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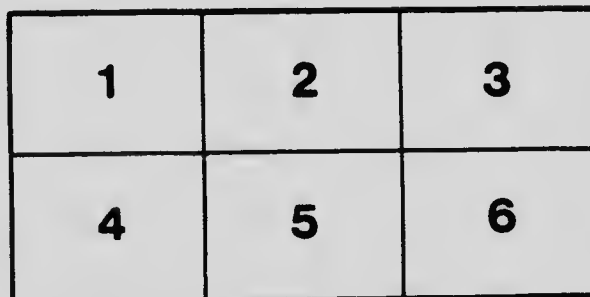
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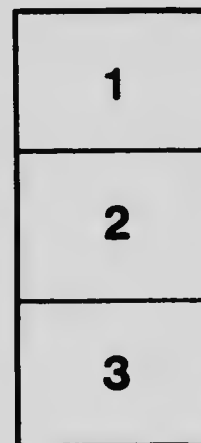
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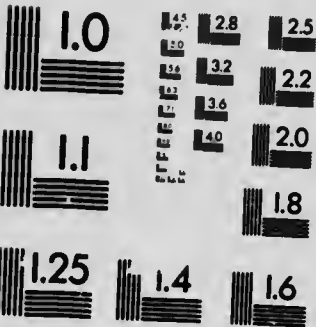
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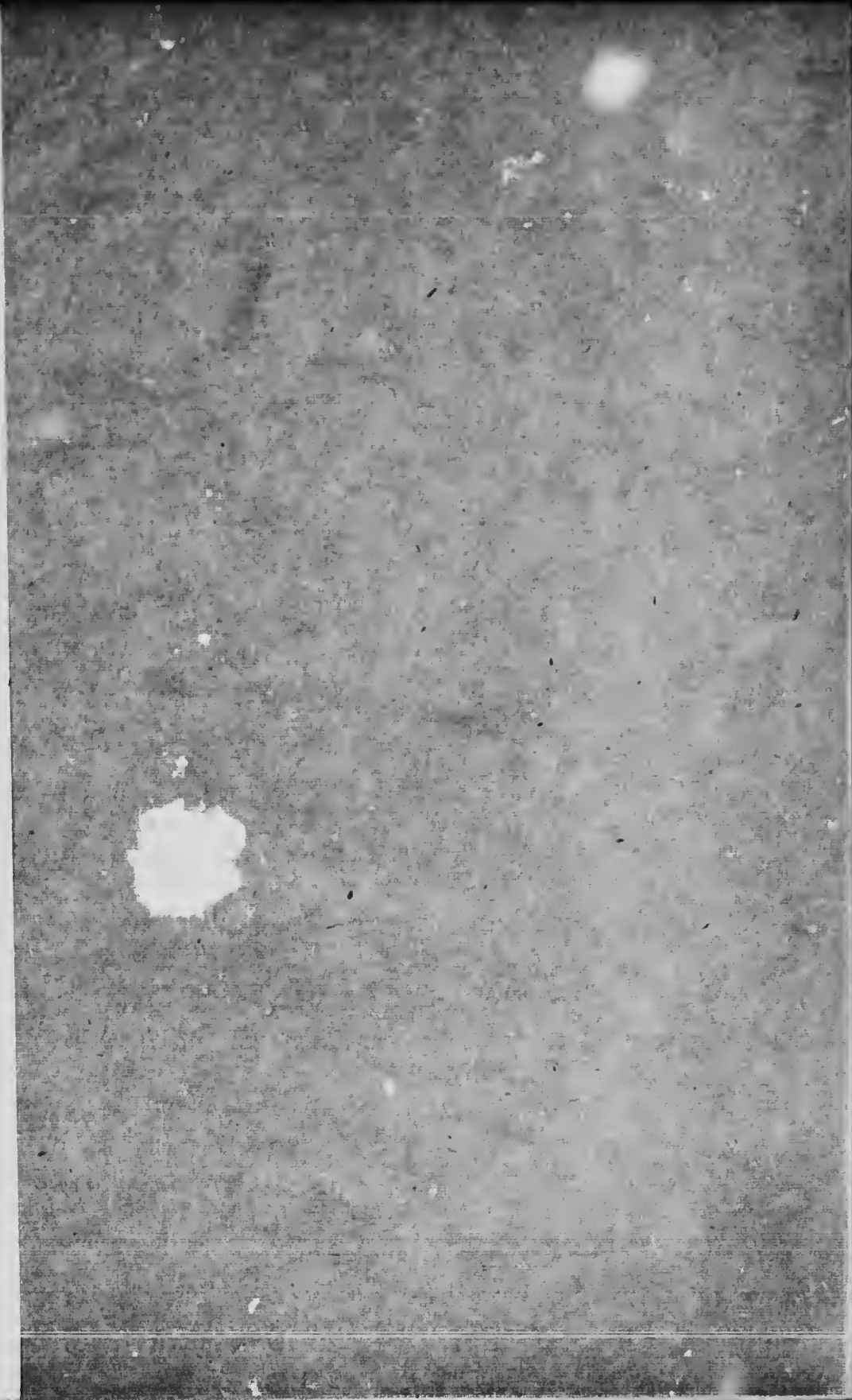
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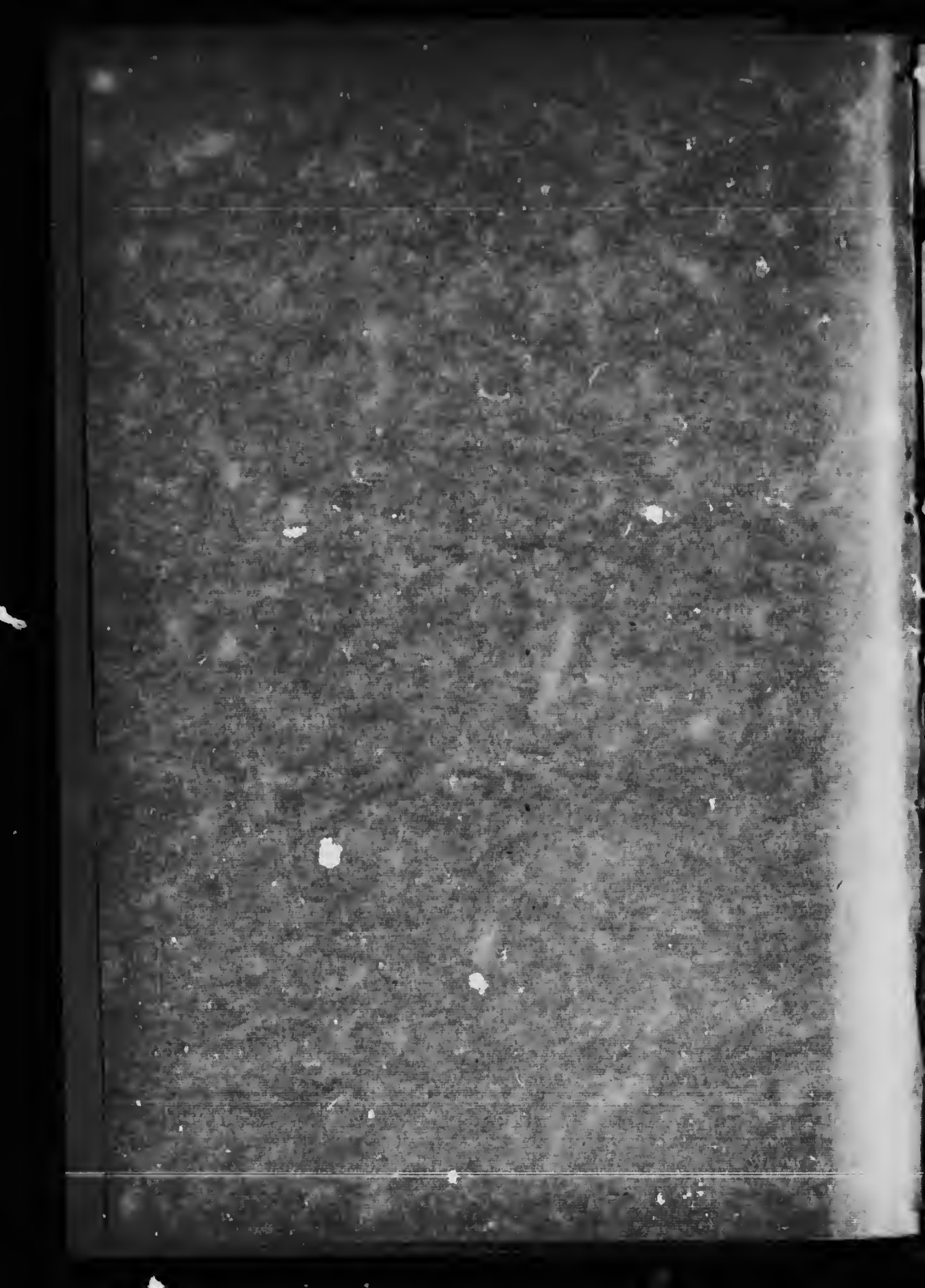
PAPERS FROM THE CHEMICAL LABORATORIES

MATHEMATICAL THEORY OF THE CHANGES OF
CONCENTRATION AT THE ELECTRODE BROUGHT ABOUT
BY DIFFUSION AND BY CHEMICAL REACTION; BY T. R.
SWANSON AND G. LANK HULL

(Translated from the Journal of Physical Chemistry, vol. XIV)

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MATHEMATICAL THEORY OF THE CHANGES OF
CONCENTRATION AT THE ELECTRODE,
BROUGHT ABOUT BY DIFFUSION
AND BY CHEMICAL REACTION

BY T. R. ROSEBRUGH AND W. LASH MILLER

Owing to the chemical changes which accompany electrolysis, the composition of the electrolyte at the electrodes is different from that in the body of the solution. Diffusion currents are consequently set up which tend to remove these differences; and if convection be avoided, the concentration of any constituent at any point in the solution will depend only on the initial composition of the solution, and on the amounts which have been carried to or from the electrodes by diffusion and by electrolytic migration.

In the simpler cases, at all events, these changes of concentration are susceptible of mathematical treatment; Weber¹ and Sand² have considered the case of electrolysis with constant currents, and Warburg³ has deduced an equation for the stationary state on electrolysis with a sinusoidal current through a diffusion layer of "infinite" length. The present paper deals with the whole problem in a systematic manner, and includes the discussion of electrolysis with intermittent, successive and sinusoidal currents, without restriction as to the duration of the electrolysis or the length of the column of liquid through which the diffusion takes place. The increasing application of the oscillograph to the study of instantaneous conditions at the electrode led us to pay particular attention to the changes which occur within the first fraction of a second after throwing on the current, while Richards'⁴ work on electrolysis with alternating currents,

¹ Wied. Ann., **7**, 536 (1879).

² Phil. Mag., [6] **1**, 45 (1901); Zeit. phys. Chem., **35**, 641 (1900).

³ Wied. Ann., **67**, 493 (1899).

⁴ Trans. Am. Electrochem. Soc., **1**, 221 (1902).

followed by the interesting experiments of LeBlanc¹ and of Reichinstein² with copper electrodes in cyanide solutions, induced us to include the case of non-instantaneous chemical reactions between the primary products of electrolysis and the other constituents of the solution.

The results of the investigation, however, are not perfectly general; for in leading up to Eqs. (iii) and (xiv) it has been assumed that both the diffusion constant and the flow due to electrolytic migration are independent of the concentration, and that the rate of the secondary reaction if any occur is proportional to the concentration of the constituent whose amount at the electrode is directly affected by the electrolysis assumptions, which, in many cases, are not even approximately true. To treat the diffusion constant as a function of the concentration, or to consider reactions whose rates are proportional to any other than the first power of the concentration under consideration, would alter the whole nature of the differential equation involved; the restrictions thus imposed have been disregarded only in the comparatively simple, though important, case of prolonged electrolysis with a constant current.

To fix the ideas, electrolysis may be supposed to take place in a vessel of uniform cross section (A cm²), bounded at the ends by the electrodes. The surface of each electrode is then identical in area and form with the cross section of the electrolyte, the current density will be uniform throughout, and the concentrations will be constant over each section of the solution taken parallel to the electrodes. The results of the argument are, however, equally applicable to the case of electrolysis with a rotating cylindrical electrode in a uniform field; in such cases, as shown by the experiments of Noyes and Whitney on rates of solution,³ the electrode may be regarded as surrounded by an adherent layer of solution of uniform thickness through which diffusion takes place,⁴

¹ *Zeit. phys. Chem.*, **46**, 213 (1903); *Zeit. Elektrochemie*, **11**, 705 (1905).

² *Zeit. Elektrochemie*, **15**, 734 (1909).

³ *Zeit. phys. Chem.*, **23**, 689 (1897).

⁴ *Ibid.*, **47**, 52 (1904).

with electrodes of ordinary dimensions this film has been found to be so thin¹ that the difference between the areas of its outer and inner surfaces may be neglected.

The direction normal to the surface of the electrodes is taken as the axis of x ; it is assumed that at some fixed point on this axis the composition of the electrolyte (or at least the concentration z of the constituent under discussion) remains unaltered throughout the experiment, and this point is taken as the origin, $x = 0$, from which the values of x are reckoned. The "solution condition," then, adopted throughout this paper is that at $x = 0$, $z = z_0$ for all values of t , or

$$[\text{For } x = 0] \quad \partial z / \partial t = 0 \quad (i).$$

In Weber's experiments, where solutions of zinc sulphate were electrolyzed for long periods of time between stationary zinc electrodes, such a point of constant concentration evidently lies midway between the two electrodes; in experiments with a rotating electrode it will lie on the outer surface of the adherent liquid film, no matter how long the electrolysis proceeds if constituents removed at the cathode are replaced at the anode and vice versa, for some time at all events if the amount of electrolyte in the cell is large compared with that destroyed per minute by the electrolysis.

The position of one of the electrodes is defined by $x = l$; the other electrode is left out of consideration altogether, for as long as there is a section of the electrolyte where the concentration of one of the constituents remains unaltered, changes in the concentration of that constituent at one of the electrodes cannot affect conditions at the other. It is true that some new substance, for instance acid formed at the anode, might on reaching the cathode affect the diffusion constants or the electrolytic migration of the others there; such cases, however, are excluded from consideration for other reasons (see pg. 820).

The distance in centimeters between the electrode under consideration and the section of fixed concentration is thus

¹ Zeit. phys. Chem., 47, 56 (1904).

denoted by l . Weber took the surface of one of his electrodes as origin and denoted the distance to the other by L ; his L is thus twice l ; with rotating electrodes, however, or stirred electrolytes, l is evidently quite independent of the distance between the electrodes.

At the moment of throwing on the current, the solution is supposed to be uniform throughout the vessel; thus the "initial condition" adopted in all the deductions of this paper is, that at $t = 0$, $z = z_0$ for all values of x or

$$[\text{For } t = 0] \quad \partial z / \partial x = 0 \quad (ii).$$

When the current is thrown on, diffusion and migration begin.

Diffusion and Migration.—The rate of diffusion of any constituent away from one of the electrodes (*i. e.*, the number of equivalents of that substance per second which is carried by diffusion across each square centimeter of the cross section of the vessel) may be different at different points of the diffusion layer. At any point x , however, it is proportional to the concentration gradient at that point in the line connecting the electrodes; that is, to the difference of concentration per centimeter in the direction of the x axis, or

$$\text{Rate of diffusion from electrode} = k \partial z / \partial x \quad \text{---} \quad \text{---} \quad \text{---} \quad (\text{Fick}),$$

where z is the concentration of the constituent in question, expressed in equivalents per cubic centimeter; if $\partial z / \partial x$ be negative, diffusion will occur *towards* the electrode.

The rate of electrolytic migration of the same constituent, or the number of equivalents per second carried across each square centimeter of the cross section of the vessel by the current \mathcal{I} amperes, is given by the expression

$$\text{Rate of migration from electrode} = \frac{\mathcal{I}}{96540} \cdot \frac{zu}{\sum zu} \quad (\text{Kohlrausch}),$$

where u is the mobility of the constituent in question and z its concentration; $\sum zu$ indicates the sum of the products of the mobilities of the various ions each into its own concentration. The sign of this expression (the direction in

which the migration takes place) evidently depends on the direction of the electric current, and on whether the constituent to which z refers acts as anion or cation; it is *negative* if the motion is *toward* the electrode.

Excluding for the present the possibility of secondary reactions in which the products of electrolysis take part, these two factors determine the total rate of flow, which accordingly is given by

$$\text{Rate of flow from electrode} = k \frac{\partial z}{\partial x} + \frac{''}{96540} \mathcal{I} \cdot \frac{zu}{\Sigma zu'}$$

and the rate of accumulation, $\partial z/\partial t$, at any point x is determined by the difference between the rates of flow to and from that point:

$$\frac{\partial z}{\partial t} = k \frac{\partial^2 z}{\partial x^2} + \frac{\partial}{\partial x} \left(\frac{''}{96540} \mathcal{I} \cdot \frac{zu}{\Sigma zu'} \right).$$

In some cases the second term on the right vanishes or may be neglected, leaving

$$\partial z/\partial t = k \partial^2 z/\partial x^2. \quad (iii)$$

This occurs, for instance, (a) if $u = 0$, *i. e.*, if the constituent in question is a non-electrolyte; (b) if $zu/\Sigma zu'$ is small, as when z refers to the concentration of copper in a solution of copper sulphate containing excess of sulphuric acid; (c) if the solution contains only one salt (in which case $zu/\Sigma zu'$ becomes Hittorf's "transport number") whose transport number is not affected by change in concentration; (d) if the solution contains several salts with a common ion (the "constituent" under consideration) and if the ions of the opposite sign all have the same mobility; when the case is analogous to (c). Throughout Parts I and II of the present paper, (iii) is assumed to hold.

Electrode condition.—Let G represent the number of equivalents per second of the constituent under consideration caused to appear in the solution at each square centimeter of the surface of the electrode by the action of the current \mathcal{I} .

G will usually be related to \mathcal{I} by an expression of the form

$$G = \frac{\mathcal{I}}{96540} \left(r + \frac{zu}{\sum zu} \right)$$

in which the first term on the right measures the amount formed by chemical changes (oxidation, reduction, solution of the electrode, etc.), and the second term the amount brought up to (but, naturally, not past) the electrode surface by migration. At the anode in a solution of copper sulphate with excess of sulphuric acid, for instance, the first term would be positive and the second term zero if the "constituent under consideration"—to which z refers—were copper; if it were sulphuric acid, the first term would be zero and the second positive; in either case, if the electrode were a cathode, G would be negative.

The effect of the electrolysis on the concentration of this constituent in the solution is the same as though it were being carried into the solution through the surface of the electrode by the concentration gradient

$$[\text{For } x = l] \quad \partial z / \partial x = G/k \quad (iv)$$

which would produce the same gain that is actually brought about by the electrolysis. Eq. (iv) is therefore introduced as the "electrode condition" corresponding to the current \mathcal{I} amperes. In the first Section of this paper, "Constant Current," G will be treated as independent of t ; under "Successive Currents" it will be supposed to change abruptly at definite moments; while under "Sinusoidal Currents" it will be treated as a continuous function of the time. In the first Part of the paper it will be assumed that for a given value \mathcal{I} , of the current, G is not affected by the composition of the solution at the electrode; in the second Part, account will be taken of the fact that the nature of the chemical action at the electrode may change abruptly when the concentration reaches a certain value; Part III admits the possibility of secondary reactions at the electrode.

The mathematical problem then is, to find a solution for the differential equation (iii) which will satisfy the "boundary conditions" (i), (ii) and (iv). In the case of linear and homogeneous equations, like (iii), where the only coefficient k is a constant, there is no difficulty in finding particular solutions; from these, general solutions can be built up by multiplying each particular solution by an arbitrary constant and taking the sum. With such general solutions, however, in which the constants have arbitrary values, "ist so gut wie nichts gewonnen."¹ The main point is to find values for these multipliers such that the boundary conditions may be satisfied; and no general rules have as yet been laid down for finding them. Eq. (iii), however, has been made the subject of detailed study by Fourier and others in connection with the theory of the flow of heat,² and Weber³ has shown how the boundary conditions of the present problem may be introduced; an equation corresponding to (15) of the present paper has already been obtained by him.

PART I

REACTIONS AT THE ELECTRODE INDEPENDENT OF THE CONCENTRATION z . SECONDARY REACTIONS EXCLUDED

Sec. 1.—Constant Current

One particular solution of (iii) is

$$z = Cx + D$$

and another is

$$z = (A \sin Ex + B \cos Ex)e^{-E^2kt}.$$

¹ Riemann, Die Partiellen Differential-Gleichungen der math. Physik, 4th Ed., Vol. i, pg. 153 (1900).

² In his "Introduction to the Theory of Fourier's Series and Integrals, and the Mathematical Theory of the Conduction of Heat" (Macmillan, 1906). H. S. Carslaw has collected a large number of cases in which problems analogous to the present have been solved, but as condition (iv) does not correspond to any easily realizable experimental condition except in the case of electrolysis, no problems satisfying that condition have been included; in the case of a heat problem, condition (iv) would correspond to a fixed rate of loss of heat from one end of a cylinder, independent of its temperature.

³ Wied. Ann., 7, 536 (1879).

The expression built up from these, viz.,

$$z = (A_1 \sin E_1 x + B_1 \cos E_1 x) e^{-E_1^2 kt} + (A_2 \sin E_2 x + B_2 \cos E_2 x) e^{-E_2^2 kt} + \text{etc.} + Cx + D,$$

or briefly

$$z = \sum_{n=1}^{\infty} \{ (A_n \sin E_n x + B_n \cos E_n x) e^{-E_n^2 kt} \} + Cx + D, \quad (1)$$

proves sufficiently general to allow the introduction of (i), (ii) and (iv).

To introduce (i).—From (1)

$$[\text{For } x = 0] \quad z = D + \sum B_n e^{-E_n^2 kt}. \quad (2)$$

The expression on the right may be made constant and equal to z_0 for all values of t , as required by condition (i), by setting

$$B_1 = 0, \quad B_2 = 0, \quad B_3 = 0, \text{ etc.} \quad (3)$$

so that, from (2), (3) and (i)

$$D = z_0. \quad (4)$$

To introduce (iv).—From (1), (3) and (4),

$$[\text{For } x = l] \quad \frac{\partial z}{\partial x} = C + \sum_{n=1}^{\infty} A_n e^{-E_n^2 kt} \cdot \cos E_n l \quad (5)$$

whence by (iv),

$$C + \sum_{n=1}^{\infty} A_n e^{-E_n^2 kt} \cdot \cos E_n l = \frac{G}{k}. \quad (6)$$

This is possible, for all values of t , only if each term involving t is separately made zero; this may be accomplished by setting

$$\cos E_n l = 0, \quad \text{i. e., } E_n = \frac{(2n-1)\pi}{2l}, \quad (7)$$

n being any integer.

From (6) and (7) there follows

$$C = G/k. \quad (8)$$

To introduce (ii).—Setting $t = 0$ in (1), and substituting

the values of B, D and E_n given by (3), (4) and (7), there follows

$$[\text{For } t = 0] \quad z = z_0 + Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}, \quad (9)$$

whence by (i)

$$0 = Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}. \quad (10)$$

Fourier has shown that for values of f between 0 and $\pi/2$ (see Appendix)

$$f = \frac{4}{\pi} (\sin f - \frac{1}{9} \sin 3f + \frac{1}{25} \sin 5f - \text{etc.}), \quad (11)$$

whence (writing $\frac{\pi x}{2l}$ for f)

$$Cx = \frac{8lC}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)^2} \sin \frac{(2n-1)\pi x}{2l}. \quad (12)$$

Substituting this expression for Cx in (10)

$$\sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l} = \frac{8lC}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)^2} \sin \frac{(2n-1)\pi x}{2l} \quad (13)$$

whence

$$A_n = \frac{(-1)^n}{(2n-1)^2} \cdot \frac{8lC}{\pi^2}. \quad (14)$$

Thus, by substituting in (1) the values for B, D, E_n and A_n from (3), (4), (7) and (14), an expression is obtained,

$$z - z_0 = \frac{Gx}{k} + \frac{8lG}{\pi^2 k} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)^2} \cdot e^{-\frac{(2n-1)^2 \pi^2 kt}{4l^2}} \cdot \sin \frac{(2n-1)\pi x}{2l}, \quad (15a)$$

which satisfies the differential equation (iii) and the conditions (i), (ii) and (iv), if the current¹ remains constant from $t = 0$, the moment of throwing on the current, up to the moment t .

Inspection of (15a) shows that the right-hand member

¹ The equations deal only with G , which however is proportional to the current, see page 821.

is divisible by G . From this it appears that in experiments with the same electrolyte, carried out at the same temperature (hence with fixed value of k) and with the same rate of stirring (fixed value of l), the amount of change in concentration ($z - z_0$) in a given time will be proportional to G and therefore to the current. It may also be concluded that if in a series of experiments (with fixed values of k and l) the currents (and therefore the values of G) be proportional to the initial concentrations (z_0), the values of z after any given duration of electrolysis (t) will likewise be proportional to the initial concentrations.

For the sake of brevity, (15a) may be written

$$z - z_0 = Cx + \frac{8lC}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{m^2} e^{-m^2 at} \sin mgx, \quad (15b)$$

where $m = 2n - 1$, $C = G/k$, $a = \pi^2 k/4l^2$, $g = \pi/2l$, and

Σ is written for $\sum_{n=1}^{\infty}$. Since $(-1)^n \sin mgx = -\cos mg(l-x)$,

(15b) may be put in the more convenient form,

$$\frac{z - z_0}{Cl} = \frac{x}{l} - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} e^{-m^2 at} \cos mg\bar{x}, \quad (15c)$$

where all the terms after the sign of summation are positive; \bar{x} is here written as an abbreviation for $l - x$, the distance of the point x from the electrode. In this equation, the term on the left expresses the change in concentration as a fraction of the maximum change that could be brought about at the electrode by the same current;¹ the first term on the right gives the distance from the origin ($x = 0$) as a fraction of the total length of the diffusion layer; and $at = \pi^2 kt/4l^2$ in the exponent gives the time in units which depend on k and l only.²

The concentrations at the electrode, which are the most important from an experimental point of view, may be ob-

¹ *i. e.*, if left to act for "infinite" time, see p. 828, footnote. This "physical" interpretation of Cl is allowable within certain limits only (see Part II); the geometrical interpretation (fig. 1) holds in all cases.

² $a = \pi^2 k/4l^2$ is spoken of later as the "time constant."

tained by substituting l for x in (15); $\cos mgz$ then becomes unity, and (15c) reduces to

$$[\text{For } x = l] \quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} e^{-m^2 at}. \quad (16)$$

Methods of Computation

First term approximation.—The first five terms of the series in (16) are:

$$e^{-at}, \quad \frac{1}{9} e^{-9at}, \quad \frac{1}{25} e^{-25at}, \quad \frac{1}{49} e^{-49at}, \quad \frac{1}{81} e^{-81at}.$$

The second term will be one percent or less of the first term if $\frac{1}{9} e^{-9at} = \frac{1}{100} e^{-at}$ or less, *i. e.*, if at be 0.301 or more; and it will be one per thousand of the first term if at be 0.589 or more; in both cases the remainder of the series is negligible. Thus in computing values of $(z - z_0)/Cl$ for values of at above 0.6, the first term of the series, neglecting all the others, will give results accurate to one tenth percent; under these conditions (17) may therefore be used in place of (16).

$$[\text{For } at \text{ large, and } x = l] \quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} e^{-at} \text{ approx.} \quad (17)$$

But as at becomes smaller, the number of terms that have to be taken into account rises rapidly. In computing $(z - z_0)/Cl$ for $x = l$ and $at = 0.03$, for instance, the values of the first five terms (each multiplied by $8/\pi^2$) are 0.78664, 0.06875, 0.01532, 0.00378, 0.00088, respectively, and all five have to be evaluated in order to find $(z - z_0)/Cl$ to three places of decimals.

Parabolic approximation.—Thomson and Cayley¹ have shewn that

$$\sum_{n=1}^{\infty} e^{-\frac{(2n-1)^2 \pi^2}{4f^2}} \cos \frac{(2n-1)\pi y}{j} = \frac{j}{2\sqrt{\pi}} (e^{-y^2} - e^{-(y-f)^2} - e^{-(y+f)^2} + e^{-(y-2f)^2} + e^{-(y+2f)^2} - \text{etc.}). \quad (18)$$

¹ Quarterly Journal of Mathematics, I, 316 (1857).

Substituting 0 for y , and at for $\pi^2/4f^2$, this gives

$$\sum_{n=1}^{\infty} e^{-(2n-1)^2 at} = \frac{1}{4} \sqrt{\frac{\pi}{at}} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \pi^2 / 4at} \right\}. \quad (19)$$

For small values of at the sum on the right may be neglected, giving

[For at small] $\sum_{n=1}^{\infty} e^{-(2n-1)^2 at} \approx \frac{1}{4} \sqrt{\frac{\pi}{at}}$ approximately. (20)

Multiplying both sides by dt and integrating between the limits 0 and t there follows

[For at small] $\sum_{n=1}^{\infty} \frac{1}{m^2} (1 - e^{-(2n-1)^2 at}) = \frac{1}{2} \sqrt{\pi at}$ approx., (21)

whence

[For $x = l$, at small] $\frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} e^{-m^2 at} \approx \frac{4}{\pi^{1/2}} \sqrt{at}$ approx., (22a)

or, substituting for at its value $\pi^2 kt / 4l^2$,

[For $x = l$ at small] $(z - z_0) / C = 1.129 \sqrt{kt}$ approximately. (22b)

TABLE I
Values of $(z - z_0) / Cl$ at the electrode

| at | Parabolic approx | | True value (Eq. 16) | First term approx. | |
|------|--------------------|---------|------------------------|--------------------|-------------------|
| | Calc. (Eq. 22a) | Error | | Error | Calc. (Eq. 17) |
| 0.4 | 0.45432 | 0.00012 | 0.45420 | 0.00246 | 0.45666 |
| 0.5 | 0.50795 | 0.00059 | 0.50730 | 0.00100 | 0.50836 |
| 0.6 | 0.55643 | 0.00169 | 0.55474 | 0.00041 | 0.55515 |

The figures of Table I show that for all practical purposes the accurate expression (16) may be replaced by the "first term approximation" (17) for values of at above 0.5, and by the "parabolic approximation" (22) for values of at below 0.5. It may not be out of place to emphasize the fact that the applicability of either of these approximations depends

not on the value of either l , k , or t alone, but on that of $at = \pi^2 kt/4l^2$; the parabolic approximation, for instance, holds not only for the case " $l = \infty$ ",¹ as shown by Sand but it also holds for any other value of l provided kt be small enough.

TABLE II
Values of $(z - z_0)/Cl$ at the electrode

| at | $(z - z_0)/Cl$ | at | $(z - z_0)/Cl$ | at | $(z - z_0)/Cl$ |
|------|----------------|------|----------------|----------|----------------|
| 0 | 0 | 0.5 | 0.507 | 1.4 | 0.800 |
| 0.05 | 0.164 | 0.6 | 0.555 | 1.5 | 0.819 |
| 0.1 | 0.227 | 0.7 | 0.597 | 2.0 | 0.890 |
| 0.2 | 0.321 | 0.8 | 0.630 | 2.786 | 0.950 |
| 0.3 | 0.393 | 0.9 | 0.670 | 4.395 | 0.990 |
| 0.4 | 0.454 | 1.0 | 0.702 | ∞ | 1.000 |

As shown by the figures of Table II, ninety-nine percent of the total change of concentration at the electrode that a given current can accomplish is completed when at reaches 4.40. The actual number of seconds corresponding to a given value of at depends, obviously, on the "time constant" $a = \pi^2 k/4l^2$, i. e., on the values of k and l ; if, for example, $k = 4 \times 10^{-6}$ cm². sec., and $l = 3.14 \times 10^{-3}$ cm (numbers within the range of those experimentally met with) at gives the duration of electrolysis in hundredths of a second; if the stirring were slower, however, and l rose to 3.14×10^{-2} cm, at would give the time in seconds.

The Stationary State

When the current has flowed long enough, the "stationary state" is reached, the equation for which may be obtained direct from (iii) by putting $\partial z/\partial t = 0$, or from (15) by setting $t = \infty$; the exponential term then becomes zero, and (15c) reduces to

$$[For $t = \infty$] $z = z_0 + Cx \quad (23)$$$

¹ Sand, Phil. Mag., [6] 1, 15 (1901).

² Practically speaking, for such values of at as make the sum term in (15) negligible. If one percent of $z - z_0$ be "negligible" from the point of view of the experimenter, $at = 4.40$ is high enough, so that for $k = 4 \times 10^{-6}$ and $l = 3.14 \times 10^{-2}$ cm, 0.044 second would be an "infinite" value of t .

i. e., there is a linear gradient of concentration throughout the diffusion layer.

The summation on the right of (15) thus shows the difference between the concentrations at any moment of the electrolysis and those at the stationary state; as with increasing t this term decreases, and ultimately vanishes, it will be spoken of as the "evanescent term" of (15) to distinguish it from the "stationary term" Cx .

The Stationary Term when k is a Function of z

Throughout this paper, the diffusion constant is supposed to be independent of the concentration; in the present paragraph, however, the important—but mathematically simple—case of the stationary state with constant current is dealt with on the assumption that k is a function of z . The equations deduced in this paragraph are not made use of in what follows.

Setting $k = f(z)$, the differential equation has the form:

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x} \left(f(z) \frac{\partial z}{\partial x} \right). \quad (A)$$

As however at the stationary state, z depends on x alone, (A) may be replaced by the "ordinary" differential relation

$$\frac{d}{dx} \left(f(z) \frac{dz}{dx} \right) = 0 \quad (B)$$

Hence $f(z) \frac{dz}{dx}$ has a constant value for all values of x ; at the electrode this is known to be equal to G ; therefore,

$$f(z) \frac{dz}{dx} = G, \quad (C)$$

and

$$\int_{z_0}^z f(z) dz = \int_0^x G dx = Gx; \quad (D)$$

therefore,

$$x = \frac{1}{G} \int_{z_0}^z f(z) dz, \quad (E)$$

which whenever $f(z)$ is known gives x explicitly in terms of z .

For example, if $f(z) = k_0 + k_1 z$ (F)

$$Gx = (k_0 z + \frac{1}{2} k_1 z^2) - (k_0 z_0 + \frac{1}{2} k_1 z_0^2), \quad (G)$$

From this, if desired, z may be expressed in terms of x , thus

$$z = \frac{-k_0 + \sqrt{k_0^2 + 2k_1(Gx + k_0 z_0 + \frac{1}{2} k_1 z_0^2)}}{k_1} \quad (H)$$

Similarly in many other cases it is possible to pass from Eq. (E) to one expressing z in terms of x ; when this is not possible, a graph may be drawn.

The "Limiting Current"

The "limiting current" for the change $z' - z_0$ is defined to be that current which at $t = \infty$ is just sufficient to bring the concentration at the electrode from z_0 to z' ; it may be denoted by \mathcal{J}' and the corresponding value of C by C' . Substituting z' for z , and l for x in (23),

$$[\text{For } t = \infty \text{ and } x = l] z' - z_0 = C'l,$$

$$\text{whence } C' = \frac{z' - z_0}{l}, \text{ and } \mathcal{J}' = \frac{96540 k \mathcal{A}(z' - z_0)}{l(1 + zu/\Sigma zu)}. \quad (24)$$

Thus any experiment in which z' , z_0 , and \mathcal{J}' are measured may serve to determine the ratio k/l . In the special case where $z' = 0$, $\mathcal{J}'/z_0 = \frac{96540 k \mathcal{A}}{(1 + zu/\Sigma zu)l}$. This relation has been used by Nernst and Merriam¹ and others for the determination of k/l .

As indicated by the heading of the table, the numbers entered in Table II give the values of $(z - z_0)/Cl$ at the electrode for different values of at . Since, however, from (24), $(z' - z_0)/Cl = C'/C = \mathcal{J}'/\mathcal{J}$, these same numbers give the limiting current \mathcal{J}' corresponding to any arbitrary change of concentration at the electrode if the time (at) is known at which some known current \mathcal{J} just brings about the same change. For example, the limiting current corresponding to

¹ Zeit. phys. Chem., 53, 235 (1905).

any change of concentration at the electrode is 0.164 times the current that will bring about the same change in the time $at = 0.05$. Conversely, the reciprocals of the numbers under $(z - z_0)/Cl$ give the current necessary to bring about any given change of concentration in a given time at , if the limiting current corresponding to the same change be known; to accomplish a given change in the time $at = 0.10$ requires 4.41 times the limiting current corresponding to that change. The "change of concentration" easiest recognized in the laboratory is often that from z_0 to 0.

Determination of k and of l

As both k and l are involved in (16), two experiments are in general required to determine both or either of them; one of these experiments may be a determination of the ratio k/l , by means of the limiting current as indicated above, and the other a measurement in which the time needed to bring about some known change of concentration at the electrode is determined. If this second measurement be so planned that $at > 0.5$, the "single term" approximation (17) may be employed: writing γ for the ratio k/l supposed known, this gives

$$l = \frac{0.4343 \pi^2 \gamma t}{4 \log_{10} \left[\frac{\pi^2}{8} \left(1 - \frac{\gamma(z' - z_0)}{G} \right) \right]}{0.09121 + \log_{10} \left(1 - \frac{\gamma(z' - z_0)}{G} \right)} \quad (25)$$

If at be less than 0.5, however, so that the "parabolic approximation" (22b) is applicable, k may be determined by means of it directly from one experiment, the change of concentration at the electrode under those circumstances being independent of l . This method of finding k has been employed by Sand; in his experiments, however, l was taken to be "infinite," and was not determined.

Graphical Representation

The curves of Fig. 1 give the values of $(z - z_0)/Cl$ through

the diffusion layer (for any fixed values of C , k , and l), for $t = 0$, for $t = \infty$ and for ten values of at ranging from 0.1 to 1.0; the curves have been drawn with fair accuracy, values of $(z - z_0)/Cl$ may be estimated from them to within one

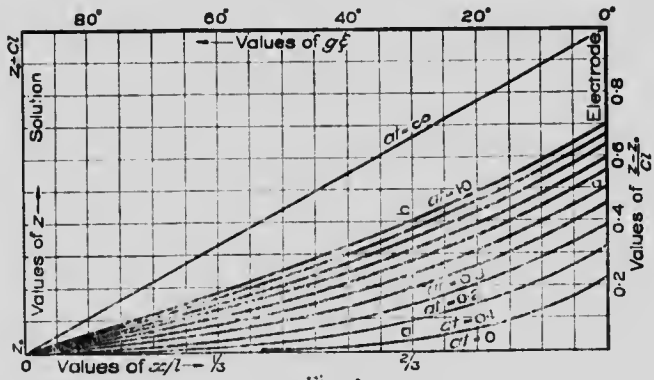


Fig. 1

percent of the value of Cl . As is clear from (15), values of z itself are not fixed by C , k , and l ; the point $z = 0$ is therefore not marked on the diagram.

In Fig. 2, the same data are plotted on a time base;

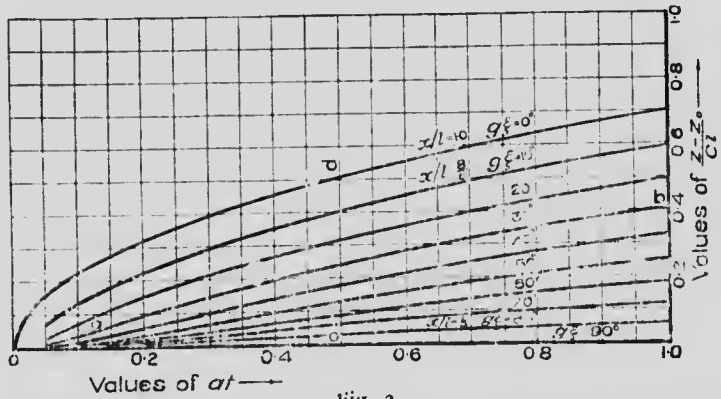


Fig. 2

the curves give the progress of the concentration change with the time (from $at = 0$, to $at = 1.0$) at ten equidistant cross-

sections of the diffusion layer. The line *ab* in Fig. 1 corresponds to the curve *ab* in Fig. 2, and the line *od* in Fig. 2 to the curve *od* in Fig. 1.

In Fig. 3, the relative change of concentration at the electrode, $(z - z_0)/Cl$ is plotted for the interval $at = 0$ to $at = 5.0$; in Fig. 4 the same data are plotted with logarithmic coordinates

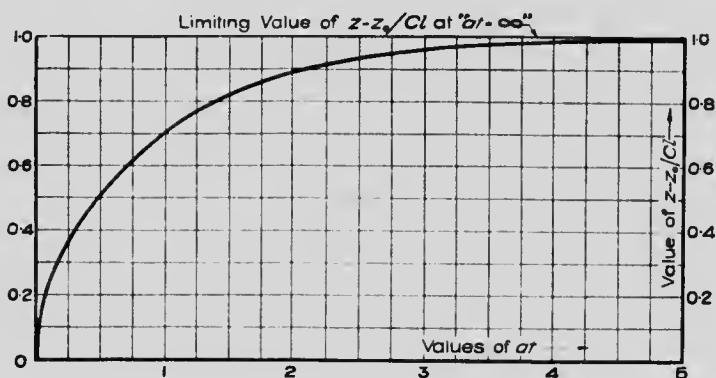


Fig. 3

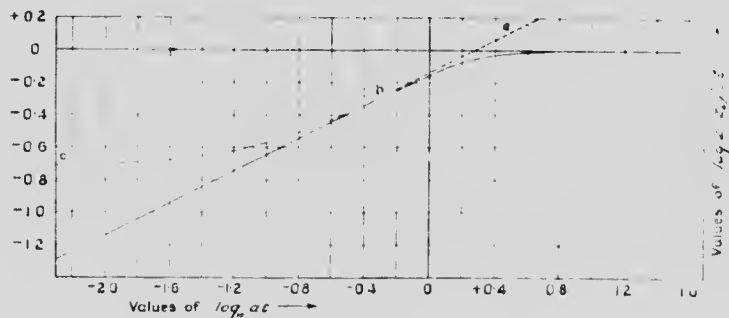


Fig. 4

(from $\log_{10} at = -2.30$ to 1.7 , *i. e.*, from $at = 0.005$ to $at = 50$). The curve *abc* represents the "first term approximation," the straight line *ca* the parabolic approximation, and the full line *abd* the true values of $\log_{10}(z - z_0)/Cl$.

Curve I of Fig. 5 gives the concentrations throughout the diffusion layer at $at = 0.5$ for fixed values of C and k

and for $l = l_1$; curve II gives the concentrations at $at = 0.1$ for the same values of C and k but for $l_2 = l_1\sqrt{5}$. Since a varies inversely as l^2 , t as well as C and k is the same for both curves, and the figure serves to illustrate the conclusion of (22b) that for small values of at , $(z - z_0)/C$ at the electrode is independent of l . As shown by the figure, the change of

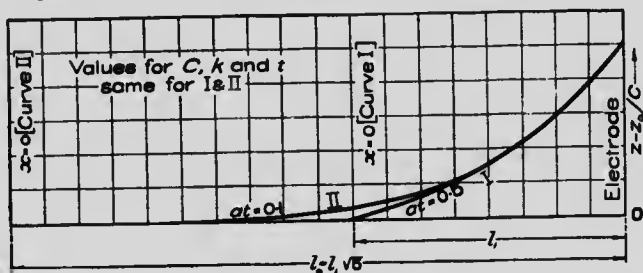


Fig. 5

concentration initiated at the electrode has hardly yet had time at $at = 0.1$ to spread more than half way to the "point of constant concentration," $x = 0$; shifting this point still further to the left could therefore have no effect on the concentration at the electrode.

Sec. 2.—Successive Currents in General

Eq. (15) and those deduced from it in the preceding paragraphs are applicable only when the current (and consequently C) remains constant during the electrolysis. It is now proposed to deal with the more general case where the currents J_1, J_2, J_3 , corresponding to C_1, C_2, C_3 , etc., act successively, C_1 from $t = 0$ to $t = t_1$, C_2 from t_1 to t_2 , C_3 from t_2 to t_3 , etc; as before, at $t = 0$, $z = z_0$ for all values of x .

Up to the moment t_1 , the values of z are given by (15); in particular,

$$[\text{For } t = t_1] z - z_0 = C_1 x - \frac{8lC_1}{\pi^2} \sum_{m^2} \frac{1}{m^2} e^{-m^2 at_1} \cos mg\zeta \quad (26a)$$

$$= C_2 x + (C_1 - C_2)x - \frac{8lC_1}{\pi^2} \sum_{m^2} \frac{1}{m^2} e^{-m^2 at_1} \cos mg\zeta \quad (26b)$$

$$= C_2 x - \frac{8l}{\pi^2} \sum_{m^2} \frac{1}{m^2} (C_1 e^{-m^2 at_1} + C_2 - C_1) \cos mg\zeta, \quad (26c)$$

the last transformation being effected by means of (12), which, since $(-1)^{n+1} \sin mgx = \cos mg\zeta$, may be brought into the form

$$Cx = \frac{8lC}{\pi^2} \sum \frac{1}{m^2} \cos mg\zeta. \quad (27)$$

Between $t = t_1$ and $t = t_2$, values of z are given by the expression

$$[For t_1 < t < t_2] \quad z - z_0 = C_2x - \frac{8l}{\pi^2} \sum \frac{1}{m^2} \{ e^{-m^2at_1} + C_2 - C_1 \} e^{-m^2a(t-t_1)} \cos mg\zeta \quad (28)$$

which satisfies *ii*, *iii*, *iv*,¹ and the condition that at $t = t_1$ the values of z along the x axis are those consequent on the action, from $t = 0$ to $t = t_1$, of the current \mathcal{J} .

In general

$$[For t_{p-1} < t < t_p] \quad z - z_0 = C_px - \frac{8l}{\pi^2} \sum \frac{1}{m^2} \{ C_1 e^{-m^2at} + C_2 - C_1 e^{-m^2a(t-t_1)} + \dots + C_r - C_{r-1} e^{-m^2a(t-t_{r-1})} + \dots + C_p - C_{p-1} e^{-m^2a(t-t_{p-1})} \} \cos mg\zeta \quad (29a)$$

$$= C_px - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \{ C_1 e^{-m^2at} + \sum_{r=2}^p C_r - C_{r-1} e^{-m^2a(t-t_{r-1})} \} \cos mg\zeta. \quad (29b)$$

The expression inside the brackets $\{\}$ can be rearranged thus:

$$\{ C_1(e^{-m^2at} - e^{-m^2a(t-t_1)}) + C_2(e^{-m^2a(t-t_1)} - e^{-m^2a(t-t_2)}) + \dots + C_r(e^{-m^2a(t-t_{r-1})} - e^{-m^2a(t-t_r)}) + \dots + C_p e^{-m^2a(t-t_{p-1})} \}$$

so that (29) may also be written

$$[For t_{p-1} < t < t_p] \quad z - z_0 = C_px - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \{ C_p e^{-m^2a(t-t_{p-1})} + \sum_{r=1}^{p-1} C_r (e^{-m^2a(t-t_{r-1})} - e^{-m^2a(t-t_r)}) \} \cos mg\zeta. \quad (29c)$$

¹ This is obvious if it be noted that the expression within the brackets $\{\}$ is a function of m only, not of x or t .

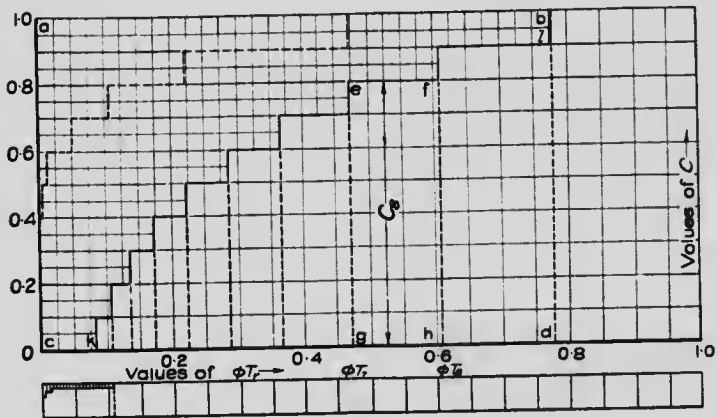
Finally, if T_r be written for $t - t_r$, the time elapsed since the current corresponding to C_r ceased to act, and ϕT_r , for $e^{-m^2 a(t-t_r)}$,

$$[For t_{p-1} < t < t_p] \quad z - z_0 = C_p x - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \{ C_p \phi T_{p-1} -$$

$$\sum_{r=1}^{p-1} C_r (\phi T_r - \phi T_{r-1}) \} \cos mg \frac{z}{2} \quad (29d)$$

which lends itself to graphical representation.

Figs. 6 and 7 illustrate the case of electrolysis by a succession of currents beginning at $t = 0$ with one ampere, followed by 2, 3, 4, . . . 10 amperes, each passing through the solution for the equal interval $at = 0.25$. The abscissae of the two



Figs. 6 and 7

figures give the values of ϕT_r , for $n = 1$ and $n = 2$ respectively, and the ordinates the values of C and of $C/9$ respectively for the ten currents; thus Fig. 6 corresponds to the first term of the n -sum in (29d) and Fig. 7 to the second term. The area $abcd$ equals $C_{10} \phi T_9$ (corresponding to $C_p \phi T_{p-1}$); $efhg$ equals $(\phi T_8 - \phi T_7) C_9$, $kefld$ equals $\sum_{r=1}^{p-1} C_r (\phi T_r - \phi T_{r-1})$, and $ackflb$ equals the whole expression within the $\{ \}$

brackets of (29d), for $n = 1$. The broken line in the upper left-hand corner of Fig. 6 represents the first term of the n -sum for the same ten currents each persisting for $at = 0.75$ instead of $at = 0.25$; the great reduction of the $\{ \}$ term of (29d) is obvious. It is quite clear from the figure, that the effect of previous history is much less on the second than on the first term, so that in deciding how far back it is necessary to go in taking account of the previous currents, the first term only need be considered.

Equation (29) in its various forms is the most general expression for $z = z_0$, all others given in Part I of this paper are deducible from it: Eq. (15) for instance results when $C_1 = C_2 = \dots = C_p$; equations for the periodic recurrence of a finite number of currents are deduced from (29) in Secs. 3 and 4, and Sec. 5 shows how the periodic recurrence of an infinite number of currents each but slightly different from the preceding may be dealt with. As usual, by substituting l for x , whereupon $\cos mgz$ becomes unity, expressions for the experimentally important concentrations at the electrode may be obtained.

Sec. 3.—Periodic Currents. I. Cycles with Two Beats

In the first "beat" the current \mathcal{C}_1 acts for θ_1 seconds, in the second beat the current \mathcal{C}_2 for θ_2 seconds; these two "beats" make up a "cycle" of duration $\theta = \theta_1 + \theta_2$ seconds, which may be repeated again and again. It is convenient to introduce the symbol τ to represent the time elapsed since the beginning of the beat which is in progress at the moment t , t being counted as always from the moment $t = 0$ when the first current is thrown on; at $t = 0$, $z = z_0$ for all values of x .

In applying (29) to this case,

$$\begin{aligned}
 C_1 &= C_3 = C_5, \text{ etc.} & \theta_1 &= t_1 - (t_3 - t_2) & (t_5 - t_4) &= (t_7 - t_6), \text{ etc.} \\
 C_2 &= C_4 = C_6, \text{ etc.} & \theta_2 &= (t_2 - t_1) - (t_4 - t_3) &= (t_6 - t_5), \text{ etc.} \\
 \theta &= \theta_1 + \theta_2 & &= (t_1 - t_2) - (t_6 - t_5), \text{ etc.} & &= \theta_1 + \theta_2.
 \end{aligned}$$

Thus, during the p th beat, if p be odd ($p = 2q + 1$), $C_p = C_1$

and $t = q\theta + \tau$; if p be even ($p = 2q$), $C_p = C_2$, and $t = (q-1)\theta + \theta_1 + \tau$.

In the first case (p odd) on making these substitutions (29) becomes

$$[p \text{ odd}] \quad z - z_0 = C_1 x - \frac{8l}{\pi^2} \sum \frac{e^{-m^2 at}}{m^2} \left\{ C_1 + (C_2 - C_1) [e^{m^2 a \theta_1} (1 + e^{m^2 a \theta} + e^{2m^2 a \theta} + \dots + e^{(q-1)m^2 a \theta}) - e^{m^2 a \theta} (1 + e^{m^2 a \theta} + e^{2m^2 a \theta} + \dots + e^{(q-1)m^2 a \theta})] \right\} \cos mg\xi, \quad (30a)$$

whence, summing the geometrical series, eliminating q , and rearranging,

$$[p \text{ odd}] \quad z - z_0 = C_1 x + \frac{8l(C_2 - C_1)}{\pi^2} \sum \frac{e^{-m^2 at}}{m^2} \cdot \frac{e^{m^2 a \theta} - e^{m^2 a \theta_1}}{e^{m^2 a \theta} - 1} \cos mg\xi - \frac{8l}{\pi^2} \sum \frac{e^{-m^2 at}}{m^2} \left\{ C_1 + (C_2 - C_1) \frac{e^{m^2 a \theta} - e^{m^2 a \theta_1}}{e^{m^2 a \theta} - 1} \right\} \cos mg\xi. \quad (30b)$$

Similarly, it may be shown that where p is even

$$[p \text{ even}] \quad z - z_0 = C_2 x + \frac{8l(C_1 - C_2)}{\pi^2} \sum \frac{e^{-m^2 at}}{m^2} \cdot \frac{e^{m^2 a \theta} - e^{m^2 a \theta_2}}{e^{m^2 a \theta} - 1} \cos mg\xi - \frac{8l}{\pi^2} \sum \frac{e^{-m^2 at}}{m^2} \left\{ C_1 + (C_2 - C_1) \frac{e^{m^2 a \theta} - e^{m^2 a \theta_1}}{e^{m^2 a \theta} - 1} \right\} \cos mg\xi. \quad (31)$$

In (30b) and (31), the term involving $e^{-m^2 at}$, which decreases with increasing t and ultimately vanishes, may be spoken of as the "evanescent term"; it is the same in both equations, so that on plotting with z and t as axes the evanescent term would be represented by a continuous curve with no abrupt changes of direction at the beginning of a new beat. A plot of the "stationary terms" from the two equations (what is left of the right-hand members of (30b) and (31) when the evanescent term has been withdrawn) would give a zigzag line.

If x be replaced by l in these equations (and consequently $\cos mg\xi$ by unity) expressions for the concentrations at the electrodes are obtained. If t be set $= \infty$ thus reducing the evanescent term to zero, expressions for the concentrations at the stationary state are obtained. If τ be set $= 0$ (and consequently $e^{-m^2 a \tau} = \text{unity}$) expressions for the con-

centrations at the beginnings of odd or even beats (*i. e.*, at the ends of even or odd beats) respectively are obtained. If $C_2 = C_1$ the expression for constant current, (15), is obtained; if $C_2 = -C_1$ the equations apply to the simplest form of alternating current, and if $C_2 = 0$ to "intermittent" currents. Special cases of the latter will be examined in detail (see pages 840 and 843).

If the first, third, etc., beats last long enough to bring about a linear distribution of concentration throughout the diffusion layer, *i. e.*, if in (31), $a\theta_1 = \infty$ (see foot-note, page 828) the concentrations throughout the even beats will be represented by

$$[\text{For } \theta_1 = \infty] z - z_0 = C_2 x + \frac{4l(C_1 - C_2)}{\pi^2} \sum \frac{e^{-m^2 a \tau}}{m^2} \cos m g \frac{z}{2}. \quad (32)$$

Centre and Amplitude of Swing

When the stationary state is reached, *i. e.*, when the evanescent term has become zero or approximately so, the concentration at any point in the diffusion layer oscillates between two extreme values, one at the end of each beat. Half the sum of the extreme values of the concentration change gives the "centre of swing" or mean value of the concentration change at that point; half their difference gives the "amplitude" or greatest deviation of the concentration above and below its mean value. An expression for the amplitude, and one for $z - z_0$ at the centre of swing, may accordingly be obtained by taking half the difference and half the sum respectively of the values of $z - z_0$ given by (30b) and (31) after setting $t = \infty$ and $\tau = 0$.

$$[\text{Amplitude}] \quad \frac{1}{2} (C_1 - C_2) x + \frac{4l(C_1 - C_2)}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 a \theta_1} + e^{m^2 a \theta_2} - 2e^{m^2 a \theta}}{e^{m^2 a \theta} - 1} \cos m g \frac{z}{2}. \quad (33)$$

$$[\text{At centre}] \quad z - z_0 = \frac{1}{2} (C_1 + C_2) x + \frac{4l(C_1 - C_2)}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2 a \theta_1} - e^{m^2 a \theta_2}}{e^{m^2 a \theta} - 1} \cos m g \frac{z}{2}. \quad (34)$$

Very Large and Very Small Values of θ

If both θ_1 and θ_2 are large, the concentration at any point oscillates between $z_0 + C_1x$ and $z_0 + C_2x$; on evaluating the θ fractions in (33) and (34), $\frac{1}{2}(C_1 + C_2)x$ is accordingly found as the expression for $z - z_0$ at the centre, and $\frac{1}{2}(C_1 - C_2)x$ for the amplitude.

When $a\theta$ is very small, the centre is $(C_1\theta_1 + C_2\theta_2)x$ and the amplitude is very small; *i. e.*, the "zigzag" becomes almost a straight line. Thus the stationary state reached by electrolysis with a rapidly interrupted, alternated, or varied two-beat current is practically the same as would be reached by electrolysis with a constant current of the same number of coulombs per second (reckoned algebraically). Progress towards the stationary state is likewise the same in the two cases, as may be seen by evaluating the evanescent term of (30b) or (31) for very small values of θ_1 and θ_2 . Stationary and evanescent terms together give:

$$[\text{For } \theta \text{ very small}] \quad z - z_0 = (C_1\theta_1 + C_2\theta_2)x - \frac{8l}{\pi^2} (C_1\theta_1 + C_2\theta_2) \sum \frac{e^{-m^2at}}{m^2} \cos m\theta z. \quad (35)$$

It may be noticed that this equation becomes equivalent to (15c) on writing $C_1\theta_1 + C_2\theta_2 = C$.

A Special Case of Intermittent Currents

To obtain an expression for the concentration changes at the electrode during electrolysis with an intermittent current, where the periods of electrolysis with the current C , and the intermissions, each last $0.5/a$ seconds, equations (30b) and (31) may be used setting $x = l$, $C_2 = 0$, $C_1 = C$, $a\theta_1 = a\theta_2 = 0.5$; so that $at = 0.5(p - 1) + a\tau$, where $a\tau$ changes from 0 to 0.5 during each beat.

The evanescent term (which of course is the same for both equations) and the two stationary terms are as follows:

$$\left. \begin{aligned}
 [\text{Evanescent term}] &= \frac{8IC}{\pi^2} \sum \frac{1}{m^2} \frac{e^{-m^2 at}}{e^{0.5m^2} + 1} \\
 [\text{Stat. term, } p \text{ odd}] &= Cl - \frac{8IC}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2(0.5 - at)}}{e^{0.5m^2} + 1} \\
 [\text{Stat. term, } p \text{ even}] &= \frac{8IC}{\pi^2} \sum \frac{1}{m^2} \frac{e^{m^2(0.5 - at)}}{e^{0.5m^2} + 1}
 \end{aligned} \right\} (36)$$

Fig. 8 gives a graph of the evanescent term, and the stationary terms of (36) and their sum, *i. e.*, the values¹ of $(z - z_0)/Cl$ at the electrode.

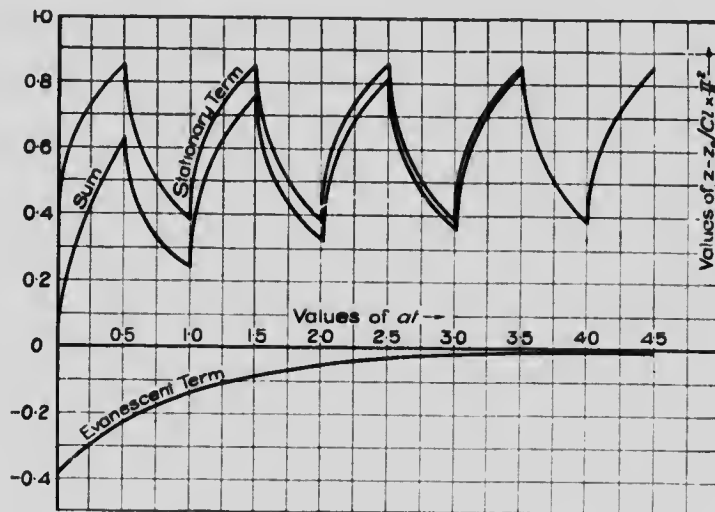


Fig. 8

Table III gives, for a number of values of a_0 , the values of $(z - z_0)/Cl$ at the electrode at the end of the 1st, 2d, 3d, 4th, and ∞ th beats of current (*i. e.*, for $p = 1, 3, 5, 7,$ and ∞). The numbers under $p = 1$ are the same as those of Table II, those under $p = \infty$ are calculated from the stationary term of (31) after setting $x = l, \tau = 0, C_2 = 0,$

¹ The values actually plotted, however, are those here described multiplied by $\pi^2/4 = 1.2337.$

$C_1 = C$; for purposes of computation this term is best put in the form:

$$[\text{For } p = \infty] \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \cdot \frac{1}{e^{m^2 a \theta_1} + 1} \quad (37)$$

The figures in a horizontal line of Table III thus give the ordinates of the peaks of $(z - z_0) - t$ -curves, such as "Sum" in Fig. 8 which corresponds to the line opposite $a\theta_1 = 0.5$. As the sum of the extreme values of $z - z_0$ at the electrode when $\theta_1 = \theta_2$ is $C_1 l$ (twice the 'centre,' Eq. 34), the difference between unity and the figure under $p = \infty$ gives the ordinates of the lowest points reached by the curve when the stationary state is attained.

Just as with Table II, however, the figures of Table III are susceptible of a second interpretation. Writing \mathcal{J}'' for the intermittent current (when $\theta_1 = \theta_2$) which just brings the concentration at the electrode from z_0 to the arbitrary value z' at the end of a beat of current, the figures of Table III obviously give $(z' - z_0)/C''l$ for various values of $a\theta_1$ and p . But by (24), $(z - z_0)/l = C'$, where C' corresponds to the limiting current \mathcal{J}' , i. e., to the constant current which at $t = \infty$ can just reduce the initial concentration by the same amount. Therefore,

$$(z_0 - z')Cl = C'/C'' = \mathcal{J}'/\mathcal{J}'' \quad (38)$$

and the reciprocals of the figures in Table III give the intermittent currents needed with different values of $\theta_1 = \theta_2$ to bring the concentration at the electrode to any arbitrary value at the end of the first, second, etc., beats of current, as multiples of the limiting current corresponding to the same change of concentration.

Thus, for example, if one ampere acting continuously is just sufficient to bring the concentration at the electrode from z_0 to any selected value z' , the table shows that 1/0.507 amp. will be needed to bring about the same change in the time $a\theta_1 = 0.5$; while 1/0.625 amp. will do, if the current is allowed to pass for $a\theta_1 = 0.5$ and then again for the same period, after a pause of equal duration.

TABLE III
Values of $(z - z_0) C_l$ at the electrode

| Values of $a\theta_1, a\theta_2$ | $p = 1$ | $p = 3$ | $p = 5$ | $p = 7$ | $p = \infty$ |
|----------------------------------|---------|---------|---------|---------|--------------|
| 2.00 | 0.800 | 0.903 | 0.903 | 0.903 | 0.903 |
| 1.50 | 0.819 | 0.851 | 0.852 | 0.852 | 0.852 |
| 1.00 | 0.703 | 0.771 | 0.781 | 0.782 | 0.782 |
| 0.50 | 0.507 | 0.625 | 0.668 | 0.684 | 0.693 |
| 0.10 | 0.227 | 0.290 | 0.353 | 0.395 | 0.586 |
| 0.05 | 0.160 | 0.212 | 0.250 | 0.281 | 0.561 |
| 0.01 | 0.072 | 0.095 | 0.112 | 0.126 | 0.527 |
| 0.005 | 0.049 | 0.067 | 0.079 | 0.089 | 0.510 |
| 0 | 0 | 0 | 0 | 0 | 0.500 |

The Simplest Alternating Currents

If C_1 and C_2 as defined by (iv) and (8) are of opposite signs, (30b) and (31) give the concentrations during electrolysis with the simplest form of alternating currents.

In the very simplest case, the two currents will be equal in strength, i. e., $C_2 = -C_1$, and the beats will be of equal duration, i. e., $\theta_1 = \theta_2$; on making these substitutions it will be found that (for both odd and even beats)

$$[For t = \infty and x = l] \frac{z - z_0}{C_l} = 2 \left[\frac{z - z_0}{C_l} \right] - 1 \quad (39)$$

where the expression in square brackets denotes the corresponding values of $(z - z_0) C_l$ (at $t = \infty$ and $x = l$) calculated for electrolysis with the simplest intermittent current, $C_2 = 0, \theta_1 = \theta_2$.

Thus by doubling the ordinates of the "stationary" curve in Fig. 8 and subtracting unity, points may be obtained for a graph of the concentrations at the stationary state when electrolyzing with the simplest alternating current, where $a\theta_1 = a\theta_2 = 0.5$. Similarly, ordinates for the peaks of the stationary curves for different values of $a\theta$ may be obtained by doubling the numbers under $p = \infty$ in Table III and subtracting unity.

In some cases it may be interesting to know the relation between C_1, C_2, θ_1 , and θ_2 that will just bring $z = z_0$ to some

previously determined value at the end of a given beat of current. At the surface of a silver electrode in a solution of copper salt, it may be assumed, for the purpose of illustration, that when C is positive silver will go into solution, and that when C is negative silver (and not copper) will be redeposited so long as there is any left in the solution at the electrode. If there were no silver in the solution originally, part of that dissolved by the current (during the "anode beat," $C = C_1$) would diffuse away from the electrode; so in order to prevent the deposition of copper during the succeeding "cathode" beat ($C = C_2$, where C_2 as defined by (8) and (iv) is negative) either C_2 must be arithmetically less than C_1 or θ_2 must be less than θ_1 .

Assuming that the two beats are of equal duration ($\theta_1 = \theta_2$), and that the stationary state has been reached, the concentration at the electrode at the end of a cathode beat will be represented by

$$\frac{z - z_0}{C_1 l} = 1 + \frac{8}{\pi^2} \left(\frac{C_2}{C_1} - 1 \right) \sum_{m=1}^{\infty} \frac{1 - e^{-m^2 a \theta_1}}{m^2 e^{m^2 a \theta_1} + 1} \quad (40)$$

Supposing $z_0 = 0$, *i. e.*, that there is (practically) no silver in the main body of the solution, the smallest value of C_1 that will prevent the deposition of copper during the cathode beats (where the current corresponds to C_2) may be calculated by setting $z = 0$ and solving for C_1/C_2 .

The result is:

$$1 - C_2/C_1 = \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1 - e^{-m^2 a \theta_1}}{m^2 e^{m^2 a \theta_1} + 1} \quad (41a)$$

Values of the expression on the right have been tabulated (for another purpose) under $p = \infty$ in Table III; indicating them for the moment by N ,

$$C_1/C_2 = 1 - N \quad (41b)$$

The values in the following Table (IV) have been calculated by (41b). As an instance of their application, if $a\theta_1 = a\theta_2 = 0.5$, a current of 2.26 amperes while the silver was anode would be needed to prevent the deposition of copper by a current of one ampere in the opposite direction;

and a quantity of silver equal to that dissolved by the action of $\frac{1}{2}(2.26 - 1.00) = 0.63$ amperes acting for $\theta_1 + \theta_2 = 1.0/a$ seconds would pass through the diffusion layer into the outside solution during each cycle of $1.0/a$ seconds duration.

TABLE IV

| | | | | | | | | | |
|-------------------------|------|-------|------|------|------|------|------|------|------|
| $a\theta_1 = a\theta_2$ | 0 | 0.005 | 0.01 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 | 2.00 |
| $-C_1/C_2$ | 1.00 | 1.08 | 1.11 | 1.28 | 1.42 | 2.26 | 3.59 | 5.76 | 9.31 |

Conversely, the concentration of the electrode solution at which black copper begins to be deposited during the electrolysis of copper sulphate solutions, and the effect of acid, etc., on that concentration, might be determined by measuring θ_1 , θ_2 , C_1 , and C_2 in suitably planned experiments.

Sec. 4. -Periodic Currents. II. Cycles with Four Beats.

One case only need be considered in detail. If the two currents referred to in the discussion of cycles with two beats be obtained from a commutator made of copper bars separated by some insulating material, (30b) and (31) are not strictly applicable; for in reality the cycle will consist of four beats, the first lasting θ_1 seconds with a current corresponding to C_1 , the second for the short period d seconds during which the brush is passing the insulation and no current flows, the third for θ_2 seconds with current corresponding to C_2 , and finally the fourth with no current for d seconds again. The duration of the cycle may be represented by $\theta = \theta_1 + \theta_2 + 2d$.

By inserting the proper values in (29c) the following expressions may be obtained:

$$[For p = 4q + 1] z = z_0 = C_1 \left\{ \frac{Sl}{\pi^2} \sum \frac{e^{-m \cdot at}}{m^2} (C_1 + B_m \cos mqz) + \frac{Sl}{\pi^2} \sum \frac{e^{-m \cdot at}}{m^2} B_m \cos mqz \right\} \quad (42)$$

$$[For p = 4q + 3] z = z_0 = C_2 \left\{ \frac{Sl}{\pi^2} \sum \frac{e^{-m \cdot at}}{m^2} [(C_2 + C_1) e^{-m \cdot a(\theta_1 + d)} e^{-m \cdot at}] + B_m e^{-m \cdot a(\theta_1 + d)} \cos mqz \right\} + \frac{Sl}{\pi^2} \sum \frac{e^{-m \cdot at}}{m^2} B_m \cos mqz \quad (42)$$

where

$$B_m(e^{m^2 a \theta} - 1) = C_1(1 - e^{m^2 a \theta_1}) + C_2\{e^{m^2 a(\theta_1 + d)} - e^{m^2 a(\theta_1 + \theta_2 + d)}\}.$$

If $d = 0$, the two equations (42) reduce to (30b) and (31) respectively. It may be noticed that their evanescent terms are identical.

Sec. 5.—Periodic Currents. III. Sinusoidal Currents, Fourier Form.

If the difference between any two successive currents be infinitely small, and the number of currents be infinite, the difference $C_r - C_{r-1}$ in (29b) becomes a differential, and the summation with respect to r becomes an integration. Values for the concentration-changes during electrolysis with a sinusoidal current, where

$$[At and after t = 0] C = M \sin(\omega t + \alpha)$$

may thus be obtained.

Writing u in place of t_r to save printing, (29b) becomes:

$$z - z_0 = Mx \sin(\omega t + \alpha) - \frac{8l}{\pi^2} \sum_{m^2}^1 \{ M e^{-m^2 a t} \sin \alpha + \int_0^t M \omega e^{-m^2 a(t-u)} \cos(\omega u + \alpha) du \} \cos mg \xi, \quad (43a)$$

$$= Mx \sin(\omega t + \alpha) - \frac{8l}{\pi^2} \sum_{m^2}^1 \{ M e^{-m^2 a t} \sin \alpha + \frac{M \omega e^{-m^2 a t}}{m^4 a^2 + \omega^2} [e^{m^2 a t} (\omega \sin \omega t + \alpha + m^2 a \cos \omega t + \alpha) - (\omega \sin \alpha + m^2 a \cos \alpha)] \} \cos mg \xi. \quad (43b)$$

$$= Mx \sin(\omega t + \alpha) - \frac{8lM\omega}{\pi^2} \sum_{m^2}^1 \frac{\omega \sin \omega t + \alpha + m^2 a \cos \omega t + \alpha}{m^4 a^2 + \omega^2} \cos mg \xi - \frac{8lMa}{\pi^2} \sum_{m^2}^1 \frac{m^2 a \sin \alpha - \omega \cos \alpha}{m^4 a^2 + \omega^2} e^{-m^2 a t} \cos mg \xi. \quad (43c)$$

$$= \frac{2Mk}{l} \sum_{m^2}^1 \frac{m^2 a \sin \omega t + \alpha - \omega \cos \omega t + \alpha}{m^4 a^2 + \omega^2} \cos mg \xi - \frac{2Mk}{l} \sum_{m^2}^1 \frac{m^2 a \sin \alpha - \omega \cos \alpha}{m^4 a^2 + \omega^2} e^{-m^2 a t} \cos mg \xi. \quad (43d)$$

(43d) being derived from (43c) by using (27) and writing $\pi^2 k/4l^2$ for a in the coefficient of the summation.

The last term on the right of (43c) and (43d) constitutes the "evanescent term", while the first term and the first sum together in (43c) or the first sum in (43d) form the "stationary term" which alone remains when the stationary state is reached. If $\omega = 0$, (43) reduces to (15) with $M \sin a$ in place of C .

The same method may obviously be employed for expressing the concentration changes produced by currents which vary with the time according to any other law. Writing $C = f(t)$, (29) becomes

$$z - z_0 = xf(t) - \frac{2k}{l} \sum \left\{ \frac{f(t)}{m^2 a} - e^{-m^2 at} \int_0^t e^{m^2 au} f(u) du \right\} \cos mg\xi. \quad (44a)$$

$$= \frac{2k}{l} \sum \left\{ e^{-m^2 at} \int_0^t e^{m^2 au} f(u) du \right\} \cos mg\xi. \quad (44b)$$

The Stationary State When $l\sqrt{\frac{\omega}{k}}$ is Large

The exponential multiplier, $e^{-m^2 at}$, causes the series in the evanescent term to converge more rapidly than that in the stationary term; with large values of l particularly, the convergence of the latter is very slow. In the next section another form of the stationary term will be obtained which is more suitable for computation; here it is proposed to find the special value assumed by the stationary term of (43d)

when $l\sqrt{\frac{\omega}{k}} = \infty$.

The stationary term may be written

$$\sum_{n=1}^{\infty} \frac{2m^2 akM \sin \omega t + \alpha}{m^4 a^2 + \omega^2} \cos mg\xi - \sum_{n=1}^{\infty} \frac{2kM\omega \cos \omega t + \alpha}{m^4 a^2 + \omega^2} \cos mg\xi. \quad (45a)$$

Defining¹ $H = \xi \sqrt{\frac{\omega}{k}}$, $\mu = \sqrt{\frac{\omega}{2k}}$, and $\phi = m \sqrt{\frac{a}{\omega}} = \frac{(2n-1)\pi}{2l} \sqrt{\frac{k}{\omega}}$;

while n increases by unity, ϕ increases by $\Delta\phi = \frac{\pi}{l} \sqrt{\frac{k}{\omega}}$.

Introducing these symbols (45a) becomes

$$\sqrt{2} \frac{M \sin \omega t + \alpha \sum_{n=1}^{\infty} \frac{\phi^2 \cos H\phi}{\phi^4 + 1} \Delta\phi}{\pi\mu} - \frac{\sqrt{2} M \cos \omega t + \alpha \sum_{n=1}^{\infty} \frac{\cos H\phi}{\phi^4 + 1} \Delta\phi}{\pi\mu}. \quad (45b)$$

As $l \sqrt{\frac{\omega}{k}}$ increases, ϕ decreases; until when $l \sqrt{\frac{\omega}{k}} = \infty$, $\Delta\phi = d\phi$ and the summation from $n = 1$ (or $\phi = \frac{\pi}{2l} \sqrt{\frac{k}{\omega}}$) to $n = \infty$ becomes an integration between the limits 0 and ∞ .

$$[\text{For } l \sqrt{\frac{\omega}{k}} = \infty] \text{ Stat. term} = \frac{\sqrt{2} M \sin \omega t + \alpha \int_0^{\infty} \frac{\phi^2 \cos H\phi}{\phi^4 + 1} d\phi}{\pi\mu} - \frac{\sqrt{2} M \cos \omega t + \alpha \int_0^{\infty} \frac{\cos H\phi}{\phi^4 + 1} d\phi}{\pi\mu}. \quad (46a)$$

By using the partial fractions $\frac{2\phi^2}{1 + \phi^4} = \frac{i}{1 + \phi^2 i} - \frac{i}{1 - \phi^2 i}$ and $\frac{2}{1 + \phi^4} = \frac{1}{1 + \phi^2 i} + \frac{1}{1 - \phi^2 i}$, where $i = \sqrt{-1}$, and setting ϕ^2 alternately equal to $\phi^2 i$ and to $-\phi^2 i$ these integrals may be made to depend upon the known form

$$\int_0^{\infty} \frac{\cos n\phi}{\phi^2 + 1} d\phi = \frac{\pi}{2} e^{-n}.$$

Their values are:

$$\left. \begin{aligned} \int_0^{\infty} \frac{\phi^2 \cos H\phi}{\phi^4 + 1} d\phi &= -\frac{\pi}{2} e^{-\frac{H}{\sqrt{2}}} \sin\left(\frac{H}{\sqrt{2}} - \frac{\pi}{4}\right) \\ \int_0^{\infty} \frac{\cos H\phi}{\phi^4 + 1} d\phi &= \frac{\pi}{2} e^{-\frac{H}{\sqrt{2}}} \sin\left(\frac{H}{\sqrt{2}} + \frac{\pi}{4}\right). \end{aligned} \right\} \quad (47)$$

¹This use of the letters H , ϕ and ψ , is restricted to equations (45) and (46).

Introducing these values in (46a) and rearranging

$$[\text{For } l \sqrt{\frac{\omega}{k}} = \infty] \text{ Stat. term} = \frac{-M}{\mu\sqrt{2}} e^{-\mu\xi} \cos(\omega t + \alpha - \mu\xi + \frac{\pi}{4}) \quad (46b)$$

$$= \frac{M}{\mu\sqrt{2}} e^{-\mu\xi} \sin(\omega t + \alpha - \mu\xi - \frac{\pi}{4}). \quad (46c)$$

This expression has already been obtained by Warburg,¹ for “ $l = \infty$,” direct from the differential equation, by means of a Fourier’s integral.

Sec. 6. —Sinusoidal Currents Continued (Hyperbolic Form)

The expression (43) for the concentrations throughout the diffusion layer during electrolysis with a sinusoidal current, which has been deduced in the preceding section, is in many cases very inconvenient for purposes of computation. In the present section another form will be obtained; for this purpose, however, it is necessary to go back to the original differential equation.

In (1), viz.:

$$z - D = Cx + \Sigma(A_n \sin E_n x + B_n \cos E_n x)e^{-E_n kt} \quad (1)$$

the “stationary term” (S) is to fulfil the conditions

[Solution condition] At $x = 0$, $\partial S / \partial x = 0$ for all values of t (v)

[Electrode condition] At $x = l$, $\partial S / \partial x = C$ for all values of t (vi)

while the “evanescent term” (V), viz. the summation, is made to fulfil the conditions

[Solution condition] At $x = 0$, $\partial V / \partial x = 0$ for all values of t (vii)

[Electrode condition] At $x = l$, $\partial V / \partial x = 0$ for all values of t (viii)

[Initial condition] At $t = 0$, $V + S = 0$ for all values of x (ix)

by assigning suitable values to A_n , B_n and E_n . Each term separately is a particular solution of the differential equation (ii).

By the use of Fourier’s series, as illustrated on pg. 824, it is obviously possible to make the evanescent term comply

¹ Wied. Ann., 67, 493 (1899).

² See page 854.

with the three conditions *vii*, *viii*, and *ix*, no matter what S may be; so that if it were possible to construct a stationary term which was a solution of (*iii*) and for which in addition

[Solution condition] At $x = 0$, $\partial S / \partial t = 0$ for all values of t (v)

[Electrode condition] At $x = l$, $\partial S / \partial x =$

$$M \sin(\omega t + \alpha) \text{ for all values of } t, \quad (x)$$

an expression could be obtained directly for the values assumed by z during electrolysis with the current $\mathcal{I} = 96540 \frac{Mk \sin(\omega t + \alpha)}{1 + zu / \Sigma zu}$ amperes (see pg. 821).

This course is followed in the succeeding paragraphs, and the resulting equation (59), while identical in meaning with (43), is much more convenient in form for certain computations.

(a) The Stationary Term, S

A hint as to the general form with which to begin is furnished by the exponential form of the evanescent term in (1).

$$\text{Let } S = (A_1 e^{rx} + A_2 e^{-rx}) e^{r^2 kt} + (B_1 e^{ix} + B_2 e^{-ix}) e^{i \omega t}. \quad (48)$$

By differentiating it will be seen at once that to satisfy (v) it is necessary to set

$$A_2 = -A_1, \text{ and } B_2 = -B_1. \quad (49)$$

Because of (v) — writing A for A_1 , and B for B_1 , and putting $M \sin(\omega t + \alpha)$ in the exponential form¹ —

$$\gamma A (e^{rl} + e^{-rl}) e^{r^2 kt} + \lambda B (e^{il} + e^{-il}) e^{i^2 kt} = \frac{M}{2i} (e^{i(\omega t + \alpha)} - e^{-i(\omega t + \alpha)}) \quad (50)$$

¹ The relations used in making the transformations of these paragraphs are:

$$\begin{aligned} i &= \sqrt{-1} \\ 2 \cos y &= e^{iy} + e^{-iy} & 2i \sin y &= e^{iy} - e^{-iy} \\ 2 \cosh y &= e^y + e^{-y} & 2 \sinh y &= e^y - e^{-y} \\ \sinh 2y &= 2 \sinh y \cdot \cosh y \\ \cosh 2y &= \cosh^2 y + \sinh^2 y \\ \cosh^2 y - \sinh^2 y &= 1 \\ \sqrt{1+i} &= \sqrt{2} & \log \text{nat } i &= (-1)^{n+1} (2n-1) i \pi / 2 \\ \sqrt{1-i} &= (1-i) / \sqrt{2} \end{aligned}$$

which can be satisfied by setting

$$\gamma^2 k = i\omega, \quad \text{whence } \gamma = (1 + i) \sqrt{\frac{\omega}{2k}} \quad (51)$$

$$\lambda^2 k = -i\omega, \quad \text{whence } \lambda = (1 - i) \sqrt{\frac{\omega}{2k}}, \quad (52)$$

$$A = \frac{M e^{i\alpha}}{2i\gamma(e^{\gamma l} + e^{-\gamma l})}, \quad B = \frac{-M e^{-i\alpha}}{2i\lambda(e^{\lambda l} + e^{-\lambda l})}. \quad (53)$$

Introducing these values of A , B , γ , l into (48), (iii) (v) and (x) are satisfied, and the result may be written

$$S = \frac{M}{2\mu} \{ (J - H)(F \cos - G \sin) + (J + H)(F \sin + G \cos) \} \quad (54a)$$

$$= \frac{-M}{2\mu} \{ (JG - HF)(\sin - \cos) - (HG + JF)(\sin + \cos) \}, \quad (54b)$$

$$= \frac{-M}{\mu\sqrt{2}} \{ (JG - HF) \cos \omega t + \alpha - \frac{3}{4}\pi + (HG + JF) \sin \omega t + \alpha - \frac{3}{4}\pi \} \quad (54c)$$

$$= \frac{M}{\mu\sqrt{2}} \sqrt{(F^2 + G^2)(H^2 + J^2)} \cdot \sin(\omega t + \alpha + \gamma - \frac{1}{4}\pi), \quad (54d)$$

where

$$\mu = \sqrt{\frac{\omega}{2k}},$$

$$F = \cosh l\mu \cdot \cos l\mu / (\cos^2 l\mu + \sinh^2 l\mu),$$

$$G = -\sinh l\mu \cdot \sin l\mu / (\cos^2 l\mu + \sinh^2 l\mu),$$

$$H = \sinh \mu x \cdot \cos \mu x,$$

$$J = \cosh \mu x \cdot \sin \mu x,$$

$$\gamma = \tan^{-1}(JF + HG) / (HF - JG),$$

“sin” and “cos” are written, in (54a) and (54b) only, for $\sin(\omega t + \alpha)$ and $\cos(\omega t + \alpha)$ respectively.

Conversion of the Hyperbolic Form of S into the Fourier Form

To check this result, (54) may be converted into the stationary term of (43); the form (54a) is the most convenient for the transformation. It is first neces-

sary to develop J and H as series of sines of odd multiples of $\pi x/2l$

Writing $m = 2n - 1$, $P = 2l\mu/\pi$, $\Theta = \pi x/2l$, the series are:

$$J = \cosh \mu x \cdot \sin \mu x = \cosh P\Theta \cdot \sin P\Theta = \\ 4^P (-1)^{\frac{m-1}{2}} \sum (m^2 + 2P^2) \cosh l\mu \cdot \cos l\mu - (m^2 - 2P^2) \sinh l\mu \cdot \sin l\mu \sin m\Theta.$$

$$H = \sinh \mu x \cdot \cos \mu x = \sinh P\Theta \cdot \cos P\Theta = \\ 4^P (-1)^{\frac{m-1}{2}} \sum (m^2 + 2P^2) \cosh l\mu \cdot \cos l\mu - (m^2 - 2P^2) \sinh l\mu \cdot \sin l\mu \sin m\Theta.$$

On carrying out the multiplications and additions indicated in (54a), writing g for $\pi/2l$, and replacing $(-1)^{\frac{m-1}{2}} \sin m\Theta$ by $\cos mg\frac{1}{2}$, the expression for S becomes

$$S = \frac{2Mk}{l} \sum \frac{m^2 g^2 k \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{m^4 g^4 k^2 + \omega^2} \cos mg\frac{1}{2}, \quad (54c)$$

which is identical with the stationary term of (43)

(b). *The Evanescent Term, V.*

$$\text{Let } V = (Ae^{\beta x} + Be^{-\beta x})e^{\beta t}. \quad (55)$$

As in the case of the stationary term, condition (vii) requires that

$$B = -A.$$

Condition (viii) requires that

$$A\beta(e^{\beta t} + e^{-\beta t})e^{\beta t} = 0 \text{ for all values of } t$$

which may be satisfied by setting

$$e^{\beta t} + e^{-\beta t} = 0, \text{ i. e. } e^{2\beta t} = -1, \text{ or } \beta t = \log nat i,$$

whence

$$\beta = \frac{(-1)^n - 1}{2l} (2n - 1)i\pi$$

where n is any positive integer. On substituting these values

¹ This use of the letter β is restricted to (55).

of B and β , (writing one term for each value of β) and converting into the trigonometrical form, (55) becomes

$$V = \sum 2A_n i (-1)^{n-1} e^{-\frac{(2n-1)^2 \pi^2 k t}{4l^2}} \sin \frac{(2n-1)\pi x}{2l}, \quad (56a)$$

$$= \sum 2i (-1)^{\frac{m-1}{2}} A_n e^{-m^2 g^2 k t} \sin mgx, \quad (56b)$$

$$= \sum 2i A_n e^{-m^2 g^2 k t} \cos mg\xi, \quad (56c)$$

m being written for $2n - 1$, g for $\pi/2l$, and ξ for $l - x$.

But, by (ix)

$$\sum 2i A_n \cos mg\xi = \frac{-2Mk}{l} \sum \frac{m^2 g^2 k \sin \alpha - \omega \cos \alpha}{m^4 g^4 k^2 + \omega^2} \cos mg\xi, \quad (57)$$

Therefore,

$$V = \frac{-2Mk}{l} \sum \frac{m^2 g^2 k \sin \alpha - \omega \cos \alpha}{m^4 g^4 k^2 + \omega^2} e^{-m^2 g^2 k t} \cos mg\xi, \quad (58)$$

which is identical with the evanescent term of (43d) since $g^2 k = a$.

(c) The Complete Expression, $S + V$

Thus from (54) and (58)

$$\begin{aligned} \text{[For sinusoidal current]} \quad z - z_0 &= S + V \\ &= \frac{M}{\mu \sqrt{2}} \sqrt{(I^2 + G^2)(H^2 + J^2)} \sin(\omega t + \alpha + \gamma - \frac{1}{2}\pi) \\ &\quad - \frac{2Mk}{l} \sum \frac{m^2 a \sin \alpha - \omega \cos \alpha}{m^4 a^2 + \omega^2} e^{-m^2 a t} \cos mg\xi, \end{aligned} \quad (59)$$

Equation (59) is the "hyperbolic form" of (43).

Values of $z - z_0$ at the electrode may be obtained by replacing x by l (and consequently $\cos mg\xi$ by unity). Thus, when the stationary state is reached

[Stat. at elec.] $z - z_0 =$

$$\frac{M}{2} \sqrt{\frac{k}{\omega}} \frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l} \sin(\omega t + \alpha + \gamma - \frac{1}{2}\pi), \quad (60)$$

where

$$\mu = \sqrt{\frac{\omega}{2k}}$$

and

$$[\text{at electrode}] \gamma = \tan^{-1} \frac{\sin 2l\mu}{\sinh 2\mu l} \quad (61)$$

With increasing values of $l\mu$, $\cos l\mu$ and $\sin l\mu$ vanish in comparison with $\sinh l\mu$, while $\sinh 2l\mu$ approaches equality with $2 \sinh^2 l\mu$. The value of the fraction $\frac{\sinh^2 2l\mu + \sin^2 2l\mu}{\sinh^2 l\mu + \cos^2 l\mu}$ thus approaches 2, and the value of " γ at the electrode" (61) approaches zero. Thus from (60)

$$[\text{For } t = \infty, \text{ at electrode}] z - z_0 = M \sqrt{\frac{k}{\omega}} \sin(\omega t + \alpha - \frac{1}{2}\pi). \quad (62)$$

The same results may be obtained by setting $\xi = 0$ in (46c); by means of (60), however, the limits within which the convenient equation (62) may be used can be ascertained. By looking up tables¹ of the hyperbolic functions it will be found that the substitution of (62) for (60) cannot introduce an error of more than one-half percent if $l\mu = l \sqrt{\frac{\omega}{2k}} > 3$. Assuming $\omega = 377$ (i. e., 60 cycles per second), and $k = 4 \times 10^{-6}$ (an average value) it follows that l is practically "infinite" for the purposes of this equation when it reaches 5×10^{-4} centimeters.

Amplitude

When the stationary state is reached, the values of z swing equally above and below z_0 ; the maximum values of $z - z_0$ being reached when $\sin(\omega t + \alpha + \gamma - \frac{1}{2}\pi) = 1$. An expression for the "amplitude" may accordingly be found by substituting this value in the stationary term of (59), or in (60) if the amplitude at the electrode be sought. From (46c) it follows that when $l = \infty$ the amplitude at any point in the diffusion layer is $\frac{M}{2} \sqrt{\frac{k}{\omega}} e^{-\mu z}$.

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The electric current is at its maximum when $\omega t + \alpha = \frac{1}{2}\pi$;

¹ Smithsonian Mathematical Tables; Hyperbolic Functions, Washington, published by the Smithsonian Institution 1909.

When the stationary state is reached, the concentration reaches its maximum whenever $\omega t + \alpha + \gamma - \frac{1}{2}\pi = \frac{1}{2}\pi$ (see Eq. 59). The difference, $\frac{1}{2}\pi - \gamma$, gives the phase difference or "lag" of the concentration wave behind the wave of current at the stationary state. The lag at the electrode may be found by computing γ from (61) and subtracting from $\frac{\pi}{4}$.

The angle γ is a function of $l\mu$ whose value rapidly falls off with increase in $l\mu$, while alternating in sign.

Illustration

As an illustration, a number of values of $(z - z_0)/M$ at the electrode have been computed for the case that $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, $\omega = 377$ (60 cycles per second), and $\alpha = \frac{1}{2}\pi$ (i. e., at the moment of throwing on the current, the latter is at its maximum). Fig. 9 gives a graph of the

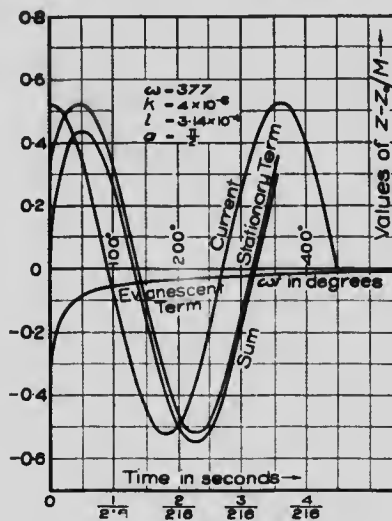
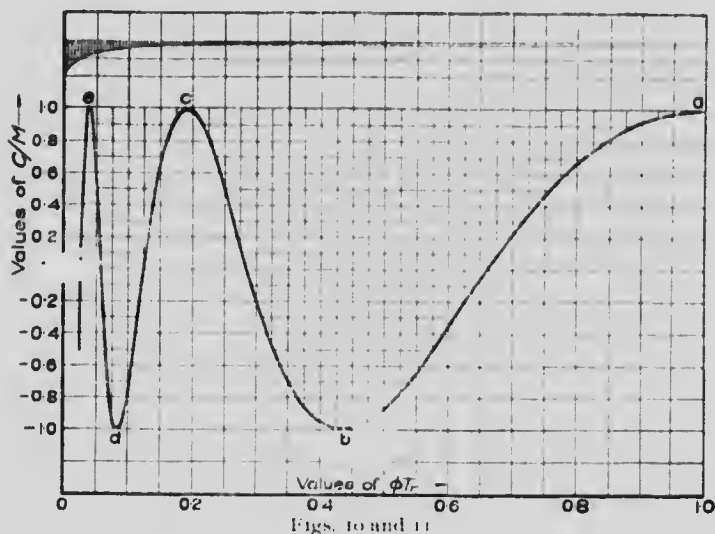


Fig. 9

evanescent term, of the stationary term, and of their sum, i. e., the values of $(z - z_0)/M$ at the electrode. The "current" wave is drawn on an arbitrary scale to illustrate the

difference in phase, (lag). Figs. 10 and 11 apply to the same case; the areas *abc*, *cde*, etc., above the curve correspond to the expression within the {} brackets of (29d).



Figs. 10 and 11

Sec. 7. Superposed Currents

Since all the equations of this Part satisfy the same "initial" condition and the same "solution" condition, and since the sum of a number of solutions of the linear differential equation (iii) is likewise a solution, the concentration changes produced by any number of currents acting simultaneously may be obtained by adding together the right hand members of the equations which give the concentration changes that would be produced by each current taken separately. Thus the effects produced by approximately sinusoidal currents could be computed if the current were analyzed in the ordinary way, and expressed as the sum of a pure sinusoidal current and its higher harmonics.

Other problems may be handled in the same way. Suppose, for instance, that the sinusoidal current for which $C = M \sin(\omega t + \alpha)$, and the direct current for which $C = C'$

both enter the solution by the same electrode; when the stationary state is reached, the amplitude of the concentration variation at the electrode caused by the sinusoidal current alone would be

$$\frac{M}{2} \sqrt{\frac{k}{\omega} \frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l}} \quad (6.3)$$

while that caused by the direct current alone would be zero; (6.3) thus gives the maximum deviation of z above and below the centre of swing. If the sinusoidal current acted alone, the centre of swing would be at $z = z_0$; if the direct current acted alone, the centre would be at $z = z_0 + C_1 l$; thus

$$C_1 l = \frac{M}{2} \sqrt{\frac{k}{\omega} \frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l}} \quad (6.4)$$

gives the lowest value of $z - z_0$ reached at the electrode during electrolysis.

If the electrode were of silver, for instance, in a solution of copper sulphate practically free from silver (*i. e.*, $z_0 = 0$), the ratio between the two currents that would just prevent the concentration of the silver salt at the electrode from falling to zero during the cycle might be found by setting the expression (6.4) equal to zero and solving for $\sqrt{2} C_1 M$ (since the reading¹ on the alternating current ammeter is proportional to $M \sqrt{2}$, and that on the direct current ammeter to C_1). This ratio is a function of $l/\omega k$, *i. e.*, of the time constant and of the duration of the cycle. If $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$ cm., and $\omega = 377$, the reading on the direct current ammeter would be 0.469 times that on the alternating.

If $\mu l \gg 3$, the *sinh* fraction in (6.4) is very closely equal to 2.00, and $C_1 M = \sqrt{k l \omega}$.

Measurements of this nature might prove an easy means

¹ In order that this may be true exactly as stated in the case under consideration it is necessary that the composite current be obtained synthetically from two separate circuits having the cell in their only common part. The alternating current ammeter must then be in the alternating current circuit and not in series with the cell.

of finding the ratio k/l ; if a "limiting current" were likewise determined (see pg. 830) the two measurements would give both k and l .

PART II

THE REACTION AT THE ELECTRODE CHANGES WHEN z AT THE ELECTRODE ATTAINS THE VALUE ζ

At the cathode in an acid solution of copper sulphate, the concentration of the copper, z , decreases when the current is thrown on; all values of $z - z_0$ will therefore be negative, they may be computed by (15c) remembering that G as defined in the Introduction, and therefore C as defined by (8), are negative. The curves *oad* for $at = 0.25$, *obe* for $at = 0.35$, *ofg* for $at = 0.50$, and *oh* for $t = \infty$, in Fig. 12 were so obtained; they differ from the corresponding

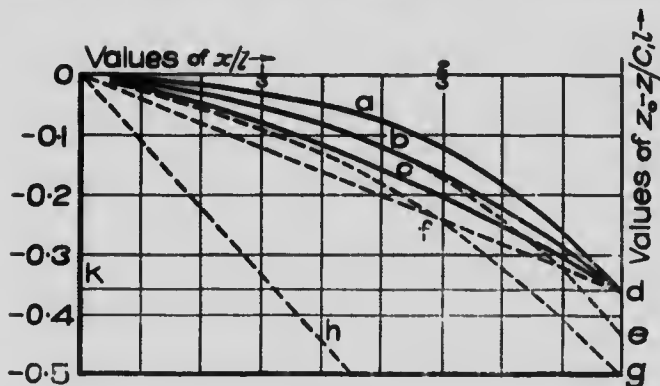


Fig. 12

curves in Fig. 1 only in scale, and in that $z - z_0$ is measured downward to indicate decrease in z as the electrode is approached.

As noted on pg. 832, (15c) merely fixes a relation between $(z - z_0)/Cl$, x/l , and at irrespective of the absolute values of z , x , and t ; the values of $(z - z_0)/Cl$ correspond to $z = 0$, and therefore the height in the figure of the horizontal line corresponding to $z = 0$, will vary from case to case. Assuming it to have the position given by *kd* in Fig.

12, z at the electrode will reach zero at $at = 0.25$; from that moment on, Eq. (15) which predicts still further fall in z (as indicated by the dotted lines *obe*, *ofg*, *oh*) ceases to be applicable, and must be replaced by another.

Sec. 8.—Constant Current

This new equation must be a solution of the differential equation (iii, Fick's law, pg. 820), it must also fulfil the "solution condition" (i, pg. 818), but the "electrode condition" (iv, pg. 821) must be replaced by

$$[\text{Electrode condition}] \text{ At } x = l, \text{ and } t > \vartheta, \partial z / \partial t = 0 \quad (vi)$$

which says that from a certain value of t (*viz.*: ϑ) onwards, the concentration at the electrode remains unaltered at the value ζ ; at the cathode in the copper solution $\zeta = 0$.

The "initial condition" (ii, pg. 819) also must be replaced, by

$$[Condition \text{ at } t = \vartheta] z = z_0 = C_1 x - \frac{8C_1 l}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} e^{-\frac{m^2 k \vartheta}{4l^2}} \cdot \cos \frac{m\pi(l-x)}{2l} \quad (vii)$$

signifying that at $t = \vartheta$, the values of z are those caused by the operation of the constant current C_1 for ϑ seconds.

From (1), introducing the special values of B_n and D from (3) and (4), and writing c instead of C_1 , q instead of n and ρ instead of E_n to avoid confusion with the formulas of Part I, the equation

$$z - z_0 = cx + \sum_{q=1}^{\infty} A_q e^{-\rho^2 t} \sin \rho x \quad (65)$$

may be obtained, which satisfies (iii) and (i). To satisfy (xi) it is necessary that

$$\rho = \frac{q\pi}{l} \quad (66)$$

as may be found by differentiating, etc., in the manner illustrated on pg. 823.

At the electrode, $z = \zeta$, and $x = l$, (hence $\sin \rho x = 0$) so that

$$c = \frac{\zeta - z_0}{l} \quad (67)$$

Introducing these values of ρ and c , (65) becomes

$$z - z_0 = \frac{\zeta - z_0}{l} x + \sum_{q=1}^{\infty} A_q e^{-\frac{q^2 \pi^2 k t}{l^2}} \sin \frac{q \pi x}{l}. \quad (68)$$

and satisfies *i*, *iii*, and *xi*.

To introduce (*xii*), the two expressions for $z - z_0$ at the moment $t = \vartheta$ obtainable from (*xii*) and (68) may be equated; replacing $(\zeta - z_0)/l$ by its value from (*xii*), viz.:

$$\frac{\zeta - z_0}{l} = C_1 \frac{8C_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} e^{-\frac{(2n-1)^2 \pi^2 k \vartheta}{4l^2}} \cos \frac{(2n-1)\pi(l-x)}{2l} \quad (69)$$

and rearranging

$$\sum_{q=1}^{\infty} A_q e^{-\frac{q^2 \pi^2 k t}{l^2}} \sin \frac{q \pi x}{l} = -\frac{8lC_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} e^{-\frac{(2n-1)^2 \pi^2 k \vartheta}{4l^2}} \left(\cos \frac{(2n-1)\pi(l-x)}{2l} - \frac{x}{l} \right) \quad (70a)$$

$$= \frac{8lC_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} e^{-\frac{(2n-1)^2 \pi^2 k \vartheta}{4l^2}} \sum_{q=1}^{\infty} \frac{2(2n-1)^2 (-1)^q}{q\pi(2n-1^2-4q^2)} \sin \frac{q \pi x}{l} \quad (70b)$$

(70b) being obtained by substituting an equivalent Fourier's series for the expression in brackets at the right of (70a) (see Appendix).

The value of A_q may now be found, for any fixed value of q , by removing the $\sum_{q=1}^{\infty}$ sign from both sides of (70b) and simplifying. Inserting the value so found in (68), there results:

$$z - z_0 = \frac{\zeta - z_0}{l} x + \frac{16lC_1 (-1)^{q+1}}{\pi^3} \sum_{n=1}^{\infty} \sum_{q=1}^{\infty} \frac{e^{-\frac{\pi^2 k}{4l^2} (3q^2 t - \vartheta + 2n-1^2 \vartheta)}}{q(2n-1^2-4q^2)} \sin \frac{q \pi x}{l} \quad (71)$$

which satisfies all four relations *i*, *iii*, *xi* and *xii*.

The symbol $\sum_{n=1}^{\infty} \sum_{q=1}^{\infty}$ signifies that the value of the expression on the right of (71) is to be computed for each value of q (for instance $q = 1$) combined with every value of n ($n = 1, 2, 3, \dots$) in turn; then for the next value of q , ($q = 2$) combined with every value of n , and so on; the sum of all these results is to be used in finding $z - z_0$.

Equation (71) is applicable whenever, for any reason, the concentration z at the electrode remains constant after reaching a certain value ζ . The case $\zeta = 0$ is no doubt the commonest, but cases where $\zeta - z_0 > 0$ may perhaps be met with where the product of electrolysis crystallizes at the electrode thus forming a saturated solution there; other cases where ν differs from zero may be sought in the electrolysis of solutions containing excess of a second salt whose decomposition voltage is only slightly greater than that of the salt to whose concentration z refers.

Illustration

In the case taken as illustration, ($\zeta = 0, a\theta = 0.25$) the constant current C_1 brings the concentration at the electrode from z_0 to zero in $0.25 a$ seconds; therefore, from (22a),

$$C_1 l = 2.784 z_0.$$

Hence

$$[\text{for } 0 < t < 0.25] \quad (z_0 - z)/z_0 = 2.784 \frac{\nu}{l} - 2.257 \sum_{m=1}^{\infty} \frac{1}{m^2} e^{-m^2 \nu t} \cos m \zeta_0^2, \quad (\text{from } 15c)$$

and

$$[\text{for } t > 0.25] \quad (z_0 - z)/z_0 = 1.436 (1 - \nu)^{\nu} \sum_{n=1}^{\infty} \sum_{q=1}^{\infty} \frac{e^{-4q^2(at-0.25) - 0.25m^2}}{q(m^2 - 4q^2)} \cdot \sin \frac{q\pi \nu}{l}, \quad (\text{from } 71)$$

whence,

| | | | | | |
|--|---|-------|-------|-------|-------|
| At the points $\nu l =$ | 0 | 0.25 | 0.50 | 0.75 | 1.00 |
| ¹ when $at = 0.35, (z - z_0)/C_1 l$ | 0 | 0.039 | 0.097 | 0.208 | 0.359 |
| ¹ when $at = 0.50, (z - z_0)/C_1 l$ | 0 | 0.058 | 0.138 | 0.237 | 0.359 |

¹ Corresponding values of $(z - z_0)/z_0$ may be obtained by multiplying by 2.784.

These points determine the curves *obd* and *ocd* in Fig. 12; *ofd*, the straight line joining *o* and *d*, gives the concentrations at $t = \infty$.

Sec. 9.—Successive Currents

At some moment t ($t > \vartheta$), suppose that the current corresponding to C_1 is changed to a current corresponding to C_2 . In the case chosen for illustration ($\zeta = 0$), if C_2 be numerically greater (algebraically less) than C_1 , z at the electrode will remain equal to ζ ; if C_2 lie between C_1 and the limiting current corresponding to ζ (*viz.*: $C' = (\zeta - z_0)/l$, Eq. 24) the concentration at the electrode will ultimately remain at ζ , although if $t - \vartheta$ be not too great it may momentarily rise above ζ and then fall again.

If, however, C_2 be (numerically) less than C' , the concentration at the electrode will rise permanently above ζ . From the moment t_1 at which this change of current occurs, the following conditions will hold, *viz.*:

$$[\text{Fick's law}] \quad \partial z / \partial t = k \partial^2 z / \partial x^2. \quad (iii)$$

$$[\text{Solution condition}] \quad \text{For } x = 0, \partial z / \partial t = 0. \quad (i)$$

$$[\text{Electrode condition}] \quad \text{For } x = l, \partial z / \partial x = C_2. \quad (iv)$$

$$[\text{"Initial" condition}] \quad \text{For } t = t_1, z - z_0 = \text{an expression obtainable by writing } t_1 \text{ for } t \text{ in (71)}. \quad (xiii)$$

The first three may be complied with by setting $t = t_1$ in (1), and substituting the values of B_n , D and E_n given by (3), (4), and (7) respectively; v is written instead of n to avoid confusion with the first summation. To introduce the "condition at $t = t_1$ " the expression on the right of (xiii) must be converted into a series proceeding by sines of odd multiples of $\pi x/2l$ (see Appendix); the A_n 's may then be found in the usual way. On carrying out these operations there results:

$$[\text{For } t > t_1] \quad z - z_0 = C_2 x + \frac{8l}{\pi^2} \left(\frac{\zeta - z_0}{l} - C_2 \right) \sum_{n=1}^{\infty} e^{-\frac{m^2 a(t-t_1)}{m^2}} \cos m g \xi \\ - \frac{128 C_1 l}{\pi^4} \sum_{n=1}^{\infty} \sum_{q=1}^{\infty} \sum_{r=1}^{\infty} \frac{e^{a z \rho} \cdot \cos(2v-1)\pi \xi}{(2n-1)^2 - 4q^2} (2v-1^2 - 4q^2)^2 \quad (72)$$

where, as usual, $m = 2n - 1$, $g = \pi/2l$, $a = \pi^2k/4l^2$, $\xi = l - x$ and the exponent of e (indicated by "exp" in (72)) is

$$\frac{-\pi^2k}{4l^2} [(2n - 1)^2\vartheta + 4q^2(t_1 - \vartheta) + (2v - 1)^2(t - t_1)]. \quad (73)$$

If $t_1 - \vartheta$ be very large, the exponential factor of the triple sum becomes zero, and only the first two terms of (72) remain. Large values of $t_1 - \vartheta$, however, correspond to a linear fall of concentration throughout the diffusion layer at the moment $t = t_1$; the single sum term of (72) can accordingly be deduced from (1), (3), (4), and (7) by introducing the condition.

$$[\text{For } t = t_1] z_0 - z = (z_0 - z_1)x/l. \quad (xiv)$$

in place of (xiii), or it may be derived from (31), the general equation for a cycle of two beats, by making $\theta_1 = \infty$ sec; (32).

Illustration

If for instance the constant current corresponding to C_1 which brings the concentration at the electrode to zero at $at = 0.25$ (see preceding section) persist till $at = 0.50$, the values of $(z - z_0)/C_1l$ at the electrode from $at = 0$ to $at = 0.25$ will be given by points on the curve oa of Fig. 13, which except in scale and the direction in which $(z - z_0)/C_1l$ is measured, is identical with the first part of the curve of Fig. 3. From $at = 0.25$ to $at = 0.5$ the concentration will remain stationary at $z = 0$ (Fig. 13, line ad).

Now let the current be shut off and be succeeded by a pause ($C_2 = 0$) lasting from $at = 0.50$ till $at = 1.0$, as in the "special case of interrupted currents" illustrated in Sec. 3. The concentrations at the electrode will rise, following the curve de of Fig. 13, points for which have been calculated by means of (72).

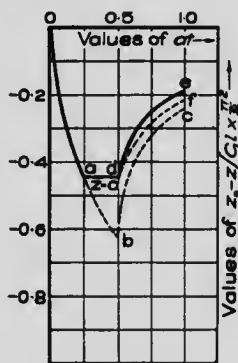


Fig. 13

To show the effect of the new electrode condition (*xi*), the curve for $at = 0$ to $at = 1.0$ of Fig. 8 has been drawn again in Fig. 13; it is represented by the broken line *oabc*. The curve *df* (points for which were computed from the first two terms only of Eq. 72) gives the concentrations that would be found during the second beat, if the first current had persisted long enough to bring about a linear concentration gradient throughout the diffusion layer. The difference between *de* and *df* in Fig. 13 corresponds to that between *cd* and *ofd* in Fig. 12.

An equation involving triple summation would suffice to trace the concentrations during the first part of the third beat, *i. e.*, until the concentration at the electrode again became zero; but each time the 'electrode condition' changes from (*iv*) to (*xi*) or back again the order of the summation is increased by unity. Simplifications are introduced if one of the beats is of long duration; but in general it would probably be easier to plan experiments in which the conditions discussed in this Part are avoided, than to carry out the computations that would otherwise be necessary. Illustrations of how this may be accomplished are given in Part III.

PART III

SECONDARY REACTIONS

In Parts I and II of this paper all changes of concentration occurring in the solution during electrolysis have been ascribed to electrolytic migration and to the diffusion of the products of electrolysis from the electrode, or, as the case may be, to the diffusion toward the electrode of such of the constituents of the solution as were consumed at that point. It will now be assumed that, apart from the effect of diffusion, the concentrations of the products of electrolysis may be lowered by the occurrence of "secondary" reactions, *i. e.*, reactions between the products of electrolysis and the other constituents of the solution; and the special assumption will be made that the rate at which such reac-

tions proceed is proportional to the concentration of the substance whose concentration is represented by z .

The rate of change of concentration of such a constituent at any point in the diffusion layer will therefore be represented by

$$[\text{Differential equation}] \quad \partial z / \partial t = k \partial^2 z / \partial x^2 - Kz, \quad (\text{xiv})$$

where K is the "velocity constant" of the secondary reaction. As is well known, K in general depends on the temperature, and on the concentrations of the other constituents of the solution, and even if these factors be kept constant many reactions have been discovered for which the rate is not proportional to the concentration of the disappearing substance; there are enough cases in which the rule holds, however, to make it worth discussion, while to assume that the rate might be proportional to any other than the first power of z would wholly change the nature of the differential equation.

The suggestion that the rates of such almost "instantaneous" reactions as that between copper salts and cyanides might be determined by electrolytic experiments is due to LeBlanc, who has already carried out a number of experiments from which the order of magnitude of such rates may be inferred. The following paragraphs suggest methods for determining K directly; if carried out at different temperatures and with different concentrations of the other reagents, the effect of these factors on the rate of the reaction might also be determined.

To simplify the discussion, it will further be assumed that the secondary reaction is practically "complete," *i. e.*, leads in time to the total destruction of the primary product of the electrolysis; thus the z_0 of Parts I and II becomes zero, and conditions (i) and (ii) are replaced by

$$[\text{Solution condition}] \quad \text{At } x = 0, z = 0 \text{ for all values of } t \quad (\text{xv})$$

$$[\text{Initial condition}] \quad \text{At } t = 0, z = 0 \text{ for all values of } x \quad (\text{xvi})$$

while the electrode condition remains the same as before

$$[\text{Electrode condition}] \quad \text{At } x = l, \partial z / \partial x = G/k = C. \quad (\text{iv})$$

Sec. 10.—Constant Current

The "stationary term" of the new equation may be found by setting $\partial z/\partial t = 0$ in (xiv), whence

$$[At t = \infty] \quad 0 = k \cdot d^2 z/dx^2 - Kz \quad (74)$$

the solution of which is

$$z = A_1 \cosh bx + A_2 \sinh bx, \text{ where } b = \sqrt{K/k}. \quad (75)$$

Condition (xv) leads to $A_1 = 0$, and (iv) to

$$A_2 = C/(b \cosh bl),$$

so that the stationary term becomes

$$[For t = \infty \quad z = C \sinh bx/(b \cosh bl.) \quad (76)$$

The evanescent term, which must satisfy (xiv) and (xv), and for which at the electrode $\partial z/\partial x$ must equal zero (so as not to interfere with iv), may be derived from the form

$$\sum_n^{\infty} A_n e^{-(K+m^2a)t} \cos \frac{(2n-1)\pi(l-x)}{2l} \quad (77)$$

by determining the coefficients A_n so that at $t = 0$ the sum of stationary and evanescent terms will vanish, *i. e.*, so that

$$\sum_n^{\infty} A_n \cos \frac{(2n-1)\pi(l-x)}{2l} = -\frac{C \cdot \sinh bx}{b \cdot \cosh bl}. \quad (78)$$

This is accomplished (as illustrated in Secs. 1 and 8) by expanding the hyperbolic expression as a series of sines of $m\pi x/2l$, and introducing in (78).

Combining stationary and evanescent terms, the solution of (xiv) which satisfies (xv), (xvi), and (iv) is found to be

$$z = \frac{C \sinh bx}{b \cosh bl} - \frac{2kC}{1} \sum \phi e^{-\psi t} \cos mg\xi \quad (79)$$

where C , k , l , t , x , have the meanings implied in (xiv), (xv) (xvi) and (iv) and explained at length in the Introduction and Part I; $m = (2n-1)$, $g = \pi/2l$, $\xi = l-x$, $b = \sqrt{K/k}$, and ϕ is written for $K + m^2a = K + (2n-1)^2\pi^2k/4l^2$.

\sum_n is used for $\sum_{n=1}^{\infty}$. An expression for the concentrations at the electrode may be obtained by setting $x = l$ in (79).

$$[\text{For } x = l] \quad z = \frac{C}{b} \tanh bl - \frac{2kC}{l} \sum_{n=1}^{\infty} \frac{e^{-\psi_n t}}{\psi_n} \quad (80)$$

On consulting tables of the hyperbolic functions, it will be found that when $bl < 0.15$, $\tanh bl$ may be replaced by bl with an error not exceeding eight-tenths of one percent; the stationary term then becomes Cl as in (15). Assuming $k = 4 \times 10^{-6}$ as in the former illustrations, $bl = l\sqrt{K/k} < 0.15$ implies $K < 0.09$ when $l = 10^{-3}$ cm, and $K < 9.0$ when $l = 10^{-4}$ cm. Perhaps the highest values of K that can be measured satisfactorily by the direct methods of chemical kinetics¹ do not exceed $K = 0.09$, corresponding to a fall of the concentration to one half its original value every eight seconds, thus if the secondary reaction takes place at any ordinarily measurable rate, the stationary term of (80) becomes Cl .

On the other hand, when $bl > 3.0$, $\tanh bl$ may be replaced by unity with an error not exceeding one-half percent; and the stationary term of (80) becomes $C\sqrt{k/K}$, = G/\sqrt{Kk} . Assuming $k = 4 \times 10^{-6}$ as before, this gives $K > 36$ if $l = 10^{-3}$ cm, and $K > 3600$ if $l = 10^{-4}$ cm as the values that must be reached by K if this approximation is to be employed.

Erf approximation. Evaluation of the evanescent part of (80) by simple addition of the terms is quite impossible when K is large, on account of the slow convergence; if at be small, however, an approximately equivalent expression, based on the equation of Thomson and Cayley (Eq. 18) may be employed.

Writing

$$\begin{aligned} \frac{2kC}{l} \sum_{n=1}^{\infty} \left(\frac{e^{-(K+m^2a)t}}{K+m^2a} - \frac{1}{K+m^2a} \right) = \\ - \frac{2kC}{l} \sum_{n=1}^{\infty} \int_0^t e^{-(K+m^2a)t} dt = - \frac{2kC}{l} \int_0^t (e^{-Kt} \sum_{n=1}^{\infty} e^{-m^2at}) dt \quad (81) \end{aligned}$$

¹ Such a case was studied by Miss Benson, Jour. Phys. Chem., 7, 356 (1903).

the summation in the last expression may be replaced by its approximate value (*viz.*: $\frac{1}{2} \sqrt{\frac{\pi}{at}}$) from (20), and the term $\frac{2kC}{l} \sum \frac{1}{K+m^2a}$ by its equivalent *viz.*: $\frac{C}{b} \tanh bl$, so that

$$\frac{C}{b} \tanh bl - \frac{2kC}{l} \sum \frac{e^{-\psi t}}{\psi} = (\text{approximately})$$

$$\frac{kC}{2l} \sqrt{\frac{\pi}{a}} \int_0^t e^{-Kt} t^{-\frac{1}{2}} dt = \frac{2C}{b\sqrt{\pi}} \int_0^y e^{-y^2} dy, \quad (82)$$

and equation (80) reduces to

$$[\text{For } at \text{ small}] \quad z = \frac{2C}{b\sqrt{\pi}} \int_0^y e^{-y^2} dy = \frac{C}{\sqrt{kK}} \frac{2}{\sqrt{\pi}} \text{Erf } y = \text{approx.} \quad (83)$$

Values of the "probability integral," $\frac{2}{\sqrt{\pi}} \text{Erf } y = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$ are tabulated in most books on Least Squares;¹ when the argument is zero, the probability integral is likewise zero, and the integral reaches 0.99⁷ when the argument reaches 1.8; the maximum value of the integral is unity.

Sec. 11.—Successive Currents in General

To obtain an expression for the concentrations when a current corresponding to C_1 , after passing for the interval $t = 0$ to $t = t_1$, is succeeded by a current corresponding to C_2 which persists from $t = t_1$ to $t = t_2$, and so on, as described in Sec. 2, (79) may be written

$$[\text{For } t = t_1] \quad z = \frac{C_2 \sinh bx}{b \cosh bl} - (C_2 - C_1) \frac{\sinh bx}{b \cosh bl}$$

$$- \frac{2k}{l} \sum \frac{C_1}{\psi} \cdot e^{-\psi t_1} \cdot \cos mg\bar{z}, \quad (84a)$$

$$= \frac{C_2 \sinh bx}{b \cosh bl} - \frac{2k}{l} \sum \frac{1}{\psi} (C_1 e^{-\psi t_1} + C_2 - C_1) \cos mg\bar{z}. \quad (84b)$$

¹For instance, Merriman and Johnson each give a four-place table, while Bertrand (*Calcul des Probabilités*) and De Morgan (*On Probabilities*) each give a seven-place table, the argument in each case advancing by 0.01. A far more elaborate table in which the argument advances generally by 0.001 is given by Burgess *Trans. Edin. Roy. Soc.*, 39, 257 (1899).

Proceeding as indicated in Sec. 2, the general expression for the concentrations during the p th beat may be obtained:

$$\begin{aligned}
 [\text{For } t_{p-1} < t < t_p] \quad z &= C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\phi^n} \{ C_1 e^{-\psi t} \\
 &+ \sum_{i=1}^p (C_i - C_{i-1}) e^{-\psi(t-t_{i-1})} \} \cos mg \xi, \quad (85a)
 \end{aligned}$$

$$\begin{aligned}
 &= C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\phi^n} \{ C_p \Phi T_{p-1} \\
 &\quad + \sum_{i=1}^{p-1} C_i (\Phi T_{i-1} - \Phi T_i) \} \cos mg \xi, \quad (85b)
 \end{aligned}$$

where

$$T_i = t - t_i, \text{ and } \Phi T_i = e^{-\psi(t-t_i)},$$

whence the expressions for the concentrations during the progress of odd and even beats in two-beat cycles:

$$\begin{aligned}
 [\text{For } p \text{ odd}] \quad z &= \frac{C_1 \sinh bx}{b \cosh bl} + \frac{2k}{l} (C_2 - C_1) \sum \frac{e^{-\psi t} \cdot e^{\psi \theta} - e^{\psi \theta_1}}{\phi \cdot e^{\psi \theta} - 1} \cos mg \xi \\
 &- \frac{2k}{l} \sum \frac{e^{-\psi t}}{\phi} \{ C_1 + (C_2 - C_1) \frac{e^{\psi \theta} - e^{\psi \theta_1}}{e^{\psi \theta} - 1} \} \cos mg \xi. \quad (86)
 \end{aligned}$$

$$\begin{aligned}
 [\text{For } p \text{ even}] \quad z &= \frac{C_2 \sinh bx}{b \cosh bl} + \frac{2k}{l} (C_1 - C_2) \sum \frac{e^{-\psi t} \cdot e^{\psi \theta} - e^{\psi \theta_2}}{\phi \cdot e^{\psi \theta} - 1} \cos mg \xi \\
 &- \frac{2k}{l} \sum \frac{e^{-\psi t}}{\phi} \{ C_1 + (C_2 - C_1) \frac{e^{\psi \theta} - e^{\psi \theta_1}}{e^{\psi \theta} - 1} \} \cos mg \xi. \quad (87)
 \end{aligned}$$

From (86) and (87) expressions for the amplitude and for the concentration at the centre of swing in the case of two-beat cycles may be obtained (see pg. 839); they are:

$$\begin{aligned}
 [\text{Amplitude}] \quad &\frac{1}{2} (C_1 - C_2) \frac{\sinh bx}{b \cosh bl} \\
 &+ \frac{k}{l} (C_1 - C_2) \sum \frac{1}{\phi} \cdot \frac{e^{\psi \theta_1} + e^{\psi \theta_2} - 2e^{\psi \theta}}{e^{\psi \theta} - 1} \cos mg \xi. \quad (88)
 \end{aligned}$$

$$\begin{aligned}
 [\text{At centre}] \quad z &= \frac{1}{2} (C_1 + C_2) \frac{\sinh bx}{b \cosh bl} \\
 &+ \frac{k}{l} (C_1 - C_2) \sum \frac{1}{\phi} \cdot \frac{e^{\psi \theta_1} - e^{\psi \theta_2}}{e^{\psi \theta} - 1} \cos mg \xi. \quad (89)
 \end{aligned}$$

When θ_1 and θ_2 are very large, the concentrations at any point in the diffusion layer oscillate between $(C_1 \sinh bx)/(b \cosh bl)$ and $(C_2 \sinh bx)/(b \cosh bl)$; when θ is very small, the amplitude is practically zero, and the concentration at the centre of swing is $(C_1 \theta_1 + C_2 \theta_2) \sinh bx/(b \cosh bl)$.

Sec. 12.—Simple Alternating Current

If the current corresponding to C_1 pass for θ_1 seconds through a copper electrode into a solution of potassium cyanide, making the copper anode, and if then the current corresponding to C_2 make the copper cathode for the same interval θ_1 seconds, and be succeeded by C_1 for θ_1 seconds and so on; the ratio between the two currents that will just bring the concentration at the electrode to zero at the end of the cathode beats when the stationary state has been reached, may be found by setting $x = l$, $t = \infty$, $z = 0$, $\tau = 0$, and $\theta = 2\theta_1$ in (86).

Making these substitutions, and dividing the numerator of the θ fraction by its denominator, the result may be put in the form

$$C_1 - C_2 = \frac{2kb}{l \tanh bl} \left\{ \sum_1^1 \phi - \sum_1^{e^{-\psi\theta_1}} \phi + \sum_1^{e^{-2\psi\theta_1}} \phi - \sum_1^{e^{-3\psi\theta_1}} \phi + \text{etc.} \right\} \quad (90)$$

and if $a\theta_1$ be small enough to justify the use of the Erf approximation,

$$C_1 - C_2 = 1 - [1 - (\coth bl) \frac{2}{\sqrt{\pi}} \text{Erf} \sqrt{K\theta_1}] + [1 - (\coth bl) \frac{2}{\sqrt{\pi}} \text{Erf} \sqrt{2K\theta_1}] - \text{etc.} \quad (91)$$

For high values of $l\sqrt{\frac{K}{k}}$, $\coth bl$ becomes unity, and the ratio between the two currents is independent of k and of l , becoming in fact a function of $K\theta_1$.

In making an actual computation, $\frac{2k}{l} \sum_1^1 \phi$ would be re-

placed by its value $(\tanh bl)/b$ and the Erf approximation would be used for the first few summations of (90) where direct summation would be too laborious; for higher values of the negative exponent, however, where the Erf approximation becomes less reliable, direct summation is easy.¹

As an example, if $k = 4 \times 10^{-6}$, $l = 3.1416 \times 10^{-4}$, $K = 400$, and the duration of each beat $\theta_1 = 0.0005$ seconds, the two currents would stand in the ratio of 68.97 to 31.03 or $G_2 = -0.4499 G_1$.

If C_1/C_2 were determined in the laboratory, K could be found by (90) and (91); the easiest way, no doubt, would be to compute C_1/C_2 for a number of assumed values of K , plot the results, and find K from the observed C_1/C_2 by interpolation. If, however, in the experimental work, the currents in the two beats had been equal, and if it were attempted to calculate K from an experimental determination of the relative amounts of copper dissolved during the anode beat and redeposited during the cathode beat (i. e., from the net loss of weight of the electrode)² or from an oscillographic determination of the moment during the cathode beat at which the concentration at the electrode fell to zero, the problem would become analogous to those of Part II; multiple summations would have to be employed, and the computations would become complicated and laborious.

¹ When $\theta_1 = 0.0005$ and $a = 100$, the following are the true values and the Erf approximations respectively of the sums in (90), beginning with the first containing an exponential factor:

| | | | | |
|-------------|-----------|-----------|-----------|-----------|
| Number | 1 | 2 | 3 | 4 |
| True value | 0.0020552 | 0.0014426 | 0.0010587 | 0.0007939 |
| Erf approx. | 0.0020552 | 0.0014426 | 0.0010587 | 0.0007939 |
| Number | 5 | 6 | 7 | 8 |
| True value | 0.0006031 | 0.0004619 | 0.0003557 | 0.0002749 |
| Erf approx. | 0.0006031 | 0.0004618 | 0.0003555 | 0.0002745 |

In the case of the last term mentioned in this table, which involves e^{-25/θ_1} , the first two terms only of the summation suffice for the determination of five significant figures and the Erf approximation can thus in this case be dispensed with before it becomes inaccurate.

² As, for instance, in LeBlanc's experiments.

The quantity of cuprion¹ per square centimeter of electrode area left in the diffusion layer at the end of the cathode beat, viz.:

$$\int_0^l z dx = \frac{C_1 k (1 - \operatorname{sech} bl)}{K} + \frac{4k}{\pi} (C_2 - C_1) \left[\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{m\psi^n} - \sum_{n=1}^{\infty} \frac{(-1)^{n+1} e^{-\psi\theta_1}}{m\psi^n} + \sum_{n=1}^{\infty} \frac{(-1)^{n+1} e^{-2\psi\theta_1}}{m\psi^n} \right] \quad (92)$$

is by no means negligible; in the case of the illustration it amounts to $4.5099 \times 10^{-4} G_1$, as against $0.000 \times 10^{-4} G_1$ equivalents brought into the solution during an anode beat (the sum of the series in square brackets in (92) is 0.0009931, and $C_2 = -0.4499 C_1$).

This is why an estimation of K from the experimentally determined ratio C_1/C_2 , based on the rough and ready hypothesis that diffusion may be altogether neglected, and that at the end of the cathode beat (when $z = 0$ at both ends of the diffusion layer) the amount of cuprion in the diffusion layer may be neglected, leads to results very wide of the mark.²

The number of equivalents of cuprion that pass out from the diffusion layer into the body of the solution, per sq. cm of electrode surface, during an anode beat, may be found by multiplying the concentration gradient at the solution (at $x = 0$) by $k dz$ and integrating:

$$k \int_0^{\theta_1} \left(\frac{\partial z}{\partial x} \right) dz = \frac{C_1 \theta_1}{\cosh bl} - \frac{k\pi}{l^2} (C_2 - C_1) \sum_{n=1}^{\infty} \frac{m (-1)^{n+1}}{\psi^{2n+1}} (e^{-\psi\theta_1} - 1). \quad (93)$$

A similar expression for the cathode beat may easily be obtained. In the case taken for illustration these quantities are not large. An approximate value for the loss during the cycle may be found, without summing the series of (93), by assuming that the loss would be the same as that caused by a constant current of average strength, $C = \frac{1}{2}(C_1 + C_2) = 0.275 C_1$, acting throughout the cycle.

¹ Copper not combined with cyanide is meant.

² See under the next heading.

Using the formula for the stationary state (Eq. 76) this gives

$$k \int_0^{\theta_1} \left(\frac{\partial z}{\partial v} \right)_z dz \approx \frac{0.275 C_1 k \theta}{\cosh bl} \text{ approximately } = 0.237 \times 10^{-4} G_1. \quad (94)$$

The loss from the diffusion layer during a complete cycle ($\theta = 2\theta_1 = 0.001$ seconds) is thus about five percent of that dissolved from the electrode during an anode beat.

Approximate Calculation of K from the Current Ratio

The quantity of cupron in the diffusion layer opposite each sq. cm of electrode surface, (which in this paragraph only will be represented by x), is thus subject to change by the operation of three causes. It is being added to by electrolysis at the rate $+G_1$ equivalents per second, it is being diminished by the chemical action of the cyanide at the rate of Kx equivalents per second, and there is a loss (which being small may be treated as constant throughout the cycle) of L equivalents per second into the main body of the solution.

Thus

$$\left[\text{Anod. beat} \right] \frac{dx}{dt} = G_1 - Kx - L, \quad \left[\text{Cathod. beat} \right] \frac{dx}{dt} = G_2 - Kx - L, \quad (95)$$

Integrating between the limits 0 and θ_1 , and θ_1 and $2\theta_1$, respectively, and writing w for the number of equivalents of cupron remaining in the diffusion layer at the end of a cathode beat ($\tau = 0$, or $\tau = 2\theta_1$), there results

$$Kw = G_1 - L = (G_2 - G_1) \frac{e^{K\theta_1}}{K\theta_1 + 1}. \quad (96)$$

Inserting the values found in the previous paragraph, viz.: $G_2 = -0.4499G_1$, $w = 4.5099 \times 10^{-4}G_1$, and $L = 0.0237G_1$, Eq. (96) gives $K = 398$ in place of the true value $K = 400$.

Suppose, however, that the current ratio had been determined experimentally, and that it was proposed to calcu-

late K without taking account of diffusion at all, *i. e.*, from

$$-G_2/G_1 = e^{-Kl} \quad (97)$$

which may be obtained from (96) by setting $w = 0$ and $L = 0$, the wholly erroneous result $K = 1597$ would be obtained. The error is mainly due to neglecting w ; if in (96) w be given its true value and L be set equal to zero, K comes out equal to 435.

Conditions Connoted by Large Values of $l\sqrt{\frac{K}{k}}$

During the discussion of (91) it was pointed out that when $l\sqrt{\frac{K}{k}}$ is large, C_1/C_2 is independent of k and l ; according to (96), however, the current ratio can be independent of k and l only when the amount of cuprion left in the diffusion layer at the end of a cathode beat is likewise independent of the same two variables. The following considerations may help to make the reason for these relations clear.

If in any series of experiments z remains constantly zero at any fixed point in the solution, that point might be taken as $x = 0$, *i. e.*, its distance from the electrode might be taken as l ; to keep $z = 0$ at any point *further* from the electrode could have no effect on the diffusion, and consequently to give l any *greater* value in any system of equations applicable to the case could have no effect on the results of the computations. By lessening k or increasing K the point at which z remains practically equal to zero is brought nearer to the electrode; and it follows from what has just been said, that when once it is nearer than the point selected as " $x = 0$ " for the given system, the "solution condition" is without effect. Large values of l bring the evanescent terms to zero, and thus destroy the influence of the "initial condition;" if both circumstances occur together, the only equations influencing the result are the "differential equation" and the "electrode condition," which for any given value of k , *viz.*: k_1 may be written

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial \xi^2} - Kz \quad (\text{viva}); \quad k_1 \frac{\partial z}{\partial \xi} = -i \quad (\text{iv a})$$

Suppose that in two cases the diffusion constants are k_1 and $k_2 = k_1/r^2$, respectively, where r is any constant multiplier. Replacing k_1 in (xiv a) and (iv a) by k_1/r^2 the equations for the second case will be

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial (r\xi)^2} - Kz; \quad k_1 \frac{\partial z}{\partial (r\xi)} = -rG \quad (98)$$

and it is obvious that (if conditions are such that the "initial" and "electrode" conditions may be neglected) the same values of z will be met with in both cases if $r\xi$ and rG in the second case have the same values as ξ and G in the first case, respectively; that is, when the current, and the distance from the electrode, of the points compared, are both r times less in the second case than in the first. Consequently (since, other things being equal, z is proportional to G) if the currents be equal in the two cases, the values of z at comparable points will be r times greater in the second case than in the first.

Hence, if the diffusion layer be imagined to be divided into corresponding laminae in the two cases, these being r times as thin in the second case as in the first and having concentrations r times greater, each will contain the same quantity of the component to which z refers. Further as explained above since the values of z in both cases fall to zero with increasing ξ and remain at zero, the impaired laminae having zero values of z will not affect the total, and therefore the total quantity of the component in the two cases being the sum of the same items must be the same. That is to say, the number of equivalents contained in the diffusion layer will be under these conditions independent of K .

Conditions that keep $z = 0$ at $\xi < l$ obviously prevent all loss from the diffusion layer into the main body of the solution, by destroying the concentration gradient at $\xi = l$; for large values of $l\sqrt{\frac{K}{k}}$ therefore, the integral expanded in (93) must reduce to zero.

Sec. 13.—Sinusoidal Currents, Fourier Form

The general expression where $C = f(t)$, from which the expression for the sinusoidal current may be derived as a special case is:

$$z = \frac{\sinh bx}{b \cosh bl} f(t) - \frac{2k}{l} \sum_{n=1}^{\infty} \left\{ \frac{f(t)}{\phi} e^{-\phi t} \int_0^t e^{\phi u} f(u) du \right\} \cos mgz. \quad (99a)$$

$$= \frac{2k}{l} \sum_{n=1}^{\infty} \left\{ e^{-\phi t} \int_0^t e^{\phi u} j(u) du \right\} \cos mgz. \quad (99b)$$

Setting $f(t) = M \sin(\omega t + \alpha)$, this becomes

$$z = M \sin(\omega t + \alpha) \frac{\sinh bx}{b \cosh bl} - \frac{2kM\omega}{l} \sum_{n=1}^{\infty} \frac{1}{\phi} \frac{\omega \sin(\omega t + \alpha) + \phi \cos(\omega t + \alpha)}{\phi^2 + \omega^2} \cos mgz \\ - \frac{2kM}{l} \sum_{n=1}^{\infty} e^{-\phi t} \frac{\phi \sin \alpha - \omega \cos \alpha}{\phi^2 + \omega^2} \cos mgz. \quad (100a)$$

$$= \frac{2kM}{l} \sum_{n=1}^{\infty} \frac{\phi \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{\phi^2 + \omega^2} \cos mgz \\ - \frac{2kM}{l} \sum_{n=1}^{\infty} e^{-\phi t} \frac{\phi \sin \alpha + \omega \cos \alpha}{\phi^2 + \omega^2} \cos mgz. \quad (100b)$$

Where the harmonic analysis of a current is known it can be seen that for each component of the current there will be in the value of z a term expressible either in this form or in that of the next section.

Sec. 14. —Sinusoidal Currents, Hyperbolic Form

As in Part I, the stationary term may be expressed in a form more suitable for computation by the use of hyperbolic functions.

Starting out from (48), and introducing the new conditions, it will be found that the values obtained for A and B are those given by (49), but that the exponents γ and λ must be defined as follows:

¹ With regard to the applicability of these results see under Sec. 15.

$$\gamma^2 k = K + i\omega \text{ and } \lambda^2 k = K - i\omega, \quad (101a)$$

whence

$$\gamma = \beta + \delta i \text{ and } \lambda = \beta - \delta i, \quad (101b)$$

where

$$\beta^2 + \delta^2 = \frac{\sqrt{K^2 + \omega^2}}{k}, \beta^2 - \delta^2 = K/k, \text{ and } 2\beta\delta = \omega/k. \quad (101c)$$

Introducing these values in (48), the following expression for the stationary term is obtained

$$z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{2}}} \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} \sin \chi \quad (102)$$

where

$$\begin{aligned} \chi = \omega t + \alpha + \tan^{-1}(\coth x\beta, \tan x\delta) - \frac{1}{2} \tan^{-1}(\omega/K), \\ - \tan^{-1}(\tanh l\beta, \tan l\delta). \end{aligned} \quad (103)$$

On setting $K = 0$ in (102) it is reduced to (54), on setting $\omega = 0$ it is reduced to (76); and by means of suitable expansions of the hyperbolic functions it may be converted into the "Fourier" form, (stationary term of equation 100).

The evanescent term may be obtained from the general form

$$\sum_1^{\infty} A_n \frac{1}{\phi} e^{-\gamma t} \cos mg\bar{z}, \quad (104)$$

(which satisfies (xiv), (xv), and the condition that when $x = l$, $\partial z / \partial t = 0$), by expanding (102) in a series of sines of $mg\bar{z}$ and determining the values of A_n as in sec. (6b). The resulting evanescent term is identical with that of (100).

Combining both terms, the "hyperbolic form" of the expression for sinusoidal currents becomes:

$$\begin{aligned} z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{2}}} \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} \sin \chi \\ - \frac{2Mk}{l} \sum_1^{\infty} \frac{e^{-\gamma t} \phi \sin \alpha}{\phi^2 + \omega^2} \frac{\omega \cos \alpha}{\cos mg\bar{z}} \end{aligned} \quad (105)$$

in which χ has the meaning given in (103), and β and δ those implied in (101c).

An expression for the *amplitude* at the stationary state may be found by setting $\sin \chi = 1$; the concentration at the centre of swing is zero. The "lag" is given by

$$[\text{Lag}] \tan^{-1}(\tanh l\beta, \tan l\delta) + \tan^{-1}(\omega/K) - \tan^{-1}(\coth x\beta, \tan x\delta). \quad (106)$$

Concentrations at the electrode may be found by substituting l for x in (105); in the evanescent term, this has the effect of making $\cos mg\xi$ unity, while the stationary term becomes

$$[\text{For } t = \infty, x = l] z = \frac{Mk^{\frac{1}{2}}}{2(K^2 + \omega^2)^{\frac{1}{2}}} \frac{\sqrt{\sinh^2 2\beta l + \sin^2 2\delta l}}{\sinh^2 \beta l + \cos^2 \delta l} \sin \chi \quad (107)$$

where

$$\chi = \omega t + \alpha + \tan^{-1} \frac{\sin 2l\delta}{\sinh 2l\beta} - \frac{1}{2} \tan^{-1} \left(\frac{\omega}{K} \right). \quad (108)$$

If $\beta l > 3$, $\sinh \beta l$ becomes > 10 , and the circular functions may be neglected in comparison with the hyperbolic. The fraction then becomes $\sinh 2\beta l / \sinh^2 \beta l$ which for values of $\beta l > 3$ is very nearly equal to 2.00; thus (with a maximum possible error of one-half percent), when the stationary state is reached

$$[\text{For } x = l, \beta l > 3] z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{2}}} \sin \chi. \quad (109)$$

Sec. 15.—Superposed Currents

As in Part I, the effect of a number of currents acting simultaneously may be found by adding the right hand members of the equations which express the effects of each of them alone. In fact, the assumption made throughout this Part, that $z_0 = 0$, deprives many of the equations of their validity unless when thought of as parts of such a sum; according to (107), for instance, the concentrations at the electrode would be *negative* during a large part of the cycle on electrolysis with a pure sinusoidal current.

When the stationary state has been reached during electrolysis with a sinusoidal current, the amplitude of the concentration variation at the electrode may be found by setting $\sin \chi_i = 1$ in (107). The centre of swing is zero with the sinusoidal current alone, but it may be raised to any desired

height, $C_1 \frac{\tanh bl}{b}$, by superposing the direct current corresponding to C_1 . If $C_1 \frac{\tanh bl}{b}$ be greater than the amplitude, z at the electrode will never fall to zero; and the condition that z just touches zero once in the cycle is expressed by

$$0 = \frac{C_1}{b} \tanh bl - \frac{Mk^4}{2(K^2 + \omega^2)l} \frac{\sqrt{\sinh^2 2\beta l + \sin^2 2\delta l}}{\sinh^2 \beta l + \cos^2 \delta l} \quad (110)$$

whence the ratio of the two ammeter readings $\frac{C_1 \sqrt{2}}{M}$ may be found:

$$\frac{C_1}{M} = \frac{1}{2} \frac{b}{\tanh bl} \frac{k^4}{(K^2 + \omega^2)l} \frac{\sqrt{\sinh^2 2l\beta + \sin^2 2l\delta}}{\sinh^2 l\beta + \cos^2 l\delta}; \quad (111)$$

the limit of (111) for $K = 0$ is the expression obtainable by equating (64) to zero.

With the ordinary alternating current of 60 cycles per second, $\omega = 377$; assuming $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, and $K = 500$, the ratio C_1/M will be 0.912, and the ratio of the ammeter readings, 1.290 provided the arrangement is as described in the footnote to Sec. 7.

The ratio is a function of $l\sqrt{\frac{\omega}{k}}$ and $\frac{\omega}{K}$ so that if it be determined experimentally, and if in addition ω and a be known, K may be calculated. As the value of C_1 for which z at the electrode just touches zero should be recognizable by voltmeter or oscillograph or by weighing the electrode (111) should lead to a convenient experimental method of determining the velocity constants of rapid "secondary" reactions. The ratio C_1/M will vary from the value discussed in Sec. 7 when K is zero, to 1 when K increases without limit (the value 1 would imply, in the case of a copper electrode in cyanide solution, that the copper never became cathode). Other things being equal, increasing ω brings the ratio nearer zero.

For large values of K , $\tanh bl$ becomes unity, and the \sinh fraction of (111) reduces to 2.0; in this case the relation be-

tween the current ratio and the value of K takes the simple form

$$\left(\frac{C_1}{M}\right)^4 = \frac{K^2}{K^2 + \omega^2}, \quad (112)$$

and K may be determined without knowledge of k or l .

APPENDIX

Note on the Construction of Special Trigonometrical Series to Represent Arbitrary Functions

If it be required to express a given function of x , $f(x)$, between given values of x as the sum of a series of sines and cosines of multiples of a variable θ chosen so as to have its increment in a constant ratio to that of x and to vary from 0 to 2π between these given limits of x , the problem admits of but one solution; and Fourier has shown that the coefficients of the general terms of the series, *viz.*, $\sin m\theta$ and $\cos m\theta$ will be $\frac{1}{\pi} \int_0^{2\pi} f(x) \sin m\theta \cdot d\theta$ and $\frac{1}{\pi} \int_0^{2\pi} f(x) \cos m\theta \cdot d\theta$ respectively, for all integral values of m not zero, while the constant term or coefficient of $\cos 0\theta$ is $\frac{1}{2\pi} \int_0^{2\pi} f(x) \cdot d\theta$.

If, however, it be agreed that the series shall represent the given function for a limited range only (less than 2π) of values of θ , an infinite number of solutions are possible; and the problem becomes determinate only when the value of the series for the remainder of the interval 2π of θ is specified. Advantage may be taken of this to impose additional conditions on the nature of the series by which the given function is to be represented.

If, for example, it be sufficient to find a series that will represent the function over the assigned range in values of x for values of θ between $\theta = 0$ and $\theta = \pi$, no conditions being imposed as to the value of the series when θ lies between π and 2π , the value of the series in the latter range may be so chosen as to make the coefficients of either the sine terms or the cosine terms of the series equal to zero.

The first may be accomplished by making the series represent the ordinates of a curve with values of θ as abscissae, whose ordinates between $\theta = 0$ and $\theta = \pi$ are the corresponding values of $f(x)$ over the given range in the values of x , and which is continued between $\theta = \pi$ and $\theta = 2\pi$ by its mirror image in the ordinate at $\theta = \pi$. Representing by $\psi(x)$ the values of the ordinates throughout the whole

range from $\theta = 0$ to $\theta = 2\pi$, the integral $\int_0^\pi \psi(x) \sin m\theta \cdot d\theta$ will then be equal in magnitude and opposite in sign to $\int_\pi^{2\pi} \psi(x) \sin m\theta \cdot d\theta$ and therefore $\int_0^{2\pi} \psi(x) \sin m\theta \cdot d\theta$ will be zero, while $\int_0^{2\pi} \psi(x) \cos m\theta \cdot d\theta$ will be equal to $2 \int_0^\pi \psi(x) \cos m\theta \cdot d\theta$,

and the constant term $\int_0^{2\pi} \psi(x) \cdot d\theta$ to $2 \int_0^\pi \psi(x) \cdot d\theta$; so that the series which represents $\psi(x)$ for all values of θ between $\theta = 0$ and $\theta = 2\pi$, and therefore *inter alia* represents $f(x)$ over the given range in x for values of θ between $\theta = 0$ and $\theta = \pi$, will consist of cosines only (besides the constant term). Thus the coefficient of the general term $\cos m\theta$ will

be $2 \int_0^\pi f(x) \cos m\theta \cdot d\theta$ and the constant term is as just stated,

or equivalently $\int_0^\pi f(x) \cdot d\theta$.

If on the other hand the ordinates of the curve represented by the series be equal to $f(x)$ for values of θ between $\theta = 0$ and $\theta = \pi$, while the part of the curve between $\theta = \pi$ and $\theta = 2\pi$ is formed from the first part by revolution through 180° round the point $\theta = \pi$ on the axis of abscissae, the cosine terms disappear and the coefficient of the general

term $\sin m\theta$ is $2 \int_0^\pi f(x) \sin m\theta \cdot d\theta$, there being here no constant term.

These "cosine series" and "sine series" are discussed in all works dealing with Fourier series; the textbooks with which we are familiar, however, do not point out that still further conditions may be imposed on the nature of the series if the range of values of θ through which it is to represent $f(x)$ be still further restricted. Such conditions are met with in practice; for instance, in order to obtain Eq. (54e) Eq. (72) and Eq. (79) of the present paper (see also Eq. 11) it was necessary to find a series of *sines of odd multiples* of $\theta = \pi x/2l$ which would represent a given function of x between the limits $\theta = 0$ and $\theta = \pi/2$. This condition is complied with if the series be constructed to represent the ordinates of a curve, whose ordinates between $\theta = 0$ and $\theta = \pi/2$ are equal to $f(x)$, and which is continued in the second quadrant by its mirror image in the vertical through the point $\theta = \pi/2$, while the second half is formed from the first by rotation through 180° around the centre $\theta = \pi$

on the axis of abscissae. For such a case $\int_0^{2\pi} \psi(x) \cos m\theta d\theta = 0$

as stated above, while $\frac{1}{\pi} \int_0^{2\pi} \psi(x) \sin m\theta d\theta$ is zero when $m =$

$2n$, and equals $\frac{4}{\pi} \int_0^{\pi/2} \psi(x) \sin m\theta d\theta$ or $\frac{4}{\pi} \int_0^{\pi/2} f(x) \sin m\theta d\theta$ when

$m = 2n - 1$. So that the series which represents $f(x)$ for all values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$, will consist of sines

of odd multiples only of θ and the coefficient of the general term, viz., $\sin(2n - 1)\theta$ will be $\frac{4}{\pi} \int_0^{\pi/2} f(x) \sin(2n - 1)\theta d\theta$.

Similarly, the general term of the series which represents $f(x)$ for values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$ and which

consists of cosines of odd multiples only of θ , is

$$\frac{4}{\pi} \cos(2n-1)\theta \int_0^{\frac{\pi}{2}} f(x) \cos(2n-1)\theta d\theta.$$

The extension to the other three quadrants which this series is made to define is obtained as follows: revolve the curve in the first quadrant about the point $\theta = \frac{\pi}{2}$ on the axis of abscissae through 180° to define the second quadrant, and then for the second half take the mirror image of the first two quadrants in the ordinate at $\theta = \pi$.

It is to be noted, however, that these extensions are introduced merely for the purpose of explanation, and, as the results above show, do not need to be represented graphically or introduced into the formulae.

Although values different from zero may be obtained from the above formulae for the coefficients of terms which are not to appear in the series, no use is to be made of such values, as the formula is not valid for any such purpose. Similarly in the last case for which the formula is given (cosines of odd multiples) there is no constant term, whatever be the mean value of $f(x)$ over the given range in x .

*University of Toronto,
July, 1910*

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The following contractions are employed throughout:

$$a = \pi^2 k / 4l^2$$

$$b = \sqrt{\frac{K}{k}}$$

$$C = G/k$$

$$g = \pi \cdot 2l$$

$$m = 2n - 1$$

$$\mu = \sqrt{\frac{\omega}{2k}}$$

$$\sum = \sum_{n=1}^{\infty}$$

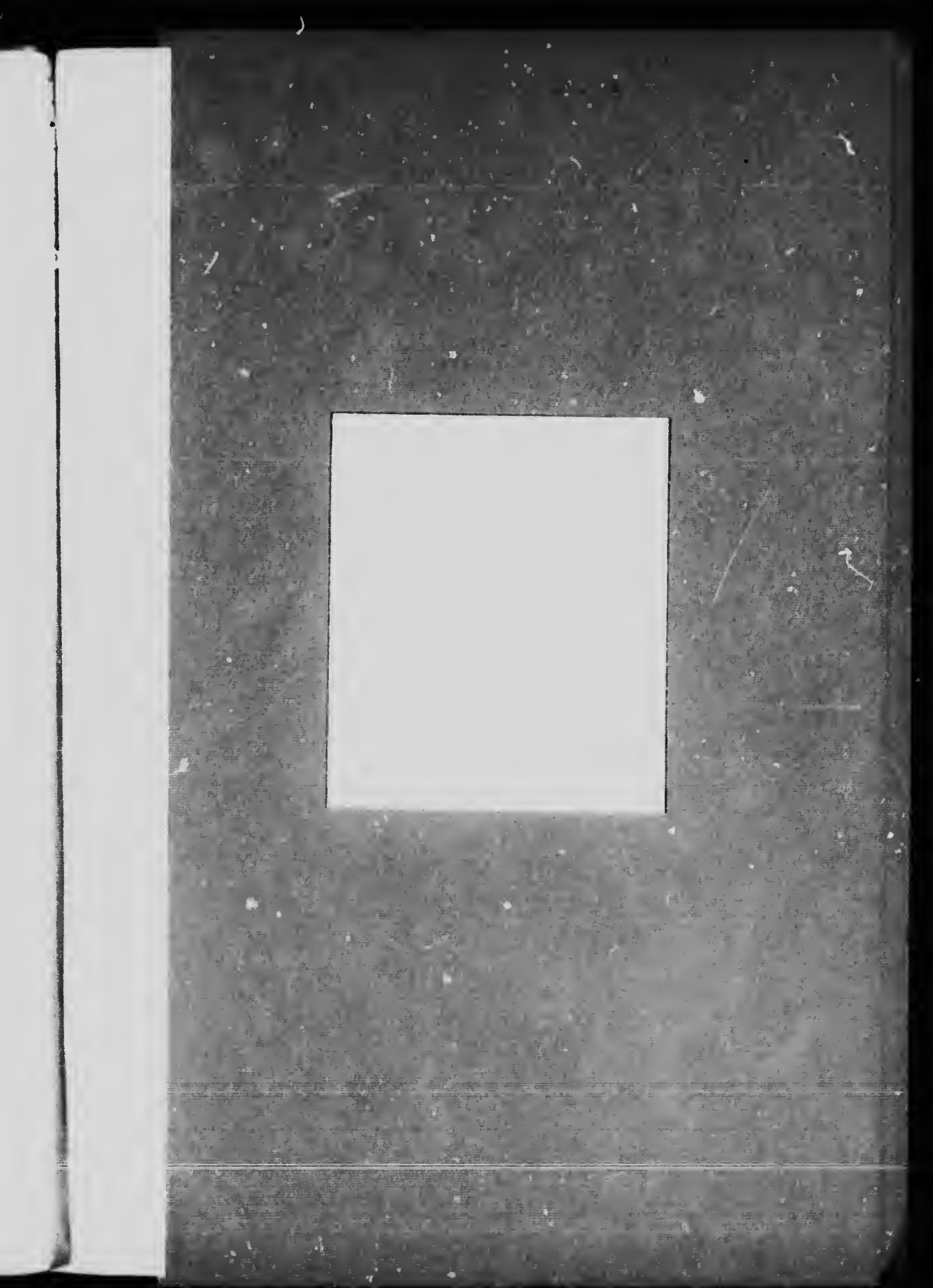
$$\xi = l - x$$

$$\phi = K + m^2 a$$

Equations presenting different algebraic forms of the same relations are given the same number, but distinguished by the use of the letters a, b, c , etc.







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