[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

# Theory of Alternating Polarographic Currents—Case of Reversible Waves

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This is a theoretical treatment of the method involving the superposition of an alternating voltage of low amplitude to the voltage applied to a polarographic cell. It is shown that the alternating current at the half-wave potential is proportional to the concentration of reducible substance and to the square root of the frequency of the alternating voltage. Theoretical results are compared with experimental data. Conclusions as to the application of the method in derivative polarography are drawn.

## Introduction

Müller and co-workers[1] were the first to demonstrate the possibility of carrying out polarographic measurements by superposing an alternating voltage of low amplitude to the voltage applied to a polarographic cell. It was shown by Müller, *et al.*, that half-wave potentials could be measured very accurately by this method.[2] Attempts to determine the concentration of reducible substance by measuring the alternating current through the polarographic cell were made by MacAleavy[3] and by Sample.[4] These authors pointed out that the alternating current exhibits a maximum at the half-wave potential; they also observed that the alternating current at $E_{1/2}$ is proportional to the concentration of reducible substance. Extensive data on the application of the method, however, were reported neither by MacAleavy nor by Sample. Recently, Breyer, Gutman and Hacobian[5] made a rather thorough experimental investigation of this method and they concluded that alternating polarographic currents have definite potentialities in analytical chemistry. These authors and those previously mentioned[1–4] applied to the polarographic cell an alternating voltage of 50 or 60 cycles per sec. Consequently, capacity currents resulting from the existence of a double layer at the electrode are rather high, and the results can be affected by a large error. This cause of error can be minimized by using low frequencies (6 cycles per sec.).[6]

Breyer and Gutman in a series of papers[7] developed a theory of alternating polarographic currents. These authors, however, did not take into account, in a satisfactory manner, the diffusion phenomenon at the electrode surface, and their views were seriously questioned by Randles.[8] No theoretical treatment of alternating polarographic currents for reversible electrode processes[9] has appeared in the literature since the publications of Breyer and Gutman, and consequently the present study was undertaken.

## Derivation of Current

**Boundary Condition.**—We consider the reversible polarographic reduction of a substance Ox to Red, and we assume that substance Red is soluble either in the aqueous phase or in mercury. Let $C(x,t)$ be the function representing the concentration of reducible substance in terms of the distance $x$ from the electrode and the time $t$ elapsed since the beginning of the electrolysis. It is shown in the classical theory of polarography that the relationship between the concentration of reducible substance at the electrode surface, $C(o,t)$, and the potential $E$ of the dropping mercury electrode is

$$E = E_{1/2} - \frac{RT}{nF}\ln\frac{C(o,t)}{C_0 - C(o,t)} \qquad (1)$$

where $E_{1/2}$ is the half-wave potential, $C_0$ the bulk concentration of substance Ox, and the other notations are conventional.[10] If potential $E$ is not very different from the half-wave potential (see below), equation (1) can be simplified by writing $C(o,t)$ as a function of $E$ and by expanding the exponential function thus obtained. By retaining the first two terms in the series, one has

$$C(o,t) = \frac{C_0}{2}\left[1 + \frac{nF}{RT}(E_{1/2} - E)\right] \qquad (2)$$

Assume now that potential $E$ varies periodically according to the function

$$E = E_{1/2} + v \sin \omega t \qquad (3)$$

where $v$ is the amplitude of a small alternating voltage superposed to the voltage applied to the cell; $\omega$ is related to the frequency $f$ of the alternating voltage by the equation $\omega = 2\pi f$.

By combining (2) and (3) one obtains the boundary condition for which the diffusion problem should be solved. Thus

$$C(o,t) - \frac{C_0}{2} = -\frac{C_0}{2}\frac{nF}{RT} v \sin \omega t \qquad (4)$$

**Variations of Concentration.**—Since the variations of potential are very rapid in comparison with the rate of the diffusion phenomenon at the electrode, it is possible to apply the differential equation of linear diffusion to the case of the dropping mercury electrode. To solve the boundary value problem, it is convenient to introduce the function $u$ defined by the equation

$$u(x,t) = C(x,t) - (C_0/2) \qquad (5)$$

In terms of this new function the initial and boundary conditions are as follows: $u(x,o) = 0$, and $u(o,t) = -\frac{C_0}{2}\frac{nF}{RT} v \sin \omega t$ (see equation (4)). The solution of the diffusion problem for this boundary condition can be obtained, for example, by the Laplace transformation[11] and the subsequent use of the inversion integral.[12] In this manner one obtains,[11] after returning to the function $C(x,t)$, the concentration as a function of time $t$ and distance $x$ from the

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(1) R. H. Müller, R. L. Garman, M. E. Droz and J. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

(2) See also J. Boeke and H. van Suchtelen, *Philips Tech. Rev.*, **4**, 213 (1939).

(3) C. MacAleavy, Belgian Patent No. 443,003 (1941).

(4) G. W. Sample, British Patent No. 599,409 (1945).

(5) B. Breyer, F. Gutman and S. Hacobian, *Australian J. Sci. Res.*, **A3**, 558, 567 (1950).

(6) P. Delahay, *Rec. trav. chim.*, **67**, 165 (1948).

(7) B. Breyer and F. Gutman, *Australian J. Sci.*, **8**, 21, 163 (1946); *Trans. Faraday Soc.*, **42**, 645, 650, 785 (1946); *Faraday Soc. Disc.*, **1**, 19 (1947).

(8) J. E. B. Randles, *ibid.*, **1**, 46 (1947).

(9) For irreversible electrode processes, see the following papers which are related to the subject: J. E. B. Randles, *ibid.*, **1**, 11 (1947); K. S. G. Doss and H. P. Agarwal, *Proc. Indian Acad. Sci.*, **34A**, 263 (1951) and J. Van Cakenberghe, *Bull. soc. chim. Belges*, **60**, 3 (1951).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y. 1941, pp. 143–144. Note that the American convention of electrode signs is used here in order to make the current increase with more positive potentials.

(11) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, Oxford, 1947, p. 259.

(12) For a detailed discussion of the method see R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., New York, N. Y., 1944, pp. 128–178. References to monographs on this subject are given in this textbook.

electrode. Thus, the alternating term in the equation for $C(x,t)$ is

$$C(x,t) = \frac{C_0}{2}\left\{1 - \frac{nF}{RT} v \exp.\left[- x\left(\frac{\omega}{2D_0}\right)^{1/2}\right] \sin\left[\omega t - x\left(\frac{\omega}{2D_0}\right)^{1/2}\right]\right\} \quad (6)$$

Equation (6) is an approximate solution of the present boundary value problem. Indeed, the initial condition was written as $u(x,o) = 0$ or $C(x,o) = C_0/2$, whereas actually the concentration varies from $C_0/2$ at $x = 0$ to $C_0$ for $x = \infty$. However, the use of an approximate initial condition is justified, because the gradient of concentration corresponding to the alternating current is much larger than the gradient corresponding to the direct electrolysis current at the half-wave potential. Therefore, the influence of the alternating current does not extend in a region of the solution where the concentration is markedly different from $C_0/2$.

Equation (6) was derived by assuming that the potential is not very different from $E^{1/2}$, *i.e.*, that $C(o,t)$ is not very different from $C_0/2$. Therefore, one concludes from (6) that the following condition should be satisfied

$$\frac{nF}{RT} v \ll 1 \quad (7)$$

For a temperature of 25°, inequality (7) is

$$v \ll 0.025 \text{ volt} \quad (8)$$

From (8) one concludes that the present treatment is valid only when the amplitude of the alternating voltage applied to the polarographic cell is of the order of a few millivolts.

**Current.**—The current is obtained by calculating the flux at the electrode surface ($x = 0$) from equation (6) and by multiplying the result by the diffusion coefficient $D$ of the reducible substance, and by the charge involved in the reduction of one mole of substance Ox. Thus, the alternating current flowing through the cell at the half-wave potential is

$$i_p = \frac{1}{2^{3/2}} \frac{n^2F^2}{RT} AD^{1/2}C_0\omega^{1/2} v(\sin \omega t + \cos \omega t) \quad (9)$$

where $A$ is the area of the electrode and the other symbols were previously defined.

Equation (9) can be transformed by combining the trigonometric functions and by calculating the area $A$ of the electrode in terms of the characteristics, $m$ and $\tau$, of the capillary. After numerical transformations, one obtains the following equation for the current corresponding to the maximum size of the mercury drop

$$i_p = Kn^2m^{2/3}\tau^{2/3}D^{1/2}\, C_0\omega^{1/2}v \sin\left(\omega t + \frac{\pi}{4}\right) \quad (10)$$

where $K$ is a numerical constant equal to 0.0160 for 25°, $i_p$ is in amperes, $m$ in mg. sec.$^{-1}$, $\tau$ in sec., $D$ in cm.$^2$ sec.$^{-1}$, $C_0$ in millimoles per liter, $\omega = 2\pi f$, $f$ being in cycles per sec., and $v$ in volts.[13]

The following properties of alternating polarographic currents are immediately derived from equation (10): (1) The current $i_p$ is proportional to the concentration of reducible substance. (2) $i_p$ is proportional to the square root of the frequency of the voltage applied to the cell. (3) Current $i_p$ leads the voltage $v$ by $\pi/4$.

It should be recalled here that the derivation of current $i_p$ is approximate. Consequently, the actual value of the numerical constant $K$ could possibly differ from the value 0.0160 obtained in the present derivation (see Experimental part).

**Admittance at $E_{1/2}$.**—Since current $i_p$ varies with the amplitude of the voltage applied to the cell it is convenient to consider the admittance at the half-wave potential. This quantity is defined by the equation

$$Y_{1/2} = Knm^{2/3}\tau^{2/3}D^{1/2}C_0\omega^{1/2} \quad (11)$$

in which $Y_{1/2}$ is in ohms$^{-1}$, and the other units are the same as in equation (10). One deduces from (11) that the admittance at the half-wave potential is proportional to $C_0$ and $\omega^{1/2}$.

**Influence of the Capacity Current and Ohmic Drop.**—In the above derivation, the influence of the capacity current and the ohmic drop was not taken into account. This matter is discussed in the present section.

In order to simplify the discussion it is convenient to use the equivalent circuit of the polarographic cell. This circuit is composed of the "polarization" impedance (sometimes referred to as the Warburg impedance[13]) in parallel with the capacity of the double layer at the half-wave potential. These two elements are in series with the resistance of the cell and that of the measuring circuit. The relationships between voltages and currents are given in the diagram of Fig. 1.[14] Vector OA, representing the amplitude of the voltage applied to the cell and the measuring circuit, is the sum of the ohmic drop BA in phase with the current and the voltage OB applied to the polarization impedance and double layer. The alternating polarographic current $i_p$ (equation (10)) leads the voltage OB by $\pi/4$, and the capacity current $i_c$ leads OB by $\pi/2$. The total current OE which is the vectorial sum of $i_p$ and $i_c$ leads the voltage OA by an angle $\varphi$.

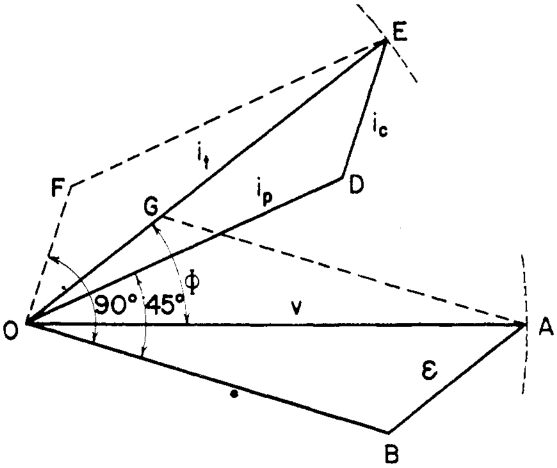

Fig. 1.—Relationship between voltages and currents.

**Determination of the Corrected Value of $i_p$.**—In actual measurements the following data are obtained: the total current $i_t$, the capacity current $i_c$ (by carrying measurements with the supporting electrolyte alone), the total resistance of the measuring circuit and the cell. The resistance of the cell is determined by carrying measurements at a frequency which should be sufficiently high (6000 cycles per sec. for example) to reduce the polarization impedance virtually to zero. From these experimental data one determines the current $i_p$ by the following method.

Trace (Fig. 1) a circle having OE = $i_t$ as radius, and construct the lines OF and OD at 90 and 45°, respectively, with respect to the arbitrarily traced radius OB. Construct OF = $i_c$ and trace FE parallel to OD; this construction yields point E and the vectors $i_t$ and $i_p$. Trace a circle of radius OA equal to amplitude $v$. The ohmic drop OG is constructed on vector OE, and GA parallel to OB is traced; the intersection A with the circle having $v$ as radius determines the vector OB representing the voltage applied to the cell. The alternating polarographic current $i_p$ corresponding to an alternating voltage of amplitude $v$ is obtained by applying the equation

$$(i_p)_{\text{corrected}} = \text{OD} \times \frac{\text{OA}}{\text{OB}} \quad (12)$$

It should be added that the value of $i_c$ which is obtained from a measurement with the supporting electrolyte alone is larger than the capacity current to be plotted in the diagram of Fig. 1. The former value of $i_c$ is obtained in an experiment in which the ohmic drop is smaller than the one existing during the actual measurement with the reducible substance. As a result, the capacity current thus obtained is too large, but the error is negligible at low frequencies (6 cycles per sec.) and for ohmic drops not exceeding 2 milli-

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(13) In connection with equations (9) and (10) see E. Warburg, *Ann. Physik*, [4] **6**, 125 (1901), and T. R. Rosebrugh and W. L. Miller, *J. Phys. Chem.*, **14**, 816 (1910). Alternating electrolytic currents are treated in these papers.

(14) For a discussion of such diagrams see for example: L. Page and N. I. Adams, Jr., "Principles of Electricity," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 453.

volts. Whenever necessary, results can be corrected for this cause of error by the following method. The diagram of Fig. 1 is constructed, and an approximate value of $i_p$ is obtained. A new value of $i_c$ taking into account the ohmic drop $\epsilon$ in the circuit is calculated, and the diagram is redrawn on the basis of this corrected value of $i_c$.

Finally, the differential double layer capacity in the case of the deposition of a metal (formation of an amalgam) could possibly differ from the capacity for pure mercury. The resulting error, however, is negligible.

**Magnitude of Capacity Current and Ohmic Drop.**—It is of interest to determine the order of magnitude of the corrections for the capacity current and ohmic drop.

If the voltage applied to the cell is $v \sin \omega t$ the capacity current is

$$i_c = 0.00852 m^{2/3}\tau^{2/3} C_1 \omega v \sin(\omega t + \pi/2) \qquad (13)$$

where the units are the same as in equation (10), and $C_1$ is the differential capacity (per unit area) of the double layer at the half-wave potential. Dividing (13) by (10) yields the ratio of the capacity current $i_c$ to the alternating polarographic current $i_p$. By introducing in the equation thus obtained the approximate values $C_1$ = 20 microfarads cm.$^{-2}$ [15] and $D = 10^{-5}$ cm.$^2$ sec.$^{-1}$, the ratio $i_c/i_p$ becomes

$$\frac{i_c}{i_p} = 3.4 \times 10^{-3} \frac{\omega^{1/2}}{nC_0} \qquad (14)$$

The capacity current can be disregarded when the ratio $i_c/i_p$ is very small. If one takes, for example, $i_c/i_p = 0.01$ it is seen from (14) that, even at low frequencies (6 cycles per sec.), the capacity current cannot be neglected unless the concentration is larger than 0.5 millimole per liter.

The ohmic drop can be calculated by using the approximate value (Fig. 1)

$$i_t \cong i_p + \frac{1}{2^{1/2}} i_c \qquad (15)$$

By combining (10), (13) and (15), one obtains

$$\frac{Ri_t}{v} = 0.0160\, n m^{2/3}\tau^{2/3} D^{1/2} C_0 \omega^{1/2} R + 0.0085 m^{2/3} C_1 \omega R \qquad (16)$$

Introducing in this equation the approximate values $C_1$ = 20 microfarads cm.$^{-2}$, $D = 10^{-5}$ cm.$^2$sec.$^{-1}$, $m^{2/3}\tau^{2/3}$ = 3 mg., one reaches the conclusion that the ohmic drop is negligible when the concentration is smaller than 0.1 millimole per liter, provided that the frequency is low (6 c.p.s.) and the resistance of the circuit does not exceed a few hundred ohms.

Summarizing, at relatively high concentrations (about 0.5 millimole per liter), the capacity current can be neglected, but the ohmic drop cannot. Conversely, the ohmic drop can be disregarded when the concentration is relatively low (less than 0.1 millimole per liter), but the capacity current cannot be neglected in this case.

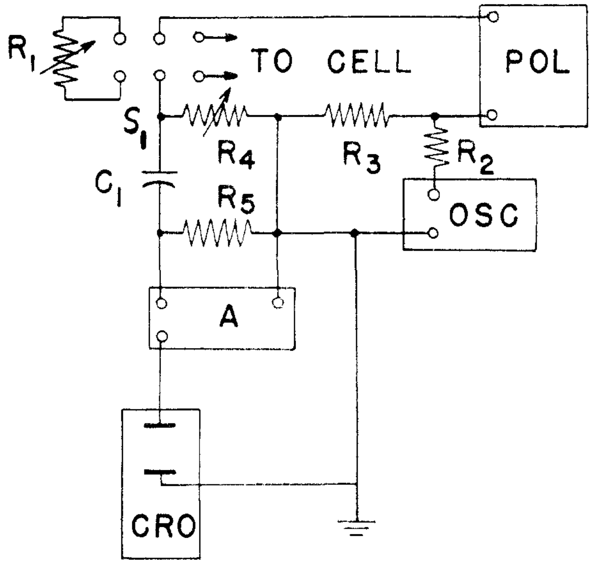

Fig. 2.—Apparatus for measuring alternating polarographic currents: R₁, 0–111,111 ohm decade box; R₂, 22,000 ohms; R₃, 6 ohm calibrated resistor; R₄, 0–9999 ohm decade box; R₅, 5000 ohms; C₁, 1000 microfarad electrolytic condenser, 35 volts; POL, manual polarograph; OSC, oscillator; A, preamplifier; C.R.O., cathode-ray oscillograph.

## Experimental

The above theory was verified by using the apparatus of Fig. 2. The polarographic cell connected to switch S₁ was polarized by means of the manual polarograph POL (Sargent, model III). Resistances R₃ and R₄ were connected in series with the cell, and an alternating voltage having an amplitude of approximately 0.005 volt was developed across resistance R₃. This alternating voltage was supplied by a precision oscillator (Hewlett-Packard, model 200 I) whose frequency was adjustable from 6 to 6300 cycles per sec. The amplitude of the alternating current through the polarographic cell was determined by measuring the ohmic drop in decade box R₄ with a cathode-ray oscillograph (DuMont, model 304 H) connected to a preamplifier (gain 20). The height of the trace on the screen of the oscillograph was adjusted to a known arbitrary value (corresponding to the maximum size of the drop) by varying R₄, the polarographic cell being inserted in the circuit; switch S₁ was then reversed and resistance R₁ was adjusted to produce a trace of the same height as the one obtained with the cell in the circuit. The current $i_t$ was calculated by applying Ohm's law, noticing that the total resistance in the circuit was $R_1 + R_3 + R_4 + X$ ($X$ resistance of polarograph with potentiometer set at $E_{1/2}$), and that the applied voltage was $2^{1/2} V \frac{R_3}{R_3 + R_2}$ ($V$, r.m.s. voltage at the output of oscillator OSC). The capacity current was determined by the same procedure, the cell being filled with the supporting electrolyte alone. The corrected value of $i_p$ was determined by the graphic procedure described above, the ohmic drop in the circuit being calculated by the equation

$$\epsilon = i_t(R_4 + X + R_c) \qquad (17)$$

in which $R_c$ represents the resistance of the cell. The latter was determined by measuring $i_t$ at 6000 cycles per sec. (see above). Whenever necessary, the alternating polarographic current was calculated by two successive approximations as described above.

The polarographic cell (H type) was not immersed in a constant temperature water-bath to avoid a stray capacity which would not have been entirely negligible at the highest frequencies used in this study. In analytical applications, however, a water-bath could be used because the frequency would be low (6 cycles per sec.). In the present work the temperature was 25 ± 2°.

The supporting electrolytes were as follows: 3 molar potassium chloride in the experiments with $Cd^{++}$ ion; 1 molar potassium oxalate + 2 molar potassium nitrate in the reduction of ferric ion; 3 molar potassium nitrate in all other cases. It was observed that gelatin causes a marked decrease in the alternating polarographic current, probably because of a decrease in the rate of the electrode process.[9] Consequently no gelatin was added to the solution being studied by the present method. Conventional waves for these solutions, however, were recorded in presence of 0.01% of gelatin.

The characteristics of the capillary were as follows: $m$ = 1.29 mg. sec.$^{-1}$, $\tau$ = 6.04 sec. in 3 $M$ KCl at −0.678 volt (*vs.* S.C.E.). The alternating polarographic currents were measured at the following potentials (*vs.* S.C.E.): $Cd^{++}$, −0.678; $Pb^{++}$, −0.428; $Tl^{+}$, −0.486; Fe(+3), −0.236; and $Cu^{++}$, −0.040 volt.

It should be pointed out that the apparatus used in the present study was constructed by making use of available equipment. Actually, the present set-up is not to be recommended for analytical applications because of its relatively low degree of accuracy (see below). In such applications, instruments composed of a low frequency phase shift oscillator[6] and a vacuum tube voltmeter would be more adequate and less expensive than the present apparatus.

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(15) See for example D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

## Description and Discussion of Results

The present theory was verified for a few electrode processes which can be regarded as virtually reversible. A set of typical data is given in Table I, and other results are presented in Figs. 3, 4 and 5.

TABLE I

DATA FOR 1 MILLIMOLAR $Cd^{++}$ IN 3 MOLAR KCl

| $f$, c.p.s. | $i_t$, micro-amp. | $i_c$, micro-amp. | $i_p$, micro-amp. | $\epsilon$,[a] milli-volts | $v'$,[b] milli-volts | Corrected $i_p$, micro-amp. |
|---|---|---|---|---|---|---|
| 6 | 8.36 | 0.17 | 8.30 | 2.06 | 3.55 | 12.1 |
| 9 | 9.56 | .27 | 9.40 | 2.30 | 3.30 | 14.7 |
| 16 | 10.65 | .48 | 10.35 | 2.47 | 3.15 | 17.0 |
| 25 | 13.34 | .77 | 12.80 | 3.01 | 2.65 | 25.0 |
| 36 | 14.65 | 1.12 | 13.90 | 3.24 | 2.45 | 29.4 |
| 49 | 15.60 | 1.51 | 14.70 | 3.42 | 2.20 | 34.6 |
| 64 | 16.70 | 1.98 | 15.30 | 3.63 | 2.05 | 38.6 |
| 81 | 17.40 | 2.51 | 15.80 | 3.74 | 1.85 | 44.3 |

[a] Ohmic drop. [b] Voltage actually applied to polarization impedance; total voltage on terminals of $R_3$ (Fig. 2) was $v$ = 5.17 millivolts.

From the data of Table I one draws the important conclusion that the magnitude of the measured current $i_t$ is markedly different from that of the corrected alternating polarographic current $i_p$. The difference between $i_t$ and $i_p$ is very large at relatively high frequencies (50–100 cycles per sec.), but even at low frequencies (6 cycles per sec.) there is a marked discrepancy. Therefore *it is essential to make corrections for the capacity current and the ohmic drop.*

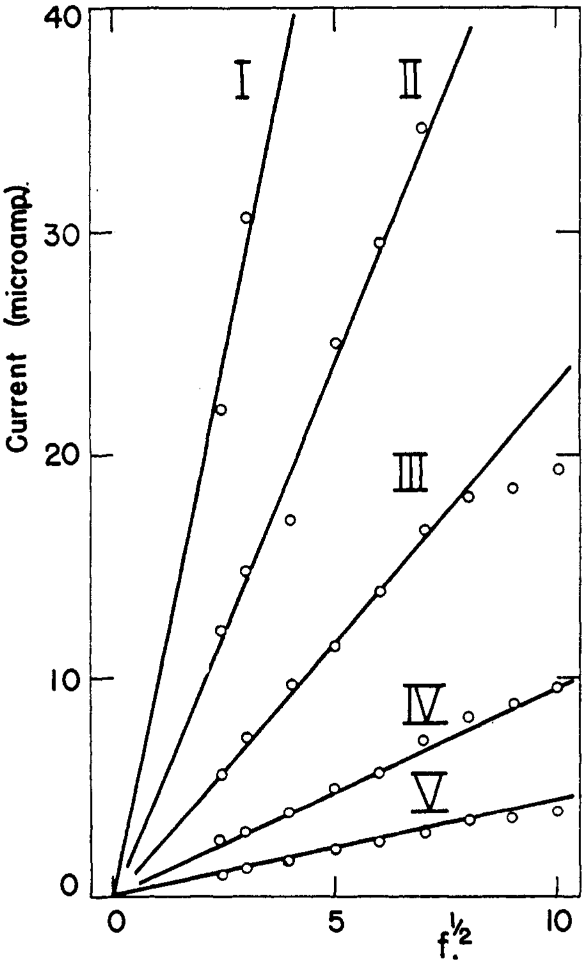

Fig. 3.—Variations of the alternating current with the square root of frequency for the reduction of cadmium ion: I, 2 m*M*; II, 1 m*M*; III, 0.5 m*M*; IV, 0.2 m*M*; V, 0.1 m*M*.

Figures 3 and 4 show that the alternating polarographic current is proportional to the square root of the frequency.[16] Figure 3 also shows that current $i_p$ is proportional to the concentration of reducible substance. The above two conclusions are in agreement with equation (10).

Equation (10) was applied to the data of Figs. 3 and 4, and currents approximately equal to one-half the experimental values were obtained. This discrepancy results from the approximate nature of the present derivation (see comments about equation (6)).

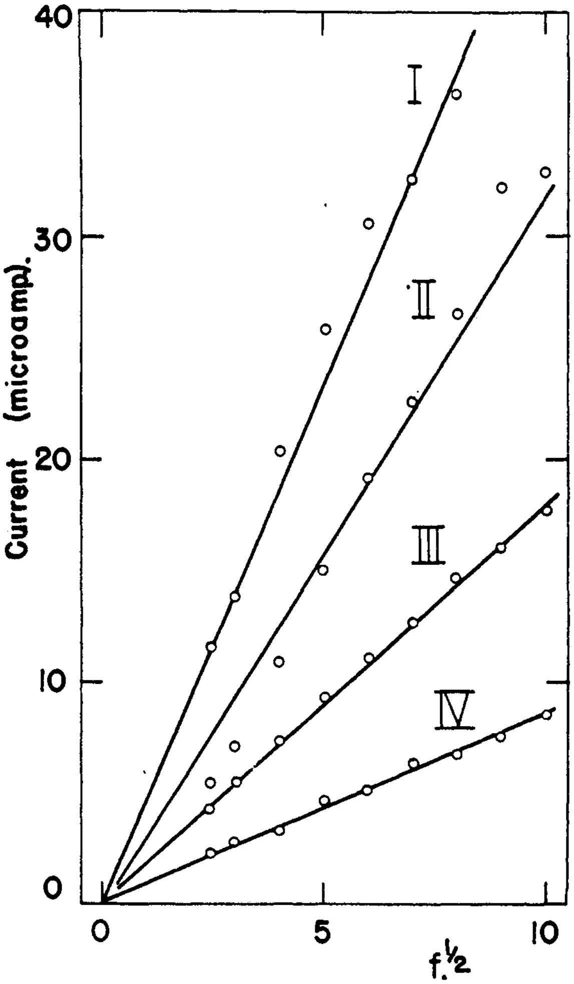

Fig. 4.—Variations of alternating polarographic current with square root of frequency: I, 1 m*M* $Pb^{++}$; II, 1 m*M* $Cu^{++}$; III, 1 m*M* $Tl^{+}$; IV, Fe(+3).

Phase shifts $\varphi$ were measured on the current–voltage diagrams (Fig. 1) for cadmium (Fig. 3),

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[16] The departure from linearity at 81 and 100 cycles per sec. for curve III probably resulted from the presence in solution of traces of a strongly adsorbed substance which caused a decrease in the rate of the electrode process (see Randles' work, ref. 9).

and the angle $\varphi$ for this case is plotted against the square root of frequency in Fig. 5. This diagram shows that $\varphi$ increases with the frequency at low concentrations of reducible substance (0.1 millimolar), and that, at high concentrations, $\varphi$ decreases when $f$ is increased. These observations can be explained in the following manner.

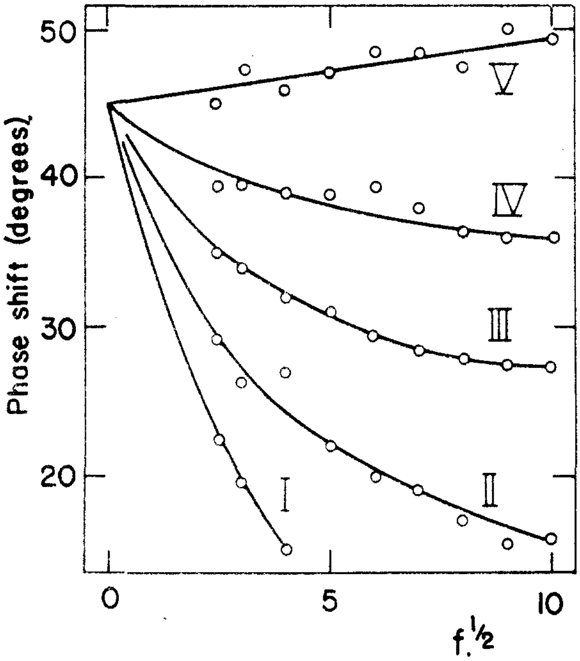

Fig. 5.—Variations of phase shift with square root of frequency for the data of Fig. 3.

At relatively high concentrations of reducible substance, the alternating polarographic current is much larger than the capacity current even at frequencies as high as 81 cycles per sec. (Table I). As a result, the phase shift between $i_t$ and the voltage *applied to the polarization impedance* is slightly smaller than 45°. The ohmic drop in the cell is relatively large (Table I), however, and consequently the angle $\varphi$ is small (see Fig. 1). Thus, the decrease of $\varphi$ with increasing frequencies is caused chiefly by an increase in the ohmic drop. At low concentrations, the capacity current is not negligible in comparison with the alternating polarographic current, but the ohmic drop is relatively small. Consequently $\varphi$ increases with frequency. At low frequencies the angle $\varphi$ approaches 45° regardless of the concentration. This is the value of $\varphi$ one would obtain if there were no ohmic drop in the circuit and no double layer capacity (equation (10)).

A phase shifter was not available, but the former conclusions were verified qualitatively by forming Lissajous patterns on the screen of the oscillograph.

## Conclusion

The present treatment is of interest since alternating polarographic currents seem to offer some advantages over the other methods of derivative polarography developed thus far. These methods involve either a twin dropping mercury electrode device[17] or a capacity differentiating circuit.[18] The former method is not satisfactory because of the difficulty of synchronizing the two dropping mercury electrodes,[19] whereas the latter method does not give a sustained reading and requires a recording device. The method, whose theory is reported here, does not have these disadvantages, although it requires a large capital outlay. However, satisfactory results with the present method cannot be expected unless the proper corrections for the ohmic drop and the capacity current are made.

The present treatment was solely concerned with so-called reversible electrode processes, and this work should also be extended to cases involving large overvoltages.[9] This matter is being investigated.

ADDED IN PROOF.—Since the preparation of this manuscript an important work on the theory of the faradaic admittance has been made available under the form of a report to the Office of Naval Research.[20]

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BATON ROUGE, LOUISIANA

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(17) G. Semerano and L. Riccoboni, *Gazz. chim. ital.*, **72**, 297 (1942).

(18) M. P. Lévêque and F. Roth, *J. chim. phys.*, **46**, 480 (1949); J. J. Lingane and R. Williams, THIS JOURNAL, **74**, 790 (1952).

(19) See, however, the mechanical synchronization device described by L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950).

(20) D. C. Grahame, "Mathematical Theory of the Faradaic Admittance," Technical Report to the Office of Naval Research, No. 8, Project NR-051-150 (June, 1952), deposited in the Library of Congress.