\epsilon} = \frac{\lambda_0}{k\Delta} = \frac{1}{R_0 K} = \frac{1}{R_{01}K_1} = \frac{1}{R_{02}K_2} \tag{3}$$

The values of these electrolytic capacities, as evaluated by experiments,[2] are so large as to indicate that the film thickness Δ is exceedingly small compared to the thickness attainable in mica condensers or air condensers, so that the capacity k per unit area is enormous. Even when there is very little evidence of the film, we may adhere to this view that Δ is very small by assuming that the film conductivity λ_0 practically short-circuits the condenser. This viewpoint then leads to the second approximation, which is generally sufficient to fit the most accurate measurements. It consists merely in viewing the cell as a leaky [3] condenser (i.e., K shunted by R_0) in series with the resistance $R_s+R_{e1}+R_{e2}$ of solution and electrodes to the whole of which the emf $E(t)$ is applied. The current $I(t)$ is then determined by the equation (where Q is the total charge on K)

$$\left(D_t+\frac{1}{R_0K}\right)Q=I \tag{4a}$$

$$E=\frac{Q}{K}+(R_s+R_e)I, \text{ where } R_e=R_{e1}+R_{e2} \tag{4b}$$

with the initial conditions $E=I=0$ when $t<t_1$, so that $Q=0$ when $t=t_1+0$.

A justification, or rather formulation, of this assumption for the general case is made in the following section. Later a case is treated which is capable of a more accurate solution and this serves to confirm the assumption that the second approximation thus outlined is generally sufficient. The elimination of Q between (4a) and (4b) gives

$$\left[D_t+\left(\frac{1}{R_0}+\frac{1}{R_s+R_e}\right)\frac{1}{K}\right]I=\left(D_t+\frac{1}{R_0K}\right)\frac{E}{R_s+R_e} \tag{5a}$$

so that

$$I(t)=\frac{1}{R_s+R_e}\left[E(t)-\frac{1}{R(_s+R_e)K}\int_{t_1}^{t}E(\tau)e^{-\left(\frac{1}{R_0}+\frac{1}{R_s+R_0}\right)\frac{t-\tau}{K}}d\tau\right] \text{ for } t>t_1 \tag{5b}$$

In case the emf is simply periodic, $E(t)$=real part of $E_0e^{i\omega t}$ a·d when transients have died out, I is $R_e\, I_0e^{i\omega t}$, where the complex ›nstant I_0 is given by

$$I_0=\frac{E_0}{R_s+R_e+\dfrac{R_0}{1+i\omega KR_0}}$$

II. OUTLINE OF METHOD IN GENERAL

The vector current density i is given at all points by $i=-\lambda\nabla V$, where $\lambda=\lambda_e$ in T_1 and T_2 and $\lambda=\lambda_s$ in T_s (6)

Since i is everywhere solenoidal, V must, at every instant, satisfy

$$\nabla^2V=0 \text{ in } T_1,\ T_2, \text{ and } T_s \tag{7}$$

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[2] Taylor, Bennett, and Acree J. Am. Chem. Soc. 38 2408, 2427 (1916).

[3] Taylor, Bennett, and Acree J. Am. Chem .Soc. 38 2408, 2415 (1916).

The boundary conditions at the small plane entrance-section S_{01} (fig. 1) and the small plane exit section S_{02} may be taken as

$$V=\frac{E(t)}{2}\text{(uniform) over } S_{01} \tag{8a}$$

$$V=\frac{-E(t)}{2}\text{(uniform) over } S_{02} \tag{8b}$$

In some cases, however, it is just as near the truth, and more convenient, to take instead of these, the boundary conditions

$i_{0n1}=\dfrac{I}{S_{01}}$ (uniform) over S_{01} and $V=\dfrac{E}{2}$ at some point on outer edge of S_{01} (8a′)

$i_{0n2}=\dfrac{I}{S_{02}}$ (uniform) over S_{02} and $V=\dfrac{-E}{2}$ at some point on outer edge of S'_{02} (8b′)

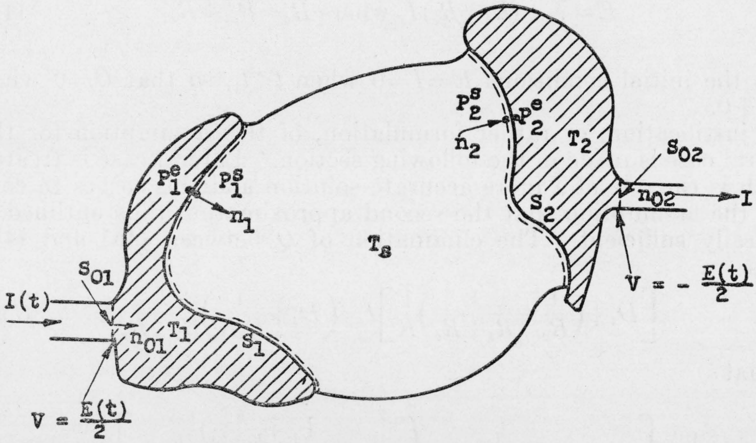


FIGURE 1.—*Electrolytic cell.*

Volumes T_1 and T_2 are electrodes and volume T_s, the solution.

The boundary conditions at the internal boundaries S_1 and S_2 are

$$i_{n_1} \text{ is continuous at } S_1 \tag{9a}$$

$$i_{n_2} \text{ is continuous at } S_2 \tag{9b}$$

and

$$(D_t+\gamma)(V_{e1}-V_{s1})=\frac{i_{n_1}}{k}=\frac{4\pi\Delta}{\epsilon}i_{n_1} \text{ at } S_1 \tag{10a}$$

$$(D_t+\gamma)(V_{s2}-V_{e2})=\frac{i_{n_2}}{k}=\frac{4\pi\Delta}{\epsilon}i_{n_2} \text{ at } S_2 \tag{10b}$$

and finally,

$$i_n=0 \text{ at all external boundaries of } T_1,\ T_2, \text{ and } T_s \tag{11}$$

The surface density of charge σ_1 on the element dS_1 of the condenser K_1 (at the point P_1^e of fig. 1) is

$$\sigma_1=k(V_{e_1}-V_{s1}) \tag{12a}$$

where V_{e1} is the potential at P_1^e in the electrode and V_{s1} at P_1^s in the solution. The conservation of electricity is represented by the equation

$$(D_t+\gamma)\sigma_1=i_{n_1} \tag{13a}$$

From the two latter equations, the boundary condition (10a) is derived. Equation 10b is similarly a consequence of

$$\sigma_2=k(V_{s2}-V_{e2}) \tag{12b}$$

and

$$(D+\gamma)\sigma_2=i_{n_2} \tag{13b}$$

The sense of the conditions (9) is that i_{n_1} at $P_1^e=i_{n_1}$ at $P_1^s=$ normal current density in the solution beyond the film which, of course, is considered to be of no thickness at all so far as we are concerned with the determination of the potential distribution outside it. If Q_1 and Q_2 are the total charges on condensers K_1 and K_2, then

$$Q_1\equiv\iint\limits_{S_1}\sigma_1dS_1 \text{ and } Q_2\equiv\iint\limits_{S_2}\sigma_2dS_2$$

and

$$\iint\limits_{S_1}i_{n_1}dS_1=\iint i_{n_2}dS_2=I$$

Let $\overline{V}_{e1}=\frac{1}{S_1}\iint\limits_{S_1}V_{e1}dS_1=$ average over S_1 of the electrode potential

and $\overline{V}_{s1}=$ the average over S_1 of the solution potential and similarly let $\overline{V}_{s2}$ and $\overline{V}_{e2}$ denote averages over S_2. Then by integration of (12) and (13) over the respective surface S_1 and S_2 we obtain, by use of (1)

$$Q_1=K_1(\overline{V}_{e1}-\overline{V}_{s1}) \tag{14a}$$

$$(D_t+\gamma)Q_1=I \tag{15a}$$

and

$$Q_2=K_2(\overline{V}_{s_2}-\overline{V}_{e_2}) \tag{14b}$$

$$(D_t+\gamma)Q_2=I \tag{15b}$$

From (15a) and (15b) we obtain $(D_t+\gamma)$ $(Q_1-Q_2)=0$. We assume that E (t) (and hence I (t), Q_1, and Q_2) is always finite, but that E and hence also I may be discontinuous at certain instants and that $E\equiv0$ if $-\infty<t<t_1$, so that $Q_1\equiv Q_2\equiv I\equiv0$ if $t<t_1$. But the last equation gives $Q_1-Q_2=Ce^{-\gamma t}$ when $t>t_1$, while (15a) and (15b) show that $Q_1(t_1+0)=Q_2(t_1+0)=0$ so that $C=0$, and we obtain

$Q_1=Q_2$ and $S_1(\overline{V}_{e1}-\overline{V}_{s1})=S_2(\overline{V}_{s2}-\overline{V}_{e2})$ at all times. (16)

Let $Q=Q_1=Q_2$. Then by (16) the two equations 15 are identical and may be written (by use of 3)

$\left(D_t+\frac{1}{R_oK}\right)Q=I$ (which is the equation 4a) (17)

Also, by dividing (14a) by K_1 and (14b) by K_2 and adding, we find, by use of (1)

$$\frac{Q}{K}=\overline{V}_{s1}-\overline{V}_{e1}+\overline{V}_{s2}-\overline{V}_{e2} \text{ which may be written}$$

$$E=\frac{Q}{K}+(\overline{V}_{s1}-\overline{V}_{s2})+\left(\frac{E}{2}-\overline{V}_{e1}\right)+\left(\overline{V}_{e2}+\frac{E}{2}\right) \tag{18}$$

The first approximation V^0 for the potential distribution is determined by placing $\Delta=0$ in the second members of the two boundary conditions (10). The initial condition used in deriving (16) then shows in similar fashion that the conditions (10), reduce merely to the requirement of continuity of V^0 at S_1 and S_2 so that $\frac{V^0}{I}$ is a function of x, y, z only throughout the compound conductor $T_1+T_s+T_2$, which represents the potential distribution when it carries unit steady current. When V^0 is found one may compute the total resistance R of this compound conductor so that R will be a known function of λ_s, λ_e and the linear dimensions entering into the description of this compound conductor. In case R comes out as the sum of two functions in one of which only the conductivity, λ_s, appears, and only λ_e in the other, the first could be called the solution resistance R_s, the second the resistance R_e of the two electrodes. In general, λ_e and λ_s will be so involved in the expression for R that in order to resolve it into $R=R_s+R_{e1}+R_{e2}$ we must adopt some arbitrary definitions of these resistances.

Since $\frac{E}{2}$ is the potential at some chosen point on the edge of the entrance surface S_{01} and $\frac{-E}{2}$ its value at some part on the edge of S_{02}, we define arbitrarily

$$R_s\equiv\frac{\overline{V}^0{}_{s1}-\overline{V}^0{}_{s2}}{I},\ R_{e1}\equiv\frac{\frac{E}{2}-\overline{V}^0{}_{e1}}{I},\ \text{and } R_{e2}\equiv\frac{\overline{V}^0{}_{e2}+\frac{E}{2}}{I} \tag{19a}$$

so that since $V^0{}_{e1}-V^0{}_{s1}=V^0{}_{s2}-V^0{}_{e2}=0$

$$\frac{E}{I}=R_s+R_{e1}+R_{e2}\equiv R \tag{19b}$$

When the first approximation V^0 for the potential has been found the use of V^0 for V in computing the mean potential drops in the second member of (18) gives

$$E=\frac{Q}{K}+(R_s+R_e)I, \text{ where } R_e=R_{e1}+R_{e2}, \tag{20}$$

which is equation 4b, so that (17) and (20) give the second approximation to the current, which is generally sufficient.

The conclusions so far are based merely upon the smallness of Δ. But the exact evaluation of the potential V^0 which is necessary to determine R is in general difficult. There is, however, another consideration equally important which results in a further simplification in the evaluation of V^0. The metallic conductivity λ_e is so large in comparison with that λ_s of the solution that the principal part of th potential V_s^0 in the solution (say $V_s^{0\prime}$), may be obtained by assuming that the contact surfaces S_1 and S_2 are equipotential surfaces. This assumption determines the principal part of R_s by (19a) (say R_s') and also the principal parts say $i_{n1}^{0\prime}$, $i_{n2}^{0\prime}$ of the normal components of current i_{n1}^0 and i_{n2}^0 at S_1 and S_2. The principal part of the potential in the electrodes is then determined by making $i_{n1}=i_{n1}^{0\prime}$ at S_1, etc., together with the remaining boundary conditions. Then using (19), the principal part of the electrode resistance R_e, say R_e' is found. Since R_e' is proportional to $\frac{1}{\lambda_e}$ and R_s' to $\frac{1}{\lambda_s}$ it is evident that R_s' is so small relatively that no further modification of it will be necessary. Neither will it be necessary to go further with the evaluation of R_s, for any further terms would be of the order of $\frac{1}{\lambda_e^2}$ as will be seen in section III.

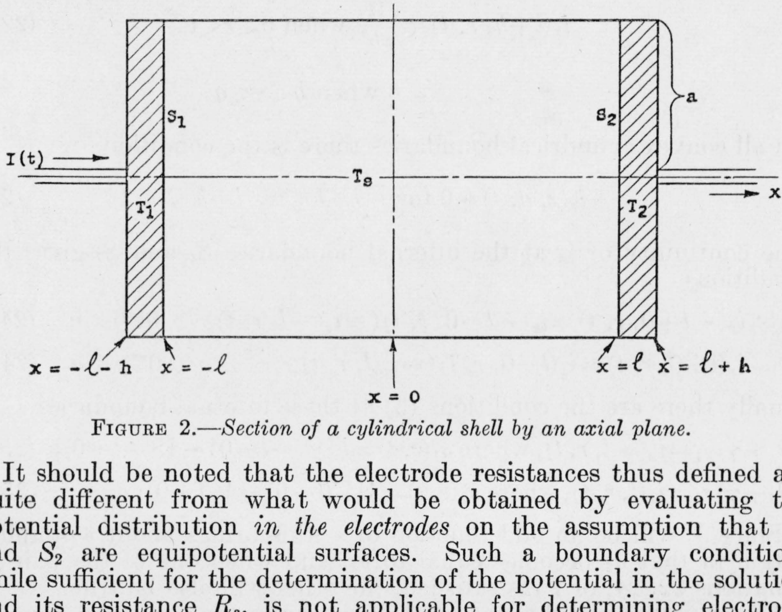


FIGURE 2.—*Section of a cylindrical shell by an axial plane.*

It should be noted that the electrode resistances thus defined are quite different from what would be obtained by evaluating the potential distribution *in the electrodes* on the assumption that S_1 and S_2 are equipotential surfaces. Such a boundary condition, while sufficient for the determination of the potential in the solution and its resistance R_s, is not applicable for determining electrode potentials. It is shown in section III that the electrode resistances obtained in this way are not even approximately correct.

III. CYLINDRICAL CELL WITH THIN DISK ELECTRODES—CURRENT IN AXIAL DIRECTION

Figure 2 represents a section by a plane through the x axis of a cylindrical cell which has as electrodes circular plates of radius a. The part $-l<x<l$ is filled with an electrolyte. The plates of thickness h, for $-l-h<x<-l$ and $l<x<l+h$ are circular disks of platinum very thin, say $h=0.02$ cm. The current $I(t)$ enters along a thin lead-in wire of radius b coaxial with the x axis, so that the potential V, either in the case of steady currents or variable with time, does

not depend upon the cylindrical coordinate θ, but only on the cylindrical coordinates x and r and the time t. As explained in equations 1 to 4

$$\left.\begin{aligned} K_1=K_2=\pi a^2 k \text{ so that } K=\frac{\pi a^2 k}{2}=\frac{\epsilon a^2}{8\Delta} \\ R_{01}=R_{02}=\frac{\Delta}{\pi a^2 \lambda_0} \text{ so that } R_0=\frac{2\Delta}{\pi a^2 \lambda_0} \end{aligned}\right\} \tag{21}$$

The boundary condition at the extreme left, where the current enters through the wire of small radius b (of the same order as h), will be taken

$$i_x(-l-h,\ r,\ t)=\frac{I(t)}{\pi b^2} \text{ when } 0\leqq r<b \tag{22a}$$

$$=0 \text{ when } b<r<a$$

At the extreme right

$$i_x(l+h,\ r,\ t)=\frac{I(t)}{\pi b^2} \text{ when } 0\leqq r<b \tag{22b}$$

$$=0 \text{ when } b<r<a$$

On all convex cylindrical boundaries there is the condition

$$i_r(x,\ a,\ t)=0 \text{ for } -l-h<x<l+h \tag{23}$$

The continuity of i_x at the internal boundaries S_1 and S_2 gives the conditions

$$i_x(-l+0,\ r,\ t)=i_x(-l-0,\ r,\ t)\,(\equiv i_x(-l,\ r,\ t)\text{----}0\leqq r<a \tag{24a}$$

$$i_x(l+0,\ r,\ t)=i_x(l-0,\ r,\ t)\,(\equiv i_x(l,\ r,\ t)\text{----------}0\leqq r<a \tag{24b}$$

Finally there are the conditions (5) at these internal boundaries

$$(D_t+\gamma)\sigma_1=i_x(-l,\ r,\ t), \text{ where } \sigma_1(r,\ t)=k[V(-l-0)-V(-l+0)] \tag{25a}$$

$$(D_t+\gamma)\sigma_2=i_x(l,\ r,\ t), \text{ where } \sigma_2(r,\ t)=k[V(l-0)-V(l+0)] \tag{25b}$$

Since V will be an odd function of x, this brings about a simplification in that σ_2 becomes equal to σ_1, and when one of the pair of equations 22, 24, or 25 is satisfied, the other will also be true.

For constructing the potential V we have the following type of particular solution of Laplace's equation

$$V=\left(A\sinh\frac{\alpha x}{a}+B\cosh\frac{\alpha x}{a}\right)J_0\left(\frac{\alpha r}{a}\right), \text{ where } J_0 \text{ is Bessel's function,}$$

the other solution of Bessel's equation being ruled out by the requirement of finiteness on the x-axis, where $r=0$.

Since $D_r J_0\left(\frac{\alpha r}{a}\right)=-\frac{\alpha}{a}J_1\left(\frac{\alpha r}{a}\right)$ the boundary condition (20) requires that α be a solution of the equation

$$J_1(\alpha)=0 \tag{26}$$

In what follows we use α_n to denote the nth positive root of this equation, of which there are an infinite number. We require the use of Dini's theorem for the development of a function of x, say $f(x)$, for the range $0 < x \leqq 1$, where $\int_0^1 f(x)dx$ converges absolutely

$$f(x)=c_0+\sum_{n=1}^{\infty} c_n J_0(\alpha_n x), \tag{27}$$

where

$$c_0=2\int_0^1 xf(x)dx \text{ and } c_n=\frac{2}{J_0^2(\alpha_n)}\int_0^1 xf(x)J_0(\alpha_n x)dx \text{ for } n>0$$

When the function has a finite discontinuity at $x=x_0$, the sum of this series is $\frac{1}{2}\left[f(x_0+0)+f(x_0-0)\right]$

As a special case of (27) we need the following development of the discontinuous function of r occurring in (22)

$$\frac{I(t)}{\pi a^2}\left\{1+\frac{2a}{b}\sum_{n=1}^{\infty}\frac{J_1\left(\frac{\alpha_n b}{a}\right)}{\alpha_n J^2{}_0(\alpha_n)}.J_0\left(\frac{\alpha_n r}{a}\right)\right\}=\frac{I(t)}{\pi b^2} \text{ ------ if } 0\leqq r<b$$

$$=o \text{ -------- if } b<r\leqq a$$

$$=\frac{I(t)}{2\pi b^2} \text{ ---- if } r=b \tag{28}$$

If $E(t)$ is the difference of potential applied to the cell, i. e., between the wire surfaces where they touch the electrodes, then

$$E(t)=V(-l-h,\ b,\ t)-V(l+h,\ b,\ t) \tag{29}$$

It is evident that the potential in the three regions T_1, T_3, and T_2, must then have the following form

$$V(x,\ r,\ t)=\frac{1}{2}E(t)-I(t)\left\{\frac{x+l+h}{\pi a^2\lambda_e}+\right.$$

$$\left.\frac{2}{\pi b\lambda_e}\sum_{n=1}^{\infty}\frac{J_1\left(\frac{\alpha_n b}{a}\right)\left[\cosh\left(\frac{\alpha_n h}{a}\right)J_0\left(\frac{\alpha_n b}{a}\right)-\cosh\frac{\alpha_n}{a}(x+l)J_0\left(\frac{\alpha_n r}{a}\right)\right]}{\alpha_n^2\sinh\left(\frac{\alpha_n h}{a}\right)J_0^2(\alpha_n)}\right\} \tag{30}$$

$$-\frac{1}{\pi a\lambda_e}\sum_{n=1}^{\infty}\frac{I_n(t)\left[\cosh\frac{\alpha_n}{a}(x+l+h)J_0\left(\frac{\alpha_n r}{a}\right)-J_0\left(\frac{\alpha_n b}{a}\right)\right]}{\alpha_n\sinh\left(\frac{\alpha_n h}{a}\right)}$$

when $-l-h<x<-l$

$$=-\frac{xI(t)}{\pi a^2\lambda_s}-\frac{1}{\pi a\lambda_s}\sum_{n=1}^{\infty}\frac{I_n(t)\sinh\left(\frac{\alpha_n x}{a}\right)}{\alpha_n\cosh\left(\frac{\alpha_n l}{a}\right)}J_0\left(\frac{\alpha_n r}{a}\right)$$

when $-l<x<l$

$$=-\frac{1}{2}E(t)+I(t)\left\{\frac{l+h-x}{\pi a^2\lambda_e}+\right.$$

$$\left.\frac{2}{\pi b\lambda_e}\sum_{n=1}^{\infty}\frac{J_1\left(\frac{\alpha_n b}{a}\right)\left[\cosh\left(\frac{\alpha_n h}{a}\right)J_0\left(\frac{\alpha_n b}{a}\right)-\cosh\frac{\alpha_n}{a}(x-l)J_0\left(\frac{\alpha_n r}{a}\right)\right]}{\alpha_n^2\sinh\left(\frac{\alpha_n h}{a}\right)J_0^2(\alpha_n)}\right\}$$

$$+\frac{1}{\pi a\lambda_e}\sum_{n=1}^{\infty}\frac{I_n(t)\left[\cosh\frac{\alpha_n}{a}(x-l-h)J_0\left(\frac{\alpha_n r}{a}\right)-J_0\left(\frac{\alpha_n b}{a}\right)\right]}{\alpha_n\sinh\left(\frac{\alpha_n h}{a}\right)}$$

when $l<x<l+h$

From this, the x component of current density is

$$i_x(x,r,t)=\frac{I(t)}{\pi a^2}\left\{1-\frac{2a}{b}\sum_{n=1}^{\infty}\frac{\sinh\frac{\alpha_n}{a}(x+l)J_1\left(\frac{\alpha_n b}{a}\right)J_0\left(\frac{\alpha_n r}{a}\right)}{\alpha_n\sinh\left(\frac{\alpha_n h}{a}\right)\cdot J^2{}_0(\alpha_n)}\right\} \tag{31}$$

$$+\frac{1}{\pi a^2}\sum_{n=1}^{\infty}\frac{I_n(t)\sinh\frac{\alpha_n}{a}(x+l+h)}{\sinh\left(\frac{\alpha_n h}{a}\right)}J_0\left(\frac{\alpha_n r}{a}\right)\text{ when } -l-h<x<-l$$

$$=\frac{I(t)}{\pi a^2}+\frac{1}{\pi a^2}\sum_{n=1}^{\infty}\frac{I_n(t)\cosh\left(\frac{\alpha_n x}{a}\right)}{\cosh\left(\frac{\alpha_n l}{a}\right)}\cdot J_0\left(\frac{\alpha_n r}{a}\right)\text{ when } -l<x<l$$

$$=\frac{I(t)}{\pi a^2}\left\{1+\frac{2a}{b}\sum_{n=1}^{\infty}\frac{\sinh\frac{\alpha_n}{a}(x-l)J_1\left(\frac{\alpha_n b}{a}\right)J_0\left(\frac{\alpha_n r}{a}\right)}{\alpha_n\sinh\left(\frac{\alpha_n h}{a}\right)J_0^2(\alpha_n)}\right\}$$

$$-\frac{1}{\pi a^2}\sum_{n=1}^{\infty}\frac{I_n(t)\sinh\frac{\alpha_n}{a}(x-l-h)J_0\left(\frac{\alpha_n r}{a}\right)}{\sinh\left(\frac{\alpha_n h}{a}\right)},\text{ when } l<x<l+h.$$

Obviously (30) is a solution of (7) satisfying the condition (23) by reason of (26) and also the conditions (24). From (31) we find

$$i_x(l,\,r,\,t)=i_x(-l,\,r,\,t)=\frac{I(t)}{\pi a^2}+\frac{1}{\pi a^2}\sum_1^\infty I_n(t)J_0\left(\frac{\alpha_n r}{a}\right). \tag{32}$$

Also, the equation 31 shows by reference to (28) that the conditions (22) are also satisfied. Hence, all but the last conditions (25) are satisfied without placing any restrictions upon the coefficients $I_n(t)$. The first approximation V^0 will only differ from the more precise potential V by the manner in which we choose these coefficients I_n.

We introduce the abbreviations for $n=1,\,2,\,3,$ — — — ∞

$$r_n\equiv\frac{2}{\pi a\lambda_e}\frac{J_0\left(\frac{\alpha_n b}{a}\right)}{\alpha_n\ \sinh\left(\frac{\alpha_n h}{a}\right)} \tag{33a}$$

$$\rho_n\equiv\frac{4}{\pi b\lambda_e}\frac{J_1\left(\frac{\alpha_n b}{a}\right)}{\alpha_n^2 J_o^2(\alpha_n)\ \sinh\left(\frac{\alpha_n h}{a}\right)} \tag{33b}$$

$$\frac{1}{\beta_n K}\equiv\frac{2}{\pi a\lambda_s\alpha_n}\left[\tanh\left(\frac{\alpha_n l}{a}\right)+\frac{\lambda_s}{\lambda_e}\coth\left(\frac{\alpha_n h}{a}\right)\right] \tag{33c}$$

$$R_e'\equiv\frac{2h}{\pi a^2\lambda_e}+\sum_{n=1}^\infty\rho_n\cosh\left(\frac{\alpha_n h}{a}\right)J_0\left(\frac{\alpha_n b}{a}\right) \tag{33d}$$

Then from (30) we find

$$V_{e1}\equiv V(-l-0,\,r,\,t)=\frac{E}{2}-\frac{R_e'}{2}I+\frac{1}{2}\sum_1^\infty r_nI_n+\frac{1}{2}\sum_1^\infty J_0\left(\frac{\alpha_n r}{a}\right)\left[\rho_nI-\frac{2I_n\coth\left(\frac{\alpha_n h}{a}\right)}{\pi a\lambda_e\alpha_n}\right] \tag{34a}$$

$$V_{s1}=V(-l+0,\,r,\,t)=\frac{l}{\pi a^2\lambda_s}I+\frac{1}{\pi a\lambda_s}\sum_1^\infty\frac{I_nJ_0\left(\frac{\alpha_n r}{a}\right)\tanh\frac{\alpha_n l}{a}}{\alpha_n} \tag{34b}$$

so that

$$V_{e1}-V_{s1}=\frac{E}{2}-\left(\frac{l}{\pi a^2\lambda_s}+\frac{R_e'}{2}\right)I+\frac{1}{2}\sum_1^\infty r_nI_n+\frac{1}{2}\sum_1^\infty J_0\left(\frac{\alpha_n r}{a}\right)\left[\rho_nI-\frac{I_n}{\beta_nK}\right] \tag{34c}$$

and

$$V_{s2}=-V_{s1}\text{ and }V_{e2}=-V_{e1}$$

so that

$$\overline{V}_{s1}-\overline{V}_{s2}=\frac{2l}{\pi a^2\lambda_s}I \tag{35}$$

and

$$\frac{E}{2}-\overline{V}_{e1}=\overline{V}_{e2}+\frac{E}{2}=\frac{R'_e}{2}I-\frac{1}{2}\sum_1^\infty r_nI_n \tag{36}$$

Now the first approximation V^0 to the potential distribution is that determined by replacing the boundary conditions (25) by the mere requirement of continuity of V^0 at the internal boundaries S_1 and S_2. This, by (34c) would require that we choose the coefficient I_n as

$$I_n=I_n^0=k\beta_n\rho_nI^0 \tag{37}$$

which, being used in (36), give

$$\frac{\frac{E}{2}-V^0_{e1}}{I}=R_{e1}=R_{e2}=\frac{1}{2}R'_e-\frac{1}{2}K\sum_1^\infty r_n\rho_n\beta_n$$

so that the total electrode resistance is

$$R_e=R_e'-K\sum_1^\infty r_n\rho_n\beta_n=\frac{2h}{\pi a^2\lambda_e}+\sum_1^\infty \rho_nJ_0\left(\frac{\alpha_nb}{a}\right)\cdot$$

$$\left\{\cosh\left(\frac{\alpha_nh}{a}\right)-\frac{\lambda_s}{\lambda_e\sinh\left(\frac{\alpha_nh}{a}\right)\left[\tanh\left(\frac{\alpha_nl}{a}\right)+\frac{\lambda_s}{\lambda_e}\coth\left(\frac{\alpha_nh}{a}\right)\right]}\right\} \tag{38}$$

$$=\frac{2h}{\pi a^2\lambda_e}+\frac{4}{\pi b\lambda_e}\sum_1^\infty\frac{J_0\left(\frac{\alpha_nb}{a}\right)J_1\left(\frac{\alpha_nb}{a}\right)}{\alpha_n^2J_0^2(\alpha_n)\sinh\left(\frac{\alpha_nh}{a}\right)}\cdot$$

$$\left\{\cosh\frac{\alpha_nh}{a}-\frac{\lambda_s}{\lambda_e\sinh\left(\frac{\alpha_nh}{a}\right)\left[\tanh\left(\frac{\alpha_nl}{a}\right)+\frac{\lambda_s}{\lambda_e}\coth\left(\frac{\alpha_nh}{a}\right)\right]}\right\}$$

On neglecting terms in $\frac{1}{\lambda^2_e}$ this becomes

$$R_e=\frac{2h}{\pi a^2\lambda_e}+\frac{4}{\pi b\lambda_e}\sum_1^\infty\frac{J_0\left(\frac{\alpha_nb}{a}\right)J_1\left(\frac{\alpha_nb}{a}\right)}{\alpha_n^2J_0^2(\alpha_n)\sinh\left(\frac{\alpha_nh}{a}\right)}$$

$$\left\{\cosh\left(\frac{\alpha_nh}{a}\right)-\frac{\lambda_s\coth\left(\frac{\alpha_nl}{a}\right)}{\lambda_e\sinh\left(\frac{\alpha_nh}{a}\right)}\right\} \tag{38'}$$

On neglecting terms in $\frac{1}{\lambda^2_e}$ this becomes

$$R_e = R_e' = \frac{2h}{\pi a^2 \lambda_e} + \frac{4}{\pi b \lambda_e} \sum_1^\infty \frac{J_0\left(\frac{\alpha_n b}{a}\right) J_1\left(\frac{\alpha_n b}{a}\right)}{\alpha_n^2 J_0^2(\alpha_n) \tanh\left(\frac{\alpha_n h}{a}\right)} \tag{38''}$$

which does not involve the conductivity λ_s of the solution, and is a function of the linear dimensions h, a, and b of the electrodes only.

Equation 35 gives $R_s = \frac{2l}{\pi a^2 \lambda_s}$ = resistance of the solution. (39)

If what we have called the second approximation to the current is sufficient, then (38″) and (39) give the total resistance $R = R_s + R'_e$ to be used in equation 4b. Equations 38 and 39 give the exact values of R_e and R_s defined by (19a) for they are derived from an exact evaluation of V^0. Since, however, (38″) differs from (39) by terms of the order $\frac{1}{\lambda_e}$, the results here obtained confirm the statements made after equation 20 as to the approximate method of evaluating R'_e.

To illustrate the general mode of the approximate evaluation of V^0, we note that the approximate potential distribution in the solution, based on the assumption that the contact surfaces S_1 and S_2 are equipotential surfaces, is given by taking $I_n = 0$ as shown by (34b). Whatever value we take for I_n, the solution resistance is given by (39). The evaluation of the potential distribution throughout the electrodes, however, is made by assuming that the normal current there is continuous with that corresponding to this approximate potential in the solution, so that with $I_n = 0$, the surfaces S_1 and S_2 are not equipotential, as shown by (34a). The value $I_n = 0$ then leads to $R_e = R'_e$ by (36), as predicted in section II.

It is worth while to illustrate at this point the misconception that might arise from calling the resistance R_e, as defined in (19), the electrode resistance. That $\frac{R'_e}{2}$ is not the resistance of one electrode when the contact surface, say S_1, is equipotential is evident from the fact that to make S'_1 equipotential (on the electrode side) we must, by equation 34a, take $I_n = I \frac{\pi a \lambda_e}{2} \rho_n \alpha_n \tanh\left(\frac{\alpha_n h}{a}\right)$ in which case we find

$$\frac{E}{2} - \overline{V}_{e1} = \frac{I}{2}\left[R'_e - \sum_1^\infty \frac{\rho_n J_0\left(\frac{\alpha_n h}{a}\right)}{\cosh\left(\frac{\alpha_n h}{a}\right)} \right]$$

which would give for the resistance of the electrodes, when S_1 and S_2 are equipotential surfaces

$$\frac{2h}{\pi a^2 \lambda_e} + \sum_1^\infty \rho_n J_0\left(\frac{\alpha_n b}{a}\right) \left[\cosh\left(\frac{\alpha_n b}{a}\right) - \frac{1}{\cosh\left(\frac{\alpha_n h}{a}\right)} \right]$$

which is not even an approximation to the value R'_e when $\frac{b}{a}$ is small.

The present problem admits of an exact formulation of the current $I(t)$ produced by an arbitrary emf E from which it is easy to derive a third approximation. This enables one to estimate the degree of validity of the second approximation.

By (25) and (34c) we find

$$\frac{\pi a^2\sigma(r,\,t)}{K} = E - (R_s + R'_e)I + \sum_1^{\infty} r_n I_n + \sum_1^{\infty} J_0\left(\frac{\alpha_n r}{a}\right)\left[\rho_n I - \frac{I_n}{\beta_n K}\right] \tag{40}$$

Since the total charge $Q = 2\int_0^a r\sigma dr$ this gives

$$E = \frac{Q}{K} + (R_s + R'_e)I - \sum_1^{\infty} r_n I_n \tag{41}$$

so that equation 40 may be written

$$\pi a^2\sigma(r,\,t) = Q + K\sum_1^{\infty} J_0\left(\frac{\alpha_n r}{a}\right)\left[\rho_n I - \frac{I_n}{\beta_n K}\right] \tag{42}$$

The boundary equation 25, which must be satisfied for all values of r in the exact solution, may be written by reference to (32)

$$(D_t + \gamma)\pi a^2\sigma(r,\,t) = I + \sum_1^{\infty} I_n J_0\left(\frac{\alpha_n r}{a}\right) \tag{43}$$

Introducing into this the expression (42) for σ gives on equating corresponding coefficients of $J\left(\frac{\alpha_n r}{a}\right)$, the relations

$$(D_t + \gamma)Q = I \text{ (which is merely equation 4a)} \tag{44}$$

and

$$(D_t + \gamma + \beta_n)\, I_n = K\rho_n\beta_n(D_t + \gamma)\, I \text{ for } n = 1, 2, 3, \text{ ----------} \infty \tag{45}$$

The integral of (44) is

$$Q(t) = \int_{t_1}^{t} I(\tau)e^{-\gamma(t-\tau)}d\tau \text{ for } t > t_1 \tag{46}$$

and the integral of (45) is

$$I_n(t) = K\beta_n\rho_n I(t) - K\beta_n^{\,2}\rho_n\int_{t_1}^{t} I(\tau)e^{-(\gamma+\beta_n)(t-\tau)}d\tau \text{ for } t > t_1 \tag{47}$$

With these values of Q and I_n the equation 41 becomes the following integral equation of Volterra's type to determine I (t) for $t > t_1$.

$$(R_s + R_e)e^{\gamma t}I(t) + \int_{t_1}^{t} e^{\gamma\tau}E(\tau).N(t-\tau)d\tau = e^{\gamma t}E(t) \tag{48}$$

where the nucleus N is defined by a convergent series for $\tau > 0$

$$N(\tau) = \sum_{n=0}^{\infty} a_n e^{-\beta_n \tau} \tag{49}$$

where

$$a_0 = \frac{1}{K},\ a_n = K r_n \rho_n \beta_n^2,\ \beta_0 = 0, \text{ and for } n > 0\ \beta_n \text{ is defined by (35c)} \tag{50}$$

If $F(\tau)$ denotes the resolving nucleus of the given nucleus N, then the unique solution of (48) is

$$\frac{e^{\gamma_1 t} E(t)}{R_s + R_e} + \int_{t_1}^{t} e^{\gamma_1 \tau} E(\tau) F(t-\tau) d\tau = e^{\gamma_1 t} I(t) \tag{51}$$

Considering I given and E unknown, this is an integral equation of the same type as (48) with a nucleus F of the same type of function as N so that reciprocally (48) is the unique solution of (51) and N the resolving nucleus of F. The particular nature of the coefficients a_n is not essential in finding F. To show this we may construct, with the coefficients a_n, a function ψ of the complex variable β by

$$\psi(\beta) \equiv R_s + R_e - \sum_{n=0}^{\infty} \frac{a_n}{\beta - \beta_n} \text{ whose poles are at } \beta = \beta_n \tag{52}$$

Let β'_s for $s = 0, 1, 2,$ ——— ∞ denote the characteristic values which are solutions of the equation

$$\psi(\beta) = 0 \tag{53}$$

Then

$$\frac{1}{2\pi i} \int \frac{d\beta'}{(\beta' - \beta)\psi(\beta')} = \frac{1}{R_s + R_e} = \frac{1}{\psi(\infty)} \tag{54}$$

where the integral is taken around a circle in the complex β' plane with center at the origin and infinite radius. Shrinking this path down to separate contours around the individual poles of the integrand which are at $\beta' = \beta$ and $\beta' = \beta'_s$ where $s = 0, 1, 2,$ ——— ∞, gives after evaluating each contour integral by Cauchy's theorem

$$\frac{1}{\psi(\beta)} = \frac{1}{R_s + R_e} - \sum_{n=0}^{\infty} \frac{A_n}{\beta - \beta'_n} \tag{55}$$

where

$$A_n = -\frac{1}{\psi'(\beta'_n)} \text{ for } n = 0, 1, 2, \text{———} \left(\text{and } \psi'(\beta) \equiv \frac{d\psi(\beta)}{d\beta}\right) \tag{56}$$

Equation 55 is in a certain respect reciprocal to (52). If β takes on one of the values β_m ($m = 0, 1, 2,$ ———), which is a pole of ψ (β) the first member of (55) vanishes, giving the relations

$$0 = \frac{1}{R_s + R_e} - \sum_{u=0}^{\infty} \frac{A_n}{\beta_m - \beta'_n} \text{ for } m = 0, 1, 2, 3 \text{———} \infty \tag{57}$$

It is easy to see that the resolving nucleus F is given by

$$F(\tau)=\sum_{n=0}^{\infty}A_n e^{-\beta'_n \tau}$$

which is similar to (49) (58)

For if this series be substituted in the integral equation 48 with series (49) for N, the equation becomes

$$\int_{t_1}^{t} e^{\gamma\tau}E(\tau)d\tau\sum_{m=0}^{\infty}\left\{e^{-\beta'_m(t-\tau)}A_m\left[R_s+R_e=\sum_{n=0}^{\infty}\frac{a_n}{\beta'_m-\beta_n}\right]\right.$$

$$\left.+e^{-\beta_m(t-\tau)}a_m\left[\frac{1}{R_s+R_e}-\sum_{n=0}^{\infty}\frac{A_n}{\beta_m-\beta'_n}\right]\right\}=0$$

that is, by reference to (52) and (55)

$$\int_{t_1}^{t} e^{\gamma\tau}.E(\tau)\,d\tau\sum_{m=0}^{\infty}\left\{e^{-\beta'_m(t-\tau)}A_m\psi(\beta'_m)+e^{-\beta_m(t-\tau)}\frac{a_m}{\psi(\beta_n)}\right\}=0$$

Since β'_m is a zero of ψ (β') and β_m a pole, this equation is satisfied for all values of t.

Hence the solution of the integral equation (48) is

$$I(t)=\frac{E(t)}{R_s+R_e}-\int_{t_1}^{t}d\tau E(\tau)e^{-\gamma(t-\tau)}\sum_{n=0}^{\infty}\frac{e^{-\beta'_n(t-\tau)}}{\psi'(\beta'_n)}\text{ for }t>t_1 \tag{59}$$

where $E(t)=0$ if $t<t_1$

If $E(t)=R_eE_0e^{i\omega t}$ for $t>t_1$ this becomes, by reference to (55)

$$I(t)=R_e\left[\frac{E_0e^{i\omega t}}{\psi(-\gamma-i\omega)}\right]+R_eE_0\sum_{s=0}^{\infty}\frac{e^{-(\gamma+\ '_n)(t-t_1)}e^{i\omega t_1}}{(\beta'_n+\gamma+i\omega)\psi'(\beta'_n)}\text{ for }t>t_1 \tag{59'}$$

so that the final periodic current is $\mathrm{I}(t)=R_eI_0e^{i\omega t}$, where

$$I_0=\frac{E_0}{\psi(-\gamma-i\omega)} \tag{59''}$$

To compute the roots β'_n of (53) we note that since λ_s is small ($\lambda_s \overline{\gtrless}.04$), while for platinum $\lambda_e=.8(10)^5$ the ratio $\frac{\lambda_s}{\lambda_e}\overline{\gtrless}5(10)^{-7}$ so that (33c) reduces practically to

$$\beta_nK=\frac{\pi a\lambda_s\alpha_n}{2}\coth\left(\frac{\alpha_n l}{a}\right) \tag{60}$$

for $n>0$, so that the coefficients a_n defined by (50) are, when $\frac{h}{a}$ is small,

$$a_n=\frac{2a}{Kb}\left(\frac{a\lambda_s}{h\lambda_e}\right)^2\cdot\frac{J_0\left(\frac{\alpha_nb}{a}\right)J_1\left(\frac{\alpha_nb}{a}\right)\coth^2\left(\frac{\alpha_nl}{a}\right)}{\alpha_n^3J_0^2(\alpha_n)}\text{ for }n>0 \tag{61}$$

The a_n's are exceedingly small $\left(\text{except } a_0=\frac{1}{K}\right)$ since if $\frac{a}{h}=100$, $\left(\frac{a\lambda_s}{h\lambda_e}\right)^2=2.5(10)^{-9}$. Hence writing (52) in the form

$$\psi(\beta)=(R_s+R_e)-\frac{1}{K\beta}-\sum_{n=1}^{\infty}\frac{a_n}{\beta-\beta_n} \tag{62}$$

it is evident that the series is negligibly small except when β is very near one of the values say β_s in which case the sth term is the only term of the series worth retaining. The nth zero β'_n of $\psi(\beta)$ is very close to the nth pole β_n so that β'_n is very approximately given by $(R_s+R_e)-\frac{1}{K\beta'_n}-\frac{a_n}{\beta'_n-\beta_n}=0$ so that

$$\beta'_n=\beta_n+\frac{a_n}{R_s+R_e} \text{ and } \frac{1}{\psi'(\beta'_n)}=\frac{a_n}{(R_s+R_e)^2}=-A_n \text{ for } n=0,1,2,3\ldots\infty \tag{63}$$

so that the resolving nucleus is

$$F(\tau)=\sum_0^{\infty}A_n e^{-\beta'_n\tau}=-\sum_0^{\infty}\frac{e^{-\beta'_n\tau}}{\psi'(\beta'_n)}=-\frac{1}{(R_s+R_e)^2}\sum_0^{\infty}a_n e^{-\beta'_n\tau} \tag{64}$$

or

$$F(\tau)=-\frac{1}{(R_s+R_e)^2K}\left\{e^{-\frac{\tau}{(R_s+R_e)K}}+K\sum_1^{\infty}a_n e^{-\beta_n\tau}\right\}, \text{ where } \beta_n \text{ is} \tag{64'}$$

given by (60) and a_n by (61) for $n>0$.

When $\frac{b}{a}$ is small, equation 61 may be written

$$a_n=\frac{\pi}{2K}\left(\frac{a\lambda_s}{h\lambda_e}\right)^2\frac{\coth\left(\frac{\alpha_n l}{a}\right)}{\alpha_n} \text{ since } \frac{\pi\alpha_n}{2}J_0^2(\alpha_n)=1 \text{ very approximately} \tag{61''}$$

Hence the equation 59 may be written

$$I(t)=\frac{1}{R_s+R_e}\left\{E(t)-\frac{1}{(R_s+R_e)K}\int_{t_1}^{t}d\tau E(\tau)e^{-\tau(t-\tau)}\right.$$
$$\left.\left[e^{-\frac{(t-\tau)}{(R_s+R_e)K}}+\left(\frac{a\lambda_s}{h\lambda_e}\right)^2\phi(t-\tau)\right]\right\} \tag{65}$$

where

$$\phi(\tau)=\frac{\pi}{2}\sum_{n=1}^{\infty}\frac{\coth^2\left(\frac{\alpha_n l}{a}\right)}{\alpha_n}e^{-\frac{\tau}{R_sK}\left(\frac{\alpha_n l}{a}\right)}\coth\left(\frac{\alpha_n l}{a}\right) \tag{65a}$$

When l is of the same order of magnitude as a or larger, $\coth\frac{\alpha_n l}{a}=1$ very approximately so that

$$\phi(\tau)=\frac{\pi}{2}\sum_{n=1}^{\infty}\frac{e^{-\frac{\tau l\alpha_n}{aR_sK}}}{\alpha_n} \text{ for } \tau>0 \tag{65b}$$

Since, however, $\alpha_n=(4n+1)\dfrac{\pi}{4}$ approximately, this may be written

$$\phi(\tau)=2\sum_{n=1}^{\infty}\frac{e^{-(4n+1)\left(\frac{\pi l\tau}{4aR_sK}\right)}}{4n+1}=\log\sqrt{\frac{1+z}{1-z}}+\tan^{-1}z-2z \tag{65c}$$

where $z=e^{-\frac{\pi l\tau}{4aR_sK}}$.

This approximation to ϕ (τ) is sufficient for those cases where it is not entirely negligible. When, however, $\left(\dfrac{a\lambda s}{b\lambda_e}\right)^2\leqq 3(10^{-9})$ as in the example quoted, the terms in ϕ $(t-\tau)$ in (65) are negligible and it reduces to equation 5b obtained at first. This may be taken as confirmation of the statement that the second approximation to the current is in general sufficient. It remains to reduce the expression (38″) to a more convenient form for computation. If we assume that $\dfrac{h}{a}$ is small, without any assumption as to b except that $0<b<a$ we may neglect the first term $\dfrac{2h}{\pi a^2\lambda_e}$ in (38″) and in the series replace $\tanh\left(\dfrac{\alpha_n h)}{a}\right)$ by $\dfrac{\alpha_n h}{a}$ which gives

$$R_e'=\frac{2}{\pi h\lambda_e}\cdot\left(\frac{2a}{b}\right)\sum_{1}^{\infty}\frac{J_0\left(\frac{\alpha_n b}{a}\right)J_1\left(\frac{\alpha_n b}{a}\right)}{\alpha_n^3J_0^2\alpha_n} \tag{65d}$$

Now by (28) when $\dfrac{r}{a}=\dfrac{b}{a}=x$ we find

$$\frac{2}{x}\sum_{1}^{\infty}\frac{J_0(\alpha_n x)\,J_1(\alpha_n x)}{\alpha_n J_0^2(\alpha_n)}=\frac{1}{2x^2}-1 \text{ ———— if } 0<x<1 \tag{66}$$

Multiplying this by $\dfrac{x}{2}\,dx$ and integrating from x to 1 gives

$$\sum_{1}^{\infty}\frac{J_0^2(\alpha_n x)}{\alpha_n^2J_0^2(n)}-\sum_{1}^{\infty}\frac{1}{\alpha_n^2}=-\tfrac{1}{2}(1-x^2+\log x) \text{ ——— if } O<x\leqq l$$

Since $\sum_{1}^{\infty}\dfrac{1}{\alpha^2 n}=\dfrac{1}{8}$ this may be written

$$\sum_{1}^{\infty}\frac{J_0^2(\alpha_n x)}{\alpha_n^2J_0^2(\alpha_n)}=\frac{1}{2}\left[\log\frac{1}{x}-\frac{3}{4}+x^2\right] \text{---- if } 0<x\eqqgtr 1 \tag{67}$$

Multiplying this by xdx and integrating from zero to x gives

$$\sum_1^\infty\left(\frac{J_0^2(\alpha_n x)+J_1^2(\alpha_n x)}{\alpha_n^2 J_0^2(\alpha_n)}\right)=\frac{1}{2}\left[\log\frac{1}{x}-\frac{1}{4}+\frac{x^2}{2}\right] \text{---- if } 0<x\overline{\gtrless}1 \quad (68)$$

whence, by (67)

$$\sum_1^\infty\frac{J_1^2(\alpha_n x)}{\alpha_n^2 J_0^2(\alpha_n)}=\frac{1}{4}(1-x^2) \text{ -------- if } 0<x\overline{\gtrless}1 \quad (69)$$

Multiplying this by xdx and integrating from 0 to x gives

$$\sum_1^\infty\frac{J_0^2(\alpha_n x)+J_1^2(\alpha_n x)}{\alpha_n^2 J_0^2(\alpha_n)}-\frac{2}{x}\sum_1^\infty\frac{J_0(\alpha_n x)J_1(\alpha_n x)}{\alpha_n^3 J_0^2(\alpha_n)}=\frac{1}{4}\left(1-\frac{x^2}{2}\right) \text{ if } 0<x\overline{\gtrless}1 \quad (70)$$

By use of (68) this becomes

$$\frac{2}{x}\sum_1^\infty\frac{J_0(\alpha_n x)J_1(\alpha_n x)}{\alpha_n^3 J_0^2(\alpha_n)}=\frac{1}{2}\left[\log\frac{1}{x}-\frac{3}{4}(1-x^2)\right] \text{ if } 0<x\overline{\gtrless}1 \quad (71)$$

Placing $x=\frac{b}{a}$ in this gives

$$\frac{2a}{b}\sum_1^\infty\frac{J_0\left(\frac{\alpha_n b}{a}\right)J_1\left(\frac{\alpha_n b}{a}\right)}{\alpha_n^3 J_0^2(\alpha_n)}=\frac{1}{2}\left[\log\frac{a}{b}-\frac{3}{4}\left(1-\frac{b^2}{a^2}\right)\right] \quad (72)$$

so that (65^d) becomes finally

$$R_e'=\frac{1}{\pi h\lambda_e}\left\{\log\frac{a}{b}-\frac{3}{4}\left(1-\frac{b^2}{a^2}\right)\right\}, \quad (73)$$

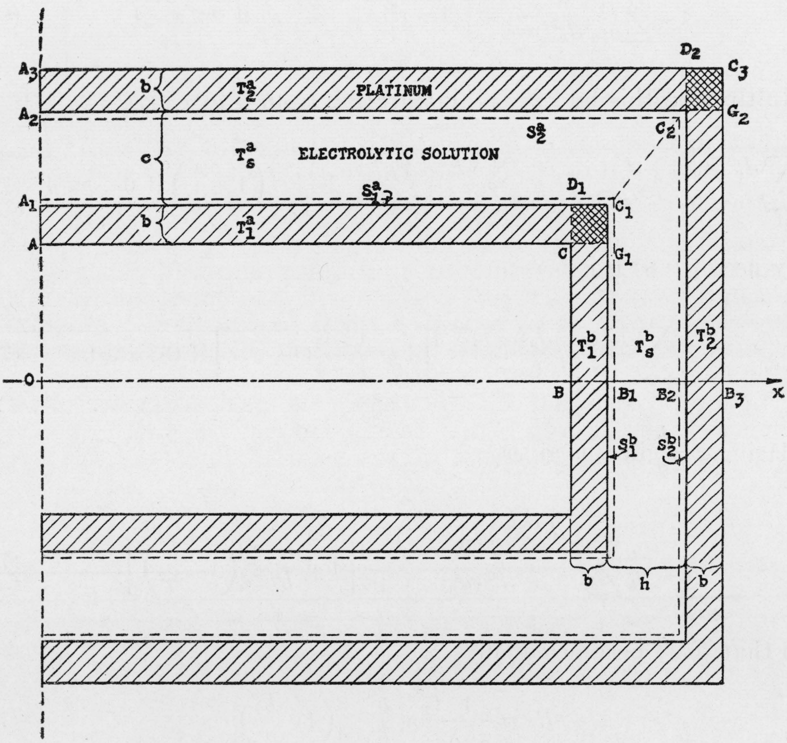
which is the principal part of R_e' when $\frac{h}{a}$ is small, and $0<b\overline{\gtrless}a$

IV. A CELL EACH OF WHOSE ELECTRODES IS A THIN CYLINDRICAL SHELL CLOSED BY A THIN DISK

In figure 3 is shown a section (by a plane through the axis) of a symmetrical cell. The cylindrical shell $T^a{}_s$ and the circular disk $T^b{}_s$ are filled with solution, these regions being fairly thin, of the order of 0.1 cm. The current enters the electrode T_1 through the face of the cylindrical shell $T^a{}_1$ at $x=0$ (trace $\overline{AA_1}$) where the potential has the uniform value $\frac{E(t)}{2}$. It leaves at the face of the shell $T^a{}_2$ at $x=0$

(trace A_2A_3), where the potential has the uniform value $-\frac{E(t)}{2}$. The total capacity K of both films is given by

$$\frac{1}{K}=\frac{1}{K^a{}_1+K^b{}_1}+\frac{1}{K^a{}_2+K^b{}_2},\ \text{where}\ \left\{\begin{array}{l} K^a{}_1=\frac{\epsilon a_1 l_1}{2\Delta},\ K^b{}_1=\frac{\epsilon a^2{}_1}{\Delta} \\ K^a{}_2=\frac{\epsilon a_2 l_2}{\Delta},\ K^b{}_2=\frac{\epsilon a^2{}_2}{\Delta} \end{array}\right\} \tag{74a}$$



SECTION 3.—*Section of concentric cylinders by a plane through the axis.*

$\overline{OA}=a$	a_1 is of order of 1 cm	$\overline{OB}=l$
$0A_1=a_1=a+b$	l_1 is of order of 5 cm	$\overline{OB}_1=l_1=l+b$
$0A_2=a_2=a_1+c$	c and b of order 0.1 cm	$\overline{OB}_2=l_2=l_1+h$
$0A_3=a_3=a_2+b$	b of order 0.01 cm	$\overline{OB}_3=l_3=l_2+b$

The resistance R_0, which shunts the condenser K, is given by

$$\left\{\begin{array}{l} R_0=R_{01}+R_{02},\ \text{where}\ \frac{1}{R_{01}}=\frac{1}{R^a{}_{01}}+\frac{1}{R^b{}_{01}}\ \text{and}\ \frac{1}{R_{02}}=\frac{1}{R^a{}_{02}}+\frac{1}{R^b{}_{02}} \\ R^a{}_{01}=\frac{\Delta}{2\pi a_1 b_1 \lambda_0},\ R^b{}_{01}=\frac{\Delta}{\pi a^2{}_1\lambda_0} \\ R^a{}_{02}=\frac{\Delta}{2\pi a_2 b_2 \lambda_0},\ R^b{}_{02}=\frac{\Delta}{\pi a^2{}_2\lambda_0} \end{array}\right\} \tag{74b}$$

Since the region T_s is everywhere thin, the first approximation to the resistance R_s of the solution, obtained by neglecting the variations of potential near the edges of C_1 and C_2, assuming a uniform radial component of current density in T_s^a, and a uniform axial component in T_s^b is given by

$$\frac{1}{R_s}=\frac{1}{R_s^a}+\frac{1}{R_s^b}, \text{ where}\left\{\begin{aligned} R_s^a&=\frac{\log\dfrac{a_2}{a_1}}{2\pi\left(l_1+\dfrac{h}{2}\right)\lambda_s}\approx\frac{c}{2\pi a_1 l_1\lambda_s}\left[1-\frac{1}{2}\left(\frac{c}{a_1}+\frac{h}{l}\right)\right]\\ R_s^b&=\frac{h}{\pi\left(a_1+\dfrac{c}{2}\right)^2\lambda_s}\approx\frac{h}{\pi a^2\lambda_s}\left(1-\frac{c}{2a_1}\right)\end{aligned}\right\} \tag{75}$$

In these expressions the mean length of the shell T_s^a is taken $\left(l_1+\frac{h}{2}\right)$ and the mean radius of the disk is $\left(a_1+\frac{c}{2}\right)$. In this way we attempt to make some allowance for the troublesome region near the edge C_1 and C_2. If the construction and measurement of dimensions of the solution-volume T_s were possible with any great precision, this expression for R_s would require a slight modification. All that is proposed here is an approximate evaluation of the electrode resistances R_{e1} and R_{e2}.

The total current is $I=I^a+I$ where I^a is that passing through the cylindrical shell T_s^a and I^b that passing through the disk T_s^b.

For the two parts $T^a{}_1$ and $T^b{}_1$ of the electrode T_1 consider the potential

$$V(x,r)=\frac{E}{2}-\frac{I^b}{2\pi a_1 b\lambda_e}x+$$

$$\frac{I^a}{\pi a_1 l^2\lambda_e}\sum_{n=1}^{\infty}\frac{\sin\alpha_n x}{i\alpha^2_n}\left[\frac{Y_1(i\alpha_n a)J_0(i\alpha_n r)-J_1(i\alpha_n a)Y_0(i\alpha_n r)}{Y_1(i\alpha_n a)J_1(i\alpha_n a_1)-J_1(i\alpha_n a)Y_1(i\alpha_n a_1)}\right] \tag{76a}$$

$$\text{in } T_1^a \text{ where } \alpha_n=\frac{(2n-1)}{2l}\pi$$

and

$$V(x,r)=\frac{E}{2}-\frac{l}{2\pi a_1 b\lambda_e}\left(\frac{I^a}{2}+I^b\right)-\frac{2I^b}{\pi a\lambda_e}\sum_{n=1}^{\infty}\frac{\cosh\beta_n\left(\dfrac{x-l}{a}\right)J_0\left(\beta_n\dfrac{r}{a}\right)}{\beta_n^2\sinh\dfrac{\beta_n b}{a}J_1(\beta_n)} \tag{76b}$$

$$\text{in } T^b{}_1$$

where β_n is the nth positive unit of $J_0(\beta)=0$.

The equation 76a reduces at the face $x=0$ of $T^a{}_1$ to $V(0,r)=\frac{E}{2}$ as it should. Also $[D_rV(x,r)]_{r=a}=0$ ie., there is no current leaving the inner boundary of $T^a{}_1$. The current density at the surface $S^a{}_1$ i. e., $r=a$ is by (71a)

$$-\lambda_e[D_rV_{(x,r)}]_{r=a_1}=i_r(x,a_1)=\frac{I^a}{2\pi a_1 l}=\frac{I^a}{\pi a_1 l^2}\sum_{n=1}^{\infty}\frac{\sin(\alpha_n x)}{\alpha_n}$$

It is evident therefore that (76a) satisfies the reasonable boundary conditions at its external boundaries.

Over the section whose trace is $\overline{CD}_1$ i. e., $x=l$ we find from (76a) $i_x(l,r)=-\lambda_e[D_xV(x,\ r)]_{x=l}=\dfrac{I^b}{2\pi a_1b}=$uniform, which is a reasonable way of ignoring the fine structure of the field at this edge, since the total current through $\overline{CD}_1$ must be I^b the total which passes to the solution through the surface $S^b{}_1$. At $S^a{}_1$, $r=a_1$, (76a) becomes

$$V(x,a_1)=\frac{E}{2}-\frac{I^b}{2\pi a_1b\lambda_e}x$$

$$+\frac{I^a}{\pi a_1l^2\lambda_e}\sum_{n=1}^{\infty}\frac{\sin\ \alpha_nx}{i\alpha_n{}^2}\left[\frac{Y_1(i\alpha_na)J_0(i\alpha_na_1)-J_1(i\alpha_na)Y_0(i\alpha_na_1)}{Y_1(i\alpha_na)J_1(i\alpha_na_1)-J_1(i\alpha_na)Y_1(i\alpha_na_1)}\right]\quad(77).$$

Since $a_1=a+b$ where b is small, this series becomes

$$\sum_{n=1}^{\infty}\frac{\sin\ \alpha_nx}{i\alpha_n{}^2}\frac{1}{i\alpha_nb}\left[\frac{Y_1J_0-J_1Y_0}{Y_1J_1{}'-J_1Y_1{}'}\right]_{(i\alpha_na)}=\sum_{1}^{\infty}\frac{\sin\ \alpha_nx}{i\alpha_n{}^2}\frac{1}{i\alpha_nb}\left[\frac{-\dfrac{2}{\pi i\alpha_na}}{-\dfrac{2}{\pi i\alpha_na}}\right]$$

$$=-\frac{1}{b}\sum_{n=1}^{\infty}\frac{\sin\ \alpha_nx}{\alpha_n{}^3}=-\frac{(2l)^3}{b}\frac{1}{\pi3}\sum_{n=1}^{\infty}\frac{\sin\ (2n-1)\dfrac{\pi x}{2l}}{(2n-1)^3}$$

so that (77) becomes

$$V(x,\ a_1)=\frac{E}{2}-\frac{1}{2\pi a_1b\lambda_e}\left[I_x{}^b+2lI^a\left(\frac{2}{\pi}\right)^3\sum_{n=1}^{\infty}\frac{\sin\ (2n-1)\dfrac{\pi x}{2l}}{(2n-1)^3}\right]\qquad(77')$$

From this we find

$$2\pi a_1\int_0^lV(x,\ a_1)dx=2\pi a_1l\left\{\frac{E}{2}-\frac{l}{2\pi a_1b\lambda_e}\left[\frac{I^b}{2}+2I^a\left(\frac{2}{\pi}\right)^4\sum_{n=1}^{\infty}\frac{1}{(2n-1)^4}\right]\right\}$$

By means of the formulas

$$\left(\frac{2}{\pi}\right)^3\sum_{1}^{\infty}\frac{-1^{n+1}}{(2n-1)^3}=\frac{1}{4}\text{ and }\left(\frac{2}{\pi}\right)^4\sum_{1}^{\infty}\frac{1}{(2n-1)^4}=\frac{1}{6}$$

we thus find

$$2\pi a_1\int_0^lV(x,\ a_1)dx=2\pi a_1l\left\{\frac{E}{2}-\frac{l}{2\pi a_1b\lambda_e}\left(\frac{I^a}{3}+\frac{I^b}{2}\right)\right\}\qquad(78)$$

and

$$V(l,\ a)=\frac{E}{2}-\frac{l}{2\pi a_1b\lambda_e}\left(\frac{I^a}{2}+I^b\right)\qquad(79)$$

Returning to the equation 76b this is evidently a solution in the region $T^b{}_1$ satisfying the boundary conditions

$V(x, a)=\frac{E}{2}-\frac{l}{2\pi a_1 b\lambda_e}\left(\frac{I^a}{2}+I^b\right)$ for $l<x<l+b$ (i. e., by 79 continuous

at C,

$D_xV=0$ at $x=l$

$$D_xV=-\frac{I^b}{\pi a^2\lambda_e} \text{ at } x=l+b\left(=-\frac{I^b}{\pi a^2\lambda_e}2\sum_1^\infty\frac{J_0\left(\frac{\beta_r}{a}\right)}{\beta_n J_1(\beta_n)}\right) \tag{80}$$

From it we find

$$2\pi\int_0^a rV(l+b, r)dr=\pi a^2\left[\frac{E}{2}-\frac{l}{2\pi a_1 b\lambda_e}\left(\frac{I_a}{2}+I^b\right)\right]-\frac{a^2}{8b\lambda_e}I^b \tag{81}$$

where we have placed $\tanh\frac{\beta_n b}{a}=\frac{\beta_n b}{a}$ and made use of the known sum

$$\sum_1^\infty\frac{1}{\beta_n{}^2}=\frac{1}{32}.$$

Hence, if $\overline{V}^0{}_{e1}$ denotes the average of V over $S_1=S^a{}_1+S^b{}_1$ we find, by use of (78) and (81)

$$\overline{V}^0{}_{e1}=\frac{E}{2}-\frac{1}{(b\lambda_e)(2\pi a_1 l+\pi a^2)}\left[\frac{l}{3}\left(l+\frac{3a}{4}\right)I^a+\frac{1}{2}\left(l+\frac{a}{2}\right)^2 I^b\right] \tag{82}$$

Since the current is determined principally by the solution resistance R_s and $R^a{}_s$ and $R^b{}_s$ are in parallel, we may replace I^a and I^b in (82) by

$$I^a=\frac{R^b{}_s}{R^a{}_s+R^b{}_s}I=\frac{hI}{h+\frac{a_1c}{2l_1}} \text{ and } I^b=\frac{R^a{}_s}{R^a{}_s+R_s{}^b}I=\frac{\frac{a_1c}{2l_1}}{h+\frac{a_1c}{2l_1}}I \tag{83}$$

Hence the "resistance of the inner" electrode defined by (19a) is

$$R_{e1}=\frac{\frac{E}{2}-\overline{V}^0{}_{e1}}{I}=\frac{\frac{l}{3}\left(2l+\frac{3a}{2}\right)2l+\frac{1}{4}(2l+a)^2a\frac{c}{h}}{2\pi ab\lambda_e(2l+a)\left(2l+a\frac{c}{h}\right)} \tag{84}$$

When the electrolytic solution has the same thickness everywhere, $c=h$ and this becomes

$$R_{e1}=\frac{l}{2\pi ab\lambda_e}\left[\frac{2l}{3(2l+a)}+\frac{al}{3(2l+a)^2}+\frac{a}{4l}\right] \tag{85}$$

Since $h=c$ is small it is similarly found as is evident from symmetry that the resistance R_{e2} of the outer electrode is practically the same as R_{e1}. To estimate the importance of this term, consider the case where $a=1$ cm, $l=5$ cm, $h=c=0.1$ cm, $b=0.01$ cm, $\lambda_s=0.04$ and $\lambda_e=0.8$ $(10)^5$. By (85) we find for the total electrode resistance $R_{e1}+R_{e2}=R_e=0.00073$ ohm, while (75) gives $R^a{}_s=0.79$ ohm, $R^b{}_s=7.95$ ohms, so that the total resistance of the electrolytic solution is

$$R_s=0.72 \text{ ohm.}$$

Hence, the electrode resistance is about one-thousandth of the solution resistance.

V. SUMMARY

In section II a plausible method of obtaining a first approximation to the effect of electrode-resistance was sketched without attempting a proof or inquiry into its limitations. The line of argument in a more detailed justification could be inferred from an examination of the equations obtained in section III for a particular shape of cells and electrodes. This exact mathematical solution confirms the method of section II as a first approximation. On the strength of this, the approximation is applied in section IV to a cylindrical cell of more complicated shape. The result of practical importance in the first case is the electrode resistance given by equation 73 and in the second case by (84). These electrode resistances were arbitrarily defined in equation 19 so that they would enter the first approximate equations of motion of electricity (4) in the familiar form. A possible source of misunderstanding due to the use of the name "electrode resistance" was pointed out in section II and illustrated in section III. The resolution of the total resistance into the sum of two parts, one being that of the solution, the other of the electrodes, is possible in the first approximation only. In a closer approximation in general, this concept goes to pieces, because the total current I is not confined to a single linear branch but is the sum of an infinite number of parallel current components having different paths and series capacities.

WASHINGTON, April 23, 1936.