[Contribution from the Department of Chemistry, Harvard University]

Derivative Polarography. I. Characteristics of the Leveque–Roth Circuit

By James J. Lingane and Richard Williams

This paper presents the results of a systematic study of the operational characteristics of the Leveque–Roth circuit, which achieves differentiation of the polarographic wave by means of a high capacity condenser in series with the galvanometer of an otherwise conventional polarograph. A limiting equation for the magnitude of the derivative maximum under the condition that the electrode reaction is reversible, and that there is no charging or recording lag, has been derived. Because of the charging and recording lags the observed derivative maxima are smaller than the ideal value, but the theoretical limiting value is closely approached when the time constant of the condenser–galvanometer circuit, the galvanometer period, and the rate of change of the applied e.m.f. are made very small. The height of the derivative maximum is directly proportional to the concentration of the electroactive substance only when the concentration and the resistance in the cell circuit are both very small; otherwise the ratio of the derivative maximum to concentration decreases with increasing concentration to an extent dependent on the cell circuit resistance. The charging lag, coupled with any galvanometer lag, results in a more or less asymmetrical derivative curve whose peak occurs later—and thus at a greater potential—than the half-wave potential.

Of the several ingenious circuits[1,2,3,4] proposed for recording derivative curves that of Leveque and Roth[5] has the appeal of greatest simplicity. The Leveque–Roth circuit, which essentially is that shown in Fig. 1, requires only a single, conventional dropping electrode. Differentiation of the current–voltage curve is achieved simply by introducing a large capacitance C_1 (electrolytic condenser) in the galvanometer or recorder circuit of an otherwise conventional polarograph.[6] The polarographic bridge is operated at a constant rate by a synchronous motor so that the rate of application of the applied e.m.f. is constant. Because the condenser C_1 does not pass constant current the galvanometer remains at zero at potentials preceding the polarographic wave, but deflects on the rising part of the wave, reaches a maximal value in the neighborhood of the potential where the wave slope is maximal, and then returns to zero when the diffusion current plateau is reached. Figure 2 shows a conventional polarogram and the corresponding derivative curve recorded with this circuit.

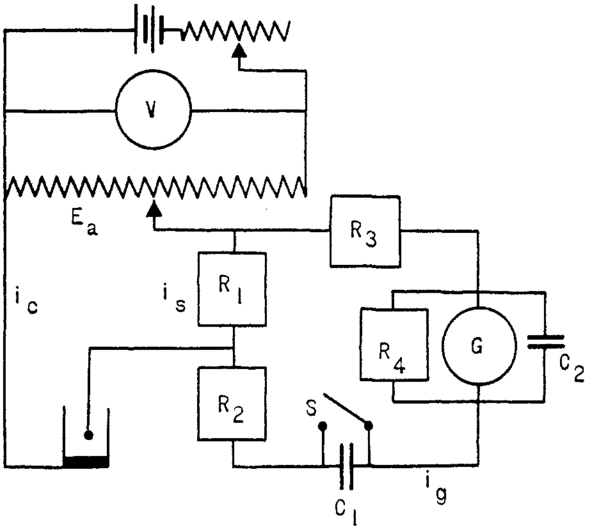

Fig. 1.—Derivative circuit.

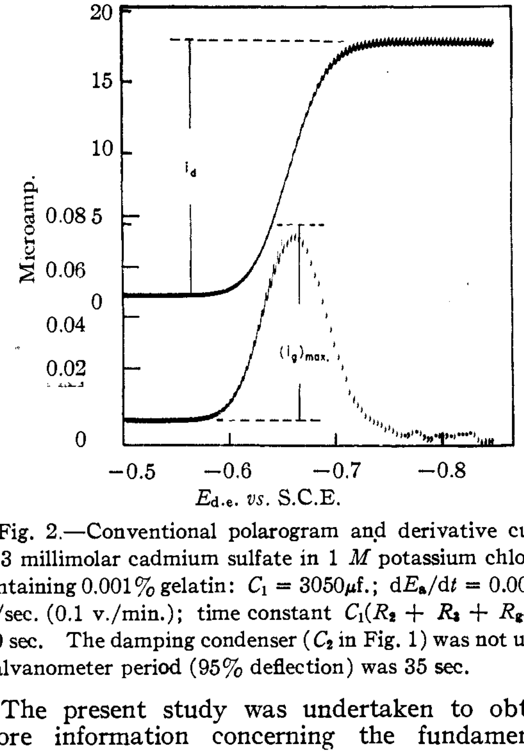

Fig. 2.—Conventional polarogram and derivative curve of 3 millimolar cadmium sulfate in 1 *M* potassium chloride containing 0.001% gelatin: $C_1 = 3050\mu$f.; $dE_a/dt = 0.00167$ v./sec. (0.1 v./min.); time constant $C_1(R_2 + R_3 + R_g) =$ 7.0 sec. The damping condenser (C_2 in Fig. 1) was not used. Galvanometer period (95% deflection) was 35 sec.

The present study was undertaken to obtain more information concerning the fundamental operational characteristics of this circuit than is given in the paper of Leveque and Roth, and especially to investigate the quantitative influence of the various factors which govern the recorded derivative maximum.

Theory of the Leveque–Roth Circuit

We shall first assume that the charging time of the differentiating capacitor C_1 in Fig. 1 is very small, *i.e.*, that the time constant of the condenser–galvanometer circuit is so small relative to the rate of change of the applied e.m.f. that there is no appreciable lag, and also that the galvanometer period is short enough not to introduce a recording lag.

Referring to Fig. 1, the charge Q (coulombs) in capacitor C_1 at any instant is

$$Q = C_1E \tag{1}$$

where E is the instantaneous voltage across the terminals of the capacitor and C_1 is the capacitance in farads. Correspondingly the instantaneous current i_g flowing through the capacitor and actuating the galvanometer G is

$$i_g = \frac{dQ}{dt} = C_1\frac{dE}{dt} \tag{2}$$

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[1] J. Heyrovsky, *Chem. Listy*, **40**, 222 (1946); *Analyst*, **72**, 229 (1947); *Chem. Listy*, **43**, 149 (1949).

[2] J. Vogel and J. Riha, *J. chim. phys.*, **47**, 5 (1950).

[3] L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950).

[4] P. Delahay, *Rec. trav. chim.*, **67**, 159, 165 (1948).

[5] M. P. Leveque and F. Roth, *J. chim. phys.*, **46**, 480 (1949); **47**, 623 (1950).

[6] Excellent discussions of the use of a capacitor to differentiate various types of electrometric curves have been given by P. Delahay, *Anal. Chim. Acta*, **1**, 19 (1947); *Bull. soc. chim. Belg.*, **56**, 7 (1947).

The voltage impressed into the galvanometer circuit is the ohmic potential drop i_sR_1 generated by the current i_s through the resistance R_1. Because the cell current i_c divides through R_1 and the galvanometer circuit it is evident that

$$i_s = i_c - i_g \qquad (3)$$

where the currents are assumed to be the average values during the life of each mercury drop. Therefore, the instantaneous voltage across the capacitor is equal to i_sR_1 or $(i_c - i_g)R_1$ minus the sum of the ohmic potential drops in R_2, R_3 and R_g; that is

$$E = (i_c - i_g)R_1 - i_g(R_2 + R_3 + R_g) \qquad (4)$$

where R_g is the net parallel resistance of the galvanometer and its damping shunt R_4. By differentiating eq. 4 and substituting the resulting expression for $\mathrm{d}E/\mathrm{d}t$ into eq. 2 we obtain

$$i_g = C_1\left[R_1\frac{\mathrm{d}i_c}{\mathrm{d}t} - (R_1 + R_2 + R_3 + R_g)\frac{\mathrm{d}i_g}{\mathrm{d}t}\right] \qquad (5)$$

When i_g attains its maximal value $\mathrm{d}i_g/\mathrm{d}t$ becomes zero, the second term in eq. 5 drops out, and

$$(i_g)_{\max} = C_1R_1\left(\frac{\mathrm{d}i_c}{\mathrm{d}t}\right)_{\max} \qquad (6)$$

In the special case of symmetrical reversible reaction the equation of the wave (i_c *vs.* $E_{d.e.}$ curve) is

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF}\ln\frac{i}{i_d - i} \qquad (7)$$

where $E_{d.e.}$ is the potential of the dropping electrode against an external reference electrode and i_d is the diffusion current. Differentiation of this equation leads to

$$\frac{\mathrm{d}i}{\mathrm{d}t} = -\frac{nF}{RT}\left[\frac{i(i_d - i)}{i_d}\right]\frac{\mathrm{d}E_{d.e.}}{\mathrm{d}t} \qquad (8)$$

The wave slope $\mathrm{d}i/\mathrm{d}t$ acquires its maximal value at the half-wave point where $i = {}^1/_2\, i_d$, and therefore

$$\left(\frac{\mathrm{d}i}{\mathrm{d}t}\right)_{\max} = -\frac{nF}{RT}\left(\frac{i_d}{4}\right)\frac{\mathrm{d}E_{d.e.}}{\mathrm{d}t} \qquad (9)$$

Substitution of eq. 9 into eq. 6, and introduction of the numerical value $(F/RT) = 39.0$ volt^{-1} at 25°, yields

$$(i_g)_{\max} = -9.75\, nC_1R_1i_d\frac{\mathrm{d}E_{d.e.}}{\mathrm{d}t} \qquad (10)$$

The negative sign conforms to the convention that $\mathrm{d}E_{d.e.}/\mathrm{d}t$ is negative for a reduction reaction.

Recorded polarograms, and recorded derivative curves, involve the total e.m.f. applied to the cell circuit, E_a, rather than the potential of the dropping electrode, $E_{d.e.}$ In general $\mathrm{d}E_{d.e.}/\mathrm{d}t$ is a function not only of $\mathrm{d}E_a/\mathrm{d}t$ but also of the total resistance in the cell circuit and the rate of change of the cell current with time. If R_c is the total resistance in the cell circuit (usually cell resistance plus R_1) then

$$-\frac{\mathrm{d}E_{d.e.}}{\mathrm{d}t} = \frac{\mathrm{d}E_a}{\mathrm{d}t} - R_c\frac{\mathrm{d}i}{\mathrm{d}t} \qquad (11)$$

When this relation is substituted into eq. 8 the expression for the maximal slope of the current-voltage curve at the half-wave point is

$$\left(\frac{\mathrm{d}i}{\mathrm{d}t}\right)_{\max} = \left(\frac{9.75ni_d}{1 + 9.75\, ni_dR_c}\right)\frac{\mathrm{d}E_a}{\mathrm{d}t} \qquad (12)$$

Correspondingly the maximal derivative current is given by

$$(i_g)_{\max} = \left(\frac{9.75\, nC_1R_1i_d}{1 + 9.75\, ni_dR_c}\right)\frac{\mathrm{d}E_a}{\mathrm{d}t} \qquad (13)$$

In this relation C_1 is expressed in farads, all of the R's in ohms, E_a in volts, and t in seconds. The i_d term in the numerator is expressed in the same units as i_g (usually microamp.), but the i_d term in the denominator must be in amperes because the product I_dR_c is in volts.

Although eq. 6 is valid for either reversible or irreversible reactions eq. 13 applies only to symmetrical reversible reactions. With irreversible reactions the constant 9.75 is replaced by a smaller constant whose value is peculiar to the particular reaction.

Equation 13 is based on the assumption that C_1 acquires its charge instantaneously. Therefore it must be regarded as a limiting relation which the actual value of $(i_g)_{\max}$ may be expected to approach when the time constant $C_1(R_2 + R_3 + R_g)$ of the condenser–galvanometer circuit is made small relative to the rate of change of the applied e.m.f. In practice it is usually necessary to employ values of $C_1(R_2 + R_3 + R_g)$ and $\mathrm{d}E/\mathrm{d}t$ of such magnitudes that the charging time of C_1 is not negligible. Under these conditions i_g lags in time behind $\mathrm{d}i_c/\mathrm{d}t$; on the rising front of the derivative curve it is smaller than the ideal value and on the decreasing side it is larger. Consequently the observed derivative curve is more or less asymmetrical, and the observed maximum is smaller than the ideal value predicted by eq. 13. The maximum occurs later than the maximum in $\mathrm{d}i_c/\mathrm{d}t$ and therefore at a potential greater (nearer the top of the wave) than the half-wave potential.

When a long period galvanometer is used there is the additional complication that the deflection lags appreciably behind the actual value of i_g. This adds to the distortion of the derivative curve and contributes to the suppression of the observed maximum.

The cumulative effect of these two types of lag is a complex function of the rate of change of the applied e.m.f. and the characteristics of the particular galvanometer or recorder used. Examples of the magnitude of each type of lag are presented below.

Experimental Technique

The circuit used, which is essentially that of Leveque and Roth,[5] is shown schematically in Fig. 1. A conventional Heyrovsky-type polarograph constructed in this Laboratory was used. The bridge consisted of a precision ten-turn 50-ohm Beckman Helipot potentiometer (linearity ± 0.1%) which was driven at a constant rate of exactly one turn per minute by a synchronous motor. The motor was reversible so that curves could be recorded with either increasing or decreasing applied e.m.f. Various values of $\mathrm{d}E_a/\mathrm{d}t$ were obtained by appropriate adjustment of the total voltage across the bridge. In case the desired total bridge voltage was too small to reach the reduction potential of a particular substance an additional constant voltage was applied in series with the cell from a low resistance radio-type potential divider powered by a 2-v. lead storage cell. This "initial voltage" was usually adjusted to be 0.1 to 0.3 v. smaller than the reduction potential.

The bridge was powered by small lead storage cells in series with a variable resistance which enabled the total bridge voltage to be adjusted to any desired integral value. The total bridge voltage was read on a precision 0–3 v. Jewel voltmeter V, which was calibrated and readable with a precision of ±1 mv.

The variable resistances R_1 and R_2, which constitute an Ayrton shunt, were two 1–1000 ohm three decade precision resistance boxes. The sum $R_1 + R_2$ was kept constant at 1000 ohms.

The resistance R_3 (10–100,000 ohm four decade resistance box) was provided in order to vary the time constant C_1 $(R_2 + R_3 + R_g)$ without altering C_1 or the total resistance of R_1 and R_2. For most of the measurements R_3 was set at 10,000 ohms.

The recording galvanometer G was a Rubicon Type 3514 with an internal resistance of 517 ohms, a critical damping resistance of *ca.* 10,000 ohms, a critically damped period of 5 sec., and an intrinsic sensitivity when critically damped of 7.20 × 10^{-4} microamp./mm. on a scale 120 cm. distant. The damping resistance R_4 was used to adjust the galvanometer period. For the majority of measurements R_4 was set at 2000 ohms, which produced a galvanometer period (95% of full deflection) of 18 sec.

The galvanometer sensitivity for both i_c and i_g was determined by closing switch S to short out C_1, replacing the d.e. cell by a precision 10,000 ohm resistance, and applying a constant voltage from the bridge. The potential drop across the precision resistance was measured with a potentiometer, and the sensitivity for i_c was computed by comparing the galvanometer deflection with the current computed from this potential drop.[7] The sensitivity for i_g was then computed *via* Ohm's law from the sensitivity for i_c and the known resistances in the galvanometer circuit. The i_g sensitivity depends only on the value of R_4 and is independent of the values of R_1, R_2 and R_3, but the i_c sen-

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(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 228.

sitivity does, of course, depend on the latter values. With R_4 = 2000 ohms the sensitivity for i_g was 9.12 $\times 10^{-4}$ microamp./mm., and with R_3 = 10,000 ohms the maximal sensitivity for i_c (corresponding to R_1 = 1000 ohms and R_2 = 0) was 1.04 $\times$ 10^{-2} microamp./mm.

The capacitor C_1 is an electrolytic condenser, or several such condensers in parallel. Its capacitance must be several thousand microfarads, but its voltage rating can be small because the voltage across it never exceeds a few millivolts. The capacitance of C_1 under the actual conditions of use was determined as follows. The dropping electrode cell was replaced by a precision resistance (*e.g.*, 10,000 ohms) and with S open the bridge was operated at a known constant rate dE_a/dt. This produces a constant rate of increase of voltage across C_1 and hence a constant current through the galvanometer and R_4 which is given by

$$i_g = C_1 \frac{dE}{dt} = C_1R_1 \frac{di_s}{dt} = C_1R_1 \frac{di_c}{dt} \quad (14)$$

where E is the voltage across the terminals of C_1. From Ohm's law di_c/dt is expressible as

$$\frac{di_c}{dt} = \frac{1}{R_s} \frac{dE_a}{dt} \quad (15)$$

where R_s is the known resistance in the cell circuit which is the sum of the resistance substituted for the cell plus the net resistance across the ends of R_1. Therefore C_1 is given by

$$C_1 = R_s i_g / R_1 \, (dE_a/dt) \quad (16)$$

Because the resistance of an electrolytic condenser is not infinitely great the value of i_g observed in the calibration includes a small "ohmic current." Correction for this is made by measuring i_g as the difference between the galvanometer deflections with the bridge operating and with it stopped at a known value of E_a. This correction amounted to only a few per cent. with a satisfactory condenser and C_1 could be determined with a precision of ± 1%.

It would be desirable to employ a pure capacitance for C_1 rather than the less-than-perfect electrolytic condenser, which at best is only a first approximation to a capacitance, but true non-electrolytic capacitors of the order of several thousand microfarads would be very expensive to construct. However, if the ohmic drop across R_1 were amplified about a thousand-fold by a linear amplifier, and the amplified signal presented to the capacitor–galvanometer circuit, it should be possible to use a precision non-electrolytic capacitor of the order of a few microfarads. This is being investigated.

Galvanometer oscillations are relatively much greater in derivative than in ordinary polarography. When a mercury drop falls the abrupt decrease in the voltage impressed across C_1 causes the condenser to discharge until the ohmic potential across R_1 recovers as the succeeding drop grows. This discharge imparts a sharp "backward" pulse to the galvanometer. The magnitude of the backward galvanometer deflection depends directly on the rate of discharge of C_1 and inversely on the period of the galvanometer. The rate of discharge, and hence the magnitude of the oscillations, can be decreased by increasing R_3 to increase the time constant $C_1(R_2 + R_3 + R_g)$, and the period can be increased by decreasing R_4. However, the first adjustment decreases the galvanometer sensitivity with respect to the cell current, and the second decreases both the i_c and i_g sensitivities, so they cannot be made beyond certain limits if adequate sensitivity is to be maintained. Furthermore, a very long galvanometer period is objectionable because it introduces appreciable recording lag. It is desirable, therefore, to augment the damping action of R_3 and R_4 by placing in parallel with the galvanometer and R_4 the electrolytic condenser C_2, through which the abrupt discharge pulse from C_1 is effectively by-passed without significantly altering the direct current characteristics of the galvanometer.[5,8,9] With the particular galvanometer used satisfactory damping was obtained when C_2 was 3000 microfarads. Care must be taken to select an electrolytic condenser that is free from parasitic e.m.f., to observe the proper polarity when connecting it into the circuit, and to short circuit it for some time to be sure it is fully discharged before placing it across the galvanometer.

Because of the relatively great time constant $C_1(R_2 + R_3 + R_g)$ care must be taken after closing the circuit to wait until the galvanometer attains its equilibrium position before starting to record the derivative curve.

The dropping electrode was of the ordinary type with a drop time of about 4 sec. in 1 *M* potassium chloride on open circuit. For most measurements a cell with an internal mercury pool anode was used, because it is essential in derivative polarography that the cell resistance be as low as possible. The cell resistance with 1 *M* potassium chloride was measured with an a.c. Wheatstone bridge (Industrial Instruments, Inc., Model RC-1B). The minimum resistance corresponding to maximum drop size was 65 ohms. Assuming as a first approximation that the resistance is inversely proportional to the drop area, this corresponds to an average resistance during the drop life of about 100 ohms.

All measurements were made at 25.00 ± 0.05°. The temperature coefficient of the derivative maximum is approximately the same as that of the diffusion current, *i.e.*, about +2% per deg.

Values of $(i_g)_{max}$ were measured as indicated in Fig. 2, using the average of the galvanometer oscillations.

Most of the experiments were performed with lead ion in 1 *M* potassium chloride containing a trace of either methyl red or gelatin as a maximum suppressor, because the reduction of lead ion is known to proceed very nearly reversibly.[10]

Results and Discussion

Influence of R_1.—When the charging and recording lags remain constant it follows from eq. 13 that $(i_g)_{max}$ should be a linear function of R_1, and this was observed by Leveque and Roth.[5] When, as in the present circuit, $R_1 + R_2$ is an Ayrton-type shunt of constant total resistance R_2 is decreased by the same amount that R_1 is increased, so that the time constant of the condenser–galvanometer circuit decreases with increasing R_1. This decreases the charging lag and causes the derivative maximum to increase at a somewhat greater-than-linear rate with increasing R_1. However, by making $R_3 + R_g$ large compared to $R_1 + R_2$ the deviation from linearity can be kept negligibly small.

For example, with 1 millimolar lead ion in 1 *M* potassium chloride, with C_1 = 3,100 microfarads, with $R_1 + R_2$ = 1000 ohms, with R_3 = 10,000 ohms, with R_g = 411 ohms, and with dE_a/dt = 0.1 v./min. (0.00167 v./sec.), the observed relation between $(i_g)_{max}$ and R_1 was

R_1, ohms	50	100	200	300	400
$(i_g)_{max}$, microamp.	0.0162	0.0342	0.0671	0.101	0.135
$[(i_g)_{max}/R_1] \times 10^4$	3.24	3.42	3.35	3.37	3.37

Influence of the Time Constant on $(i_g)_{max}$.—From eq. 13 the derivative maximum should increase directly with C_1. However, when C_1 is increased the time constant $C_1(R_2 + R_3 + R_g)$ is also increased, and correspondingly the charging lag is increased. The net result of these two opposing effects is that $(i_g)_{max}$ increases at a less-than-linear rate with increasing C_1.

When C_1 is kept constant and the time constant is increased by increasing R_3 the increased charging lag causes $(i_g)_{max}$ to decrease. This is demonstrated by the derivative curves in Fig. 3, which were recorded with all other factors except R_3 constant. The time constant was increased from 3.8 to 34.9 sec. by increasing R_3 from 0 to 10,000 ohms. The lower family of curves was recorded without the damping condenser C_2 and the upper family with C_2 = 3000 microfarads.

Comparison of corresponding curves in the two

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(8) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 750 (1940).

(9) P. Delahay, *Bull. soc. chim. France*, 527 (1948).

(10) Ref. 7, pp. 145-146.

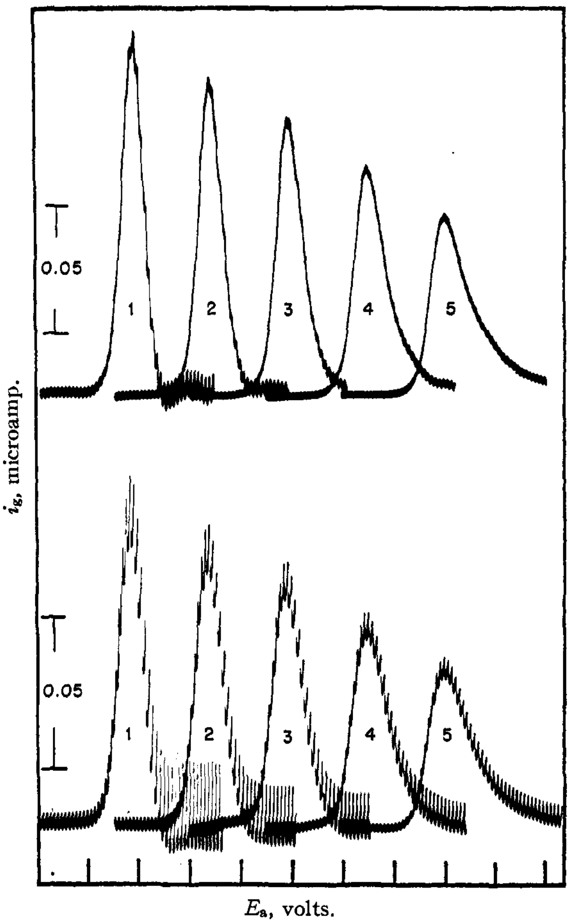

Fig. 3.—Influence of charging lag caused by increasing time constant at a constant value of C_1. All curves recorded with the same solution of 1 millimolar lead ion in 1 *M* potassium chloride, at the same value of dE_a/dt (0.00167 v./sec.) and with C_1 constant at 3120 μf. The lower family was recorded without damping condenser C_2 and the upper family with C_2 = 3000μf; R_1 = 190 ohms, R_2 = 810 ohms, R_4 = 2000 ohms. Each curve starts at 0.3 v., and the voltage marks correspond to an increment of 0.1 v. (60 sec.). The values of R_3 were (1) 0, (2) 1500, (3) 3000, (4) 6000, and (5) 10,000 ohms, the corresponding time constants $C_1 \cdot (R_2 + R_3 + R_g)$ were (1) 3.8, (2) 8.5, (3) 13.1 (4) 22.5 and (5) 34.9 sec.

sets shows the beneficial influence of the damping condenser in reducing the galvanometer oscillations without appreciably influencing the derivative maximum. Comparison of the curves in the lower set from left to right demonstrates that the relative magnitude of the oscillations decreases with increasing time constant. The reason for this latter effect is that with increasing time constant the rate of discharge of C_1 as each drop falls is diminished, and consequently the magnitude of the backward pulse imparted to the galvanometer is decreased. The oscillations are much greater following the derivative peak than preceding it because the total charge stored in C_1 is larger following the peak, and hence the charge decrement responsible for the backward pulse is greater.

The asymmetry produced by the charging lag when C_1 is very large is demonstrated by the curves in Fig. 4, obtained with values of the time constant $C_1(R_2 + R_3 + R_g)$ of 18.5 and 152 sec. at the same galvanometer period (18 sec.) and the same value of dE_a/dt. The values of R_1 were adjusted (50 ohms for curve 1 and 220 ohms for curve 2) so that the maxima would be about the same height; *i.e.*, if the recording sensitivity had been the same in both cases the maximum of curve 2 would have been only about one-fifth as large as that of curve 1.

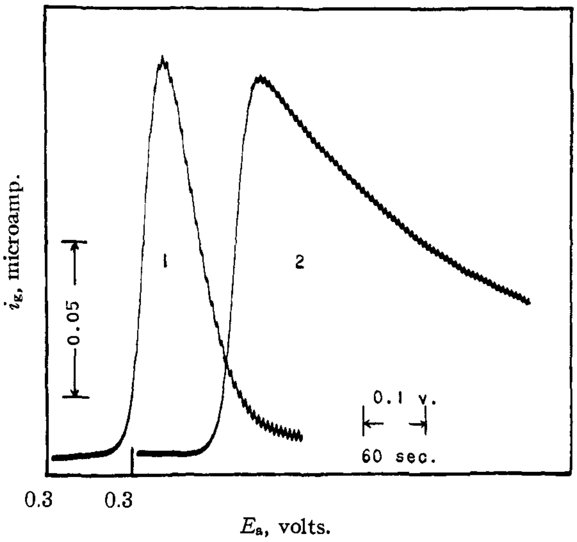

Fig. 4.—Asymmetry produced by the charging lag. Both curves were recorded with the same solution of 1 millimolar lead ion in 1 *M* potassium chloride. Each starts at E_a = 0.3 v. and dE_a/dt was 0.00167 v./sec. (0.1 v./min.). The galvanometer period (95% deflection) was 18 sec. in both cases, R_g was the same (411 ohms), and C_1 was the same (13,640μf.). (1) R_1 = 50 ohms, R_3 = 0, and $C_1(R_2 + R_3 + R_g)$ = 18.5 sec.; (2) R_1 = 220 ohms, R_3 = 10,000 ohms, and $C_1(R_2 + R_3 + R_g)$ = 152 sec. Note that sensitivity factor $R_1/(R_1 + R_2)$ for curve 1 was 0.227 that for curve 2. Time constants: (1) 18.5 sec.; (2) 152 sec.; current sens.: (1) 0.05; (2) 0.22.

In Fig. 5 observed values of the quantity $(i_g)_{max}/i_dR_1(dE_a/dt)$ are plotted against the time constant which was increased from 3.8 to 63.6 sec. by increasing R_3 at constant values of C_1 and dE_a/dt. From eq. 13 if there were no charging lag this quantity should have remained constant at a value theoretically equal to $(9.75nC_1)/(1 + 9.75ni_dR_c)$ or 6.0×10^{-2} ohm^{-1} sec. volt^{-1}, which is indicated by the horizontal dashed line. The fact that the theoretical value is closely approached as the time constant approaches zero substantiates the validity of eq. 13 as a limiting relation.

Influence of dE_a/dt.—With a given time constant the rate of change of the applied e.m.f. influences the derivative maximum in two ways. If there were no charging lag and no galvanometer lag $(i_g)_{max}$ should be directly proportional to dE_a/dt. Secondly dE_a/dt influences the derivative maximum because the greater its value the greater is the cumulative suppressive effect of the charging and recording lags. Because these effects oppose each other the next result is that $(i_g)_{max}$ increases at a less-than-linear rate with increasing dE_a/dt.

The net effect is demonstrated by the derivative curves in Fig. 6 obtained with values of dE_a/dt

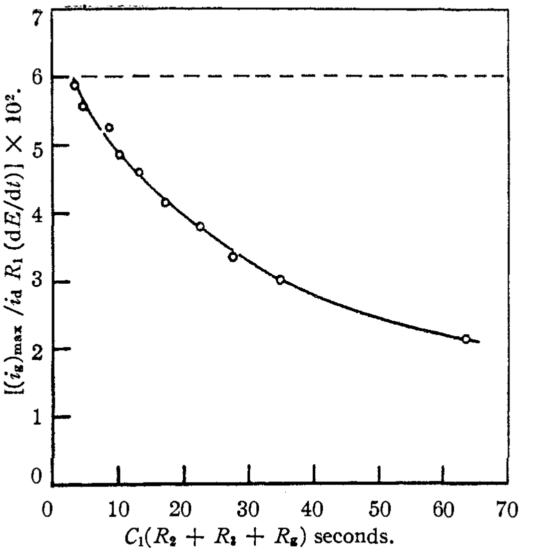

Fig. 5.—Influence of the time constant. One millimolar lead ion in 1 *M* potassium chloride: C_1 = 3120μf.; dE_a/dt = 0.00167 v./sec.; i_d = 7.4 microamp.; R_1 = 190 ohms; R_2 = 810 ohms; R_4 = 2000 ohms; R_g = 411 ohms. The time constant was varied by increasing R_3 from 0 to 20,000 ohms. The theoretical value of $(i_g)_{max}/i_d$ R_1(dE_a/dt) corresponding to no charging lag is indicated by the horizontal dashed line.

from 0.005 to 0.001 v./sec. The distinct asymmetry with a rapid rate of application of the applied e.m.f. is due chiefly to the charging lag and it tends to disappear when dE_a/dt is relatively small.

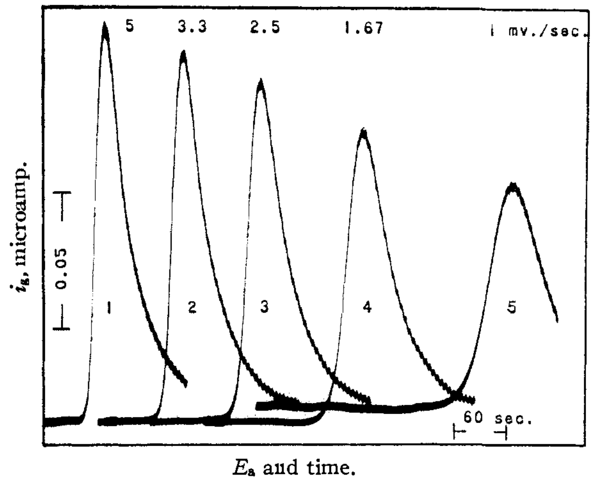

Fig. 6.—Influence of rate of change of the applied e.m.f. One millimolar lead ion in 1 *M* potassium chloride containing 10^{-4}% methyl red: C_1 = 3105μf.; C_2 = *ca.* 3000μf.; R_1 = 300 ohms; R_3 = 10,000 ohms; R_4 = 2000 ohms. Galvanometer period (95% deflection) = 18 sec. Each curve starts at E_a = 0.3 v. and dE_a/dt was (1) 0.005, (2) 0.0033, (3) 0.0025, (4) 0.00167 and (5) 0.001 v./sec.

Figure 7 shows plots of the quantity $(i_g)_{max}/i_dR_1$(dE_a/dt) against dE_a/dt at a constant value of C_1 and a constant time constant of 35 sec. with three different galvanometer periods of 11, 17 and 59 sec. The galvanometer period was varied by adjusting R_4, and R_3 was appropriately readjusted to maintain the sum $R_2 + R_3 + R_g$ constant. The i_g sensitivity of the galvanometer was determined at each value of R_4. If there were no charging or galvanometer lag it follows from eq. 13 that the above quantity should remain constant at 9.75 $nC_1/(1 + 9.75ni_dR_c)$ or 6.0 × 10^{-2} ohm^{-1} sec. volt^{-1}, as indicated by the horizontal dashed line. The observed values are much smaller than the limiting theoretical value at the larger values of dE_a/dt, and, as expected, are smaller at a given value of dE_a/dt the greater the galvanometer period. At all galvanometer periods the observed values approach the theoretical limiting value as dE_a/dt approaches zero.

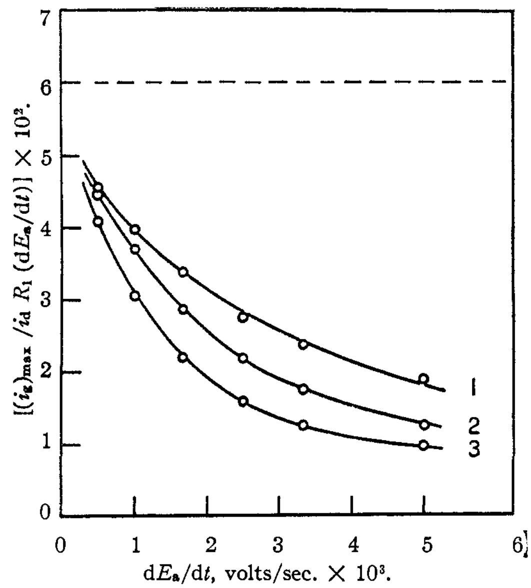

Fig. 7.—Influence of rate of change of the applied e.m.f. and galvanometer period at a constant time constant. One millimolar lead ion in 1 *M* potassium chloride containing 10^{-4}% methyl red: C_1 = 3110μf.; C_2 = *ca.* 3000μf. Galvanometer period adjusted by varying R_4 to (1) 11, (2) 17, and (3) 59 sec. for 95% deflection. The time constant $C_1(R_2 + R_3 + R_g)$ was kept constant at 35 sec. by adjusting R_3 to compensate the various values of R_1 and R_4.

Relation between $(i_g)_{max}$ and C_1.—From eq. 13 if all other factors are kept constant $(i_g)_{max}$ should be directly proportional to C_1. Using 1 millimolar lead ion in 1 *M* potassium chloride, with dE/dt = 0.1 v./min., experiments were made with C_1 ranging from 1000 to 6000 microfarads. To prevent change in the charging lag with different values of C_1 the time constant was maintained constant at 20 sec. by adjusting R_3 to compensate for the change in C_1. The expected linear relation between $(i_g)_{max}$ and C_1 was found to be obeyed to within ± 2%.

Relation between $(i_g)_{max}$ and Concentration and Cell Circuit Resistance.—Leveque and Roth[5] reported a linear relation between the height of the derivative maximum and concentration, but eq. 13 predicts that this is an approximation which approaches validity only under limited conditions. The diffusion current is directly proportional to concentration, but from the form of eq. 13 it is evident that the ratio of the derivative maximum to concentration should decrease with increasing concentration (increasing i_d in the denominator). A linear relation should be approached only when the $9.75ni_dR_c$ term in the denominator is negligibly small compared to 1; *i.e.*, when the diffusion current (concentration) and cell circuit resistance are both relatively small. These conditions happened to be satisfied in the experiments of Leveque and Roth because they used concentrations of cadmium ion from only 0.04 to 0.2 millimolar.

The effect of an increase in the cell circuit resistance on the derivative maximum is exemplified by the curves in Fig. 8.

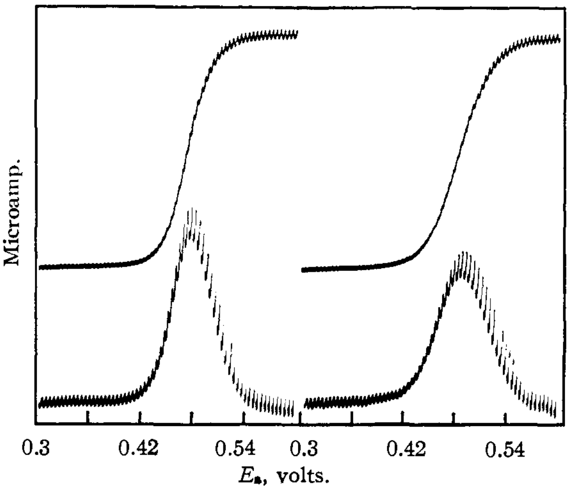

Fig. 8.—Influence of cell circuit resistance. Two millimolar lead ion in 1 *M* potassium chloride containing $10^{-4}\%$ methyl red: $C_1 = 3280\mu$f.; $dE_a/dt = 0.06$ v./min.; $R_3 =$ 1000 ohms, $R_4 = 1000$ ohms. Galvanometer period (95% deflection) = 35 sec. The damping condenser C_2 was not used. The upper ordinary polarograms were recorded with $R_1 = 70$ ohms, and the lower derivative curves with $R_1 =$ 450 ohms. The resistance of the cell alone was *ca.* 100 ohms. The curves on the left were recorded with no additional resistance, and those on the right with 5000 ohms in series with the cell.

The relation between the maximum derivative current and concentration of lead ion in 1 *M* potassium chloride is shown by the data plotted in Fig. 9. Curve 1 was obtained with no other resistance in the cell circuit except that (*ca.* 100 ohms) of the cell itself, and curve 2 resulted when 5000 ohms additional resistance was placed in series with the cell. With no additional resistance $(i_g)_{\max}$ increases linearly with concentration up to about 2 millimolar, but above this concentration it falls off due to the increasing significance of the $9.75ni_dR_c$ term. With 5000 ohms in the cell circuit (curve 2) the curve is entirely non-linear.

With 2.5 millimolar lead ion (i_d = 18 microamp.) the maximum derivative current with 5000 ohms in the circuit is 0.58 of its value without additional resistance. The ratio expected from eq. 13 is the reciprocal of $1 + (9.75 \times 2 \times 18 \times 10^{-6} \times 5000)$ or 0.36. The observed ratio is larger than this because the decreased slope of the c.v. curve produced by the additional resistance results in a longer time to polarize from the beginning of the wave to the point of maximum slope, so that the suppressive effect of the charging and recording lags are relatively smaller.

To retain the convenience of a linear relation in practical applications of the derivative technique it is evident that the cell resistance must be kept as small as possible and that measurements must be restricted to relatively small concentrations.

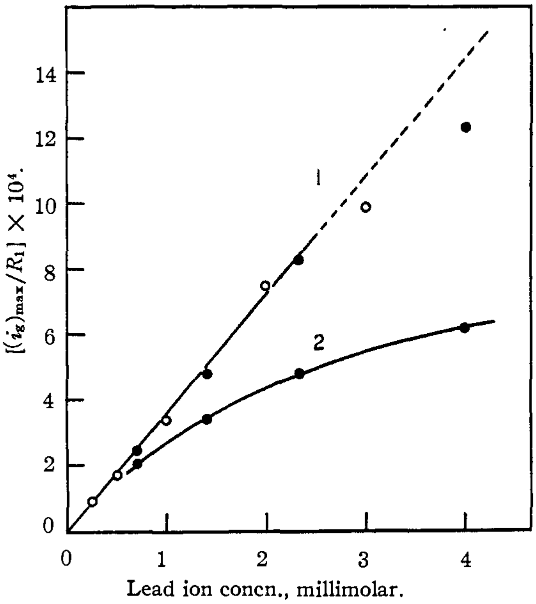

Fig. 9.—Relation between derivative maximum and concentration of lead ion without and with additional cell circuit resistance. The supporting electrolyte was 1 *M* potassium chloride. The solid points were obtained using 0.003% gelatin as a maximum suppressor, and the open points using $10^{-4}\%$ methyl red. Curve 1 was obtained with no additional resistance in the cell circuit (cell resistance *ca.* 100 ohms) and curve 2 with 5000 ohms in series with the cell: $C_1 = 3100\mu$f.; $dE_a/dt = 0.1$ v./min.; $C_1(R_2 + R_3 + R_g) =$ 35 sec.

Displacement of the Potential of the Derivative Maximum from the Half-wave Potential.—Because of the charging and recording lags the derivative maximum occurs later than the half-wave potential. This is illustrated by the curves in Fig. 10. The upper curve was recorded with increasing applied e.m.f. in the ordinary way, and the lower curve was obtained with decreasing applied e.m.f. Because the c.v. curve in this case is symmetrical about the half-wave potential the displacement of the potential of the derivative maximum with decreasing applied e.m.f. must be equal but of opposite sign to the displacement with increasing applied e.m.f. Consequently the arithmetic mean of the two derivative maximum potentials corresponds closely to the true half-wave potential. It should be noted that this technique corrects only for the charging and recording lags and not for any displacement of the apparent half-wave potential from the true value due to resistance in the cell circuit.

There is no significant difference in the value of $(i_g)_{\max}$ observed with decreasing and increasing applied e.m.f.

The displacement ΔE of the potential of the derivative maximum from the half-wave potential, measured as one half the difference between the potentials of the derivative maxima with increasing and decreasing applied e.m.f., was determined

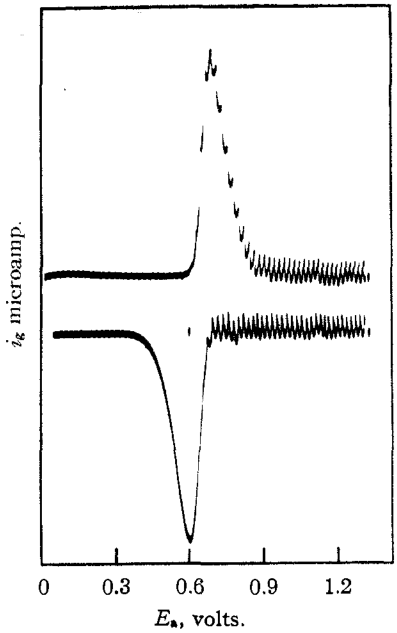

Fig. 10.—Displacement of potential of derivative maximum from half-wave potential. Three millimolar cadmium sulfate in 1 M potassium chloride containing 0.001% gelatin: C_1 = 3050μf.; $C_1(R_2 + R_3 + R_g)$ = 5.8 sec.; dE_a/dt = 0.3 v./min. Galvanometer period (95% deflection) = 30 sec. The upper curve was recorded with increasing, and the lower curve with decreasing, applied e.m.f.

at various values of dE_a/dt with the galvanometer period constant (18 sec.) and $C_1(R_2 + R_3 + R_g)$ constant (35 sec.). Measurements of ΔE were also made using various galvanometer periods with dE_a/dt constant at 0.1 v./min. and $C_1(R_2 + R_3 + R_g)$ constant at 35 sec., and finally at various values of the time constant $C_1(R_2 + R_3 + R_g)$ with dE_a/dt constant at 0.1 v./min. and the galvanometer period constant at 18 sec. The results are shown in Fig. 11.

In each case ΔE increases almost linearly with the increasing variable, the increase being greatest with increasing dE_a/dt. At a constant time constant and constant galvanometer period ΔE would evidently decrease to zero if the rate of change of the applied e.m.f. were made infinitely small. However, with dE_a/dt and the galvanometer period both constant, ΔE extrapolates to a minimal value of about 21 mv. as the time constant (T.C.) approaches zero. This represents the lag due to the galvanometer alone. Similarly with dE_a/dt and the time constant both constant, ΔE extrapolates to a minimal value of about 23 mv. as the galvanometer period (G.P.) approaches zero, and this represents the contribution due to the charging lag alone.

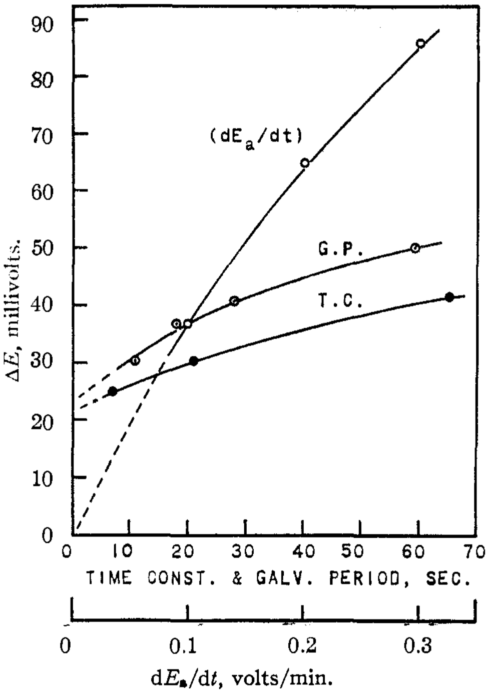

Fig. 11.—Influence of rate of change of applied e.m.f. (dE_a/dt), galvanometer period (G.P.), and time constant $C_1(R_2 + R_3 + R_g)$ (curve T.C.), on displacement ΔE of potential of derivative maximum from half-wave potential. One millimolar lead ion in 1 M potassium chloride containing 10^{-4}% methyl red: C_1 = 3110μf. For curve dE_a/dt the galvanometer period was constant at 18 sec. and the time constant was constant at 35 sec. For curve G.P. the rate of change of applied e.m.f. was constant at 0.1 v./min. and the time constant was constant at 35 sec. For curve T.C. the galvanometer period was constant at 18 sec. and dE_a/dt was constant at 0.1 v./min.

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