[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# Convection Controlled Limiting Currents (Convection Currents). II. The Convection Mercury Electrode

BY I. M. KOLTHOFF, JOSEPH JORDAN AND STEPHEN PRAGER

RECEIVED MAY 20, 1954

A stationary mercury microelectrode is described which yields typical convection currents in stirred solutions when the electrode reaction is fast enough. The reduction of mercurous, thallous and cadmium ions proceeds reversibly, linear diffusion being the controlling factor of the transport of the metal in the mercury phase, and forced convection of the electroactive species in the solution phase. Current–voltage, current–time and voltage–time interrelations are discussed and an equation is derived which accounts quantitatively for the variation with time of the potential at constant current. In spite of intense stirring of the solution the mercury in the convection electrode remains quiescent. The electrode is very suitable for the determination of diffusion coefficients of metals in dilute amalgams from anodic current–time curves, the shape of which is controlled by linear diffusion.

In a previous paper[1] characteristics of convection currents at rotated and stationary platinum wire electrodes were discussed. In the present paper a stationary mercury micro-convection electrode in stirred solutions is described. Current–voltage curves, current–time curves (at constant potential) and voltage–time curves (at constant current) in the reduction of aquo thallous, cadmium and mercurous ions are presented. The electroreduction of these ions proceeds reversibly. In a subsequent paper it will be shown that many electroreductions and oxidations, which yield waves at the dropping electrode corresponding to reversible reactions, are irreversible at the convection mercury electrode. This behavior may be a serious limitation for theoretical and practical applications. It is planned to study the "degree of reversibility" of several reactions as a function of the extent of stirring. From a practical point of view it may be mentioned that the convection mercury electrode (CME) has at least the following advantages over the dropping mercury electrode (DME) in amperometric titrations: one, easier to construct and to manipulate, and two, greater sensitivity. It therefore can be used for the titration of more dilute solutions than the DME.

## Experimental

**Materials.**—C.P. chemicals and conductivity water were used throughout. "Stock amalgams" (about 0.01 *M*) of thallium and cadmium were prepared by electrolysis of chloride solutions in an atmosphere of nitrogen. More dilute amalgams were prepared by mixing the "stock" with pure mercury.

**Cell and Electrodes.**—A 250-ml. Pyrex beaker, 9 cm. in height and 7 cm. in diameter, served as electrolysis cell. The indicator electrode consisted of a capillary cuvette filled with mercury or with an amalgam, about 1 cm. in height and with a bore of 1.5–2 mm. mounted on the center axis of the cell with the aid of a ground glass joint which protruded 25 mm. from the bottom. The mercury appeared to adhere quasi rigidly to the walls of the capillary and did not move even when exposed to violent shaking. Capillaries with a diameter greater than 2 mm. yielded irregular and irreproducible currents in stirred solutions, apparently because the surface of the mercury was set in motion. The solution had a tendency to penetrate into the capillary and disrupt the column of mercury, especially at negative potentials (v.i.). To minimize this disturbance the upper extremities of the cuvette were coated with a water-repellent silicone film, prepared from "Dri-Film SC 87," supplied by General Electric, Waterford, N.Y. Electrical contact was established through sealed-in platinum wires and mercury. The cell was closed with a rubber stopper with appropriate holes for in- and outlets for nitrogen, stirrer and salt bridge. A Hume–Harris saturated calomel electrode[2] (SCE) served as reference electrode. The resistance of the cell was 1000 ohm in 0.1 *M* potassium chloride and 350 ohm in 0.1 *M* nitric acid. Potentials reported in this paper have been corrected for *IR* drops and are referred to the SCE.

**Instrumentation.**—Current–voltage (c.v.) curves were recorded wth a Sargent XXI Polarograph at a chart speed of 2.53 cm. per minute. Unless otherwise stated the rate of change of applied potential, $\Delta V/\Delta t$, was 2.47 mv./sec. Manual measurements of limiting currents were made with a circuit previously described.[3]

Current–time (c.t.) curves at constant potential were recorded at a chart speed of 5.06 cm./min. Voltage–time (v.t.) curves were measured at constant current maintained by short-circuiting the electrolysis cell in series with a 22.5 v. Burgess "B"-Battery and resistances of 20–25 megohm. The potential was measured with a Beckman Model H AC line-operated *p*H meter and recorded as a function of time on the polarograph chart with a precision and accuracy of 0.002 v. This was accomplished by disconnecting the galvanometer of the Beckman instrument and feeding its indicating current into the polarograph.

**Procedure.**—The volume of solution was 150 ml.; a variation by ±10 ml. did not affect the results. The solution was stirred at 900 r.p.m. with the aid of a glass stirrer with six asymmetrically bent blades, about 12 mm. in length, located 5 mm. above the indicator electrode. A displacement of the stirrer up to 8 mm. had no effect on the results. Equal currents were obtained with rates of stirring between 800–1200 r.p.m., but currents decreased whenever the rate of stirring was increased or decreased beyond these limits. Solutions were very vigorously bubbled throughout the experiments with high purity Linde nitrogen. Bubbling under a pressure of at least 1.3 atm. was required to maintain solutions free of oxygen. It was ascertained that the effect of bubbling on convection coefficients[1] was negligible under the experimental conditions.

## Results

**Residual Currents.**—The residual current in dilute perchloric acid was found the same as at the DME. Identical residual c.v. curves were obtained when they were run from positive to negative potentials and *vice versa*. As shown in Fig. 1 a very pronounced maximum was obtained in potassium chloride at +0.1 v. when the residual current was recorded from positive to negative potentials. This maximum was not suppressed by gelatin and is probably due to the formation of an adhering film of mercurous chloride on the electrode. The portion of the c.v. curve with the maximum corresponds to the dissolution pattern of the film. A similar maximum was obtained in a phosphate buffer of *p*H 7. Between 0.0 and −1.5 v. the residual current of 0.1 *M* potassium chloride at the CME

---

(1) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3843 (1954).

(2) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

(3) I. M. Kolthoff and J. Jordan, *Anal. Chem.*, **25**, 1833 (1953).

TABLE I

CHARACTERISTICS OF COMPOSITE CURRENT–VOLTAGE CURVES AT THE CONVECTION ELECTRODE

| Solution | Indicator electrode | $C_s$, concn. of electroactiv. ion (moles/l.) | Zero current potential (v. *vs.* S.C.E.) Experim. value | Zero current potential (v. *vs.* S.C.E.) Thermodyn. equilibr. value[a] | $E_{1/2}$, (v. *vs.* S.C.E.) | $\Delta E_{1/2}$, (volt) |
|---|---|---|---|---|---|---|
| $Hg_2^{++}$ in 0.1 *M* $HNO_3$ | Pure mercury | $5 \times 10^{-6}$ | +0.368 | +0.378 | +0.357 | 0.033 |
| | | $5 \times 10^{-5}$ | + .400 | + .408 | + .390 | |
| $Tl^+$ in 0.1 *M* KCl | $1.615 \times 10^{-2}$ *M* thallium amalg. | $10^{-5}$ | − .631 | − .640 | − .651 | .061 |
| | | $10^{-4}$ | − .572 | − .580 | − .590 | |
| $Cd^{++}$ in 0.1 *M* $KNO_3$ | $1.012 \times 10^{-2}$ *M* cadmium amalg. | $5 \times 10^{-6}$ | − .668 | − .679 | − .680 | .030 |
| | | $5 \times 10^{-5}$ | − .637 | − .649 | − .650 | |

[a] Calculated from Latimer's standard potential for the mercury–mercurous couple ("Oxidation Potentials," 2nd Ed., Prentice–Hall, Inc., New York, N. Y., p. 175), Kolthoff and Lingane's compiled data on amalgam potentials ("Polarography," 2nd Ed., Vol. I, Interscience Publishers, Inc., New York, N. Y., p. 198), and Kielland's ionic activity coefficients (THIS JOURNAL, **59**, 1675 (1937)). Activity coefficients of the metal in the amalgam were assumed to be unity.

was of the order of 0.1 μamp. or less, and exhibited irregular oscillations at about −1.9 v., followed by an abrupt increase. Concomitantly, solution was observed to penetrate into the indicator electrode capillary, disrupting the continuity of the mercury column. Between 0.0 and −2.0 v. residual currents of potassium nitrate and of ammonia–ammonium chloride buffers were similar to those of potassium chloride.

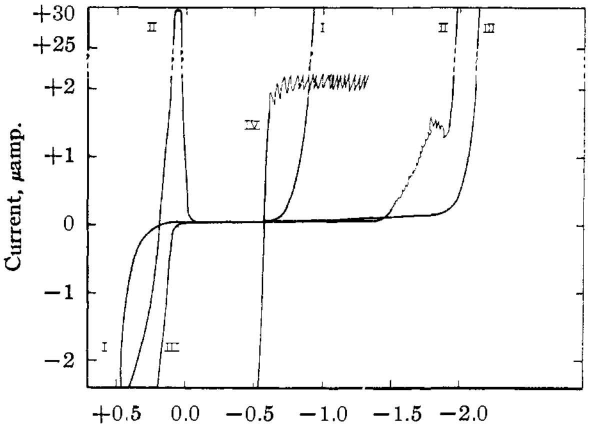

Fig. 1.—Current–voltage curves, run from positive to negative potentials: I, 0.1 *M* perchloric acid at CME; II, 0.1 *M* potassium chloride at CME; III, 0.1 *M* potassium chloride at DME; IV, $10^{-4}$ *M* thallous ion in 0.1 *M* KCl at 0.01615 *M* thallium amalgam convection electrode.

**Current–Voltage Curves.**—C.v. curves at the CME of mercurous ion solutions in 0.1 *M* nitric acid were analogous in shape to those at the DME.[4] Similar composite c.v. curves were also obtained with aquo thallous and cadmium solutions at amalgam convection electrodes. Recorded c.v. curves coincided within an experimental error of ±2% with those measured with the manual apparatus and the limiting currents in both instances exhibited fluctuations of about ±5% from a mean value. As an illustration of the oscillations the c.v. curve of thallous ion in 0.1 *M* potassium chloride is given in Fig. 1 (curve IV). Limiting currents reported in this paper are the arithmetic mean of the fluctuations, corrected for residual currents. The limiting currents were proportional to concentration in the range between $5 \times 10^{-6}$ and $5 \times 10^{-4}$ *M* and equal to $(20.6 \pm 0.4) \times 10^3$ μ amp./equiv. per l. for all three species. Cathodic half-wave and zero current potentials observed on composite waves of mercurous mercury, and of aquo thallous and cadmium ions at corresponding amalgam electrodes, are listed in Table I.

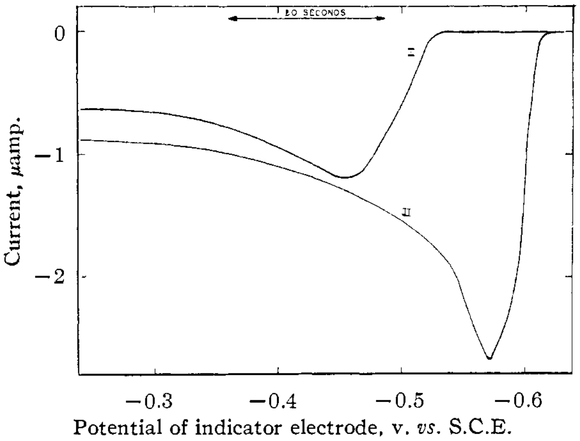

Fig. 2.—Anodic current–voltage curves of amalgams, run from negative to positive potentials: I, $1.615 \times 10^{-3}$ *M* thallium amalgam in 0.1 *M* KCl; II, $1.012 \times 10^{-3}$ *M* cadmium amalgam in 0.1 *M* $KNO_3$.

C.v. curves recorded from negative to positive potentials of dilute amalgams of thallium and cadmium in supporting electrolytes free of thallous and cadmium ions yielded anodic waves of the shape shown in Fig. 2. Identical curves were observed in quiet and in stirred solution. The current at a given potential decreased continuously with time (v.i.), which accounts for the decrease of the anodic currents (Fig. 2) in the range of potentials where constant values of limiting currents would be expected.

C.v. curves of aquo thallous and cadmium ions at a convection electrode of pure mercury resembled the shape of classical polarographic waves. However, the slope of the wave of a given solution and its half-wave potential varied with the rate of change of applied potential, while the limiting current was independent of it and the same as at the corresponding amalgam electrode. Experimental results are summarized in Table II. As can be seen in the table, the half-wave potentials at a given $\Delta V/\Delta t$ did not depend on the concentration of the electroactive species.

---

(4) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 2732 (1941).

TABLE II

CHARACTERISTICS OF CATHODIC CURRENT-VOLTAGE CURVES AT THE CONVECTION MERCURY ELECTRODE

| Solution | $C_s$, concn. of electro-active ion (moles/l.) | $E_{3/4} - E_{1/4}$ (volt) $\Delta V/\Delta t$ = 2.47, mv./sec. | $\Delta V/\Delta t$ = $1.23_5$, mv./sec. | $E_{1/2}$ (v. *vs.* SCE) $\Delta V/\Delta t$ = 2.47, mv./sec. | $\Delta V/\Delta t$ = $1.23_5$, mv./sec. |
|---|---|---|---|---|---|
| $Tl^+$ in 0.1 | $10^{-5}$ | 0.080 | 0.101 | −0.515 | −0.528 |
| *M* KCl | $10^{-4}$ | .078 | .102 | − .515 | − .526 |
| $Cd^{++}$ in | $5 \times 10^{-6}$ | .045 | .053 | − .612 | − .619 |
| 0.1 *M* $KNO_3$ | $5 \times 10^{-5}$ | .047 | .052 | − .614 | − .620 |

**Current–Time Curves at Constant Potential. (a) Anodic Amalgam Currents.**—The anodic currents at potentials of −0.2 and −0.4 v. of thallium and cadmium amalgams (Fig. 2) decreased in inverse proportion with the square root of time. For ready comparison we have evaluated in Table III the quantity *Q*, expressed in μamp. × sec.$^{1/2}$ equiv.$^{-1}$ × *l* and defined as follows

$$Q = (i_a)_t\sqrt{t}/nC_a \qquad (1)$$

where $(i_a)_t$ denotes the instantaneous anodic current at time *t*, *n* the number of electrons per mole involved in the electrode process and $C_a$ the concentration of the amalgam in moles/liter. With a given amalgam the current was found to be the same at −0.2 and −0.4 v. after the same time of electrolysis. The ratio of the currents of equinormal thallium amalgam and cadmium amalgam electrodes is given by the ratio of the *Q* values shown in Table III.

TABLE III

CHARACTERISTICS OF ANODIC CURRENT–TIME CURVES AT CONSTANT POTENTIAL OF CADMIUM AND THALLIUM AMALGAMS[a]

| Amalgam | $C_a$, amalgam concn. (moles/l.) | *t*, time, sec. | $(i_a)_t$, anodic current[b] (μamp.) at −0.4 v. | at −0.2 v. | $Q = (i_a)_t\sqrt{t}/nC_a$[c] (μamp. × sec.$^{1/2}$ × equiv.$^{-1}$ × l.) |
|---|---|---|---|---|---|
| | $1.615 \times 10^{-3}$ | 10 | 2.09 | 2.08 | $4.06 \times 10^3$ |
| | | 100 | 0.66 | 0.67 | 4.11 |
| Thallium | | 10 | 21.2 | 21.2 | 4.13 |
| | $1.615 \times 10^{-2}$ | 100 | 6.69 | 6.74 | 4.15 |
| | | 1000 | 2.10 | 2.08 | 4.09 |
| | | | | Mean | $(4.11 \pm 0.04) \times 10^3$ |
| | $1.012 \times 10^{-3}$ | 10 | 3.28 | 3.25 | $5.09 \times 10^3$ |
| | | 100 | 1.03 | 1.03 | 5.08 |
| Cadmium | | 10 | 32.6 | 32.4 | 5.08 |
| | $1.012 \times 10^{-2}$ | 100 | 10.4 | 10.3 | 5.12 |
| | | 1000 | 3.32 | 3.29 | 5.14 |
| | | | | Mean | $(5.10 \pm 0.03) \times 10^3$ |

[a] Supporting electrolytes: 0.1 *M* KCl for thallium, 0.1 *M* $KNO_3$ for cadmium. [b] Corrected for residual current. [c] Calculated from the arithmetic mean of the currents at −0.4 and −0.2 v.

**(b) Cathodic Convection Currents.**—In the electrolysis at the CME of thallous or cadmium ions the cathodic current on the ascending part of the wave decreases when the potential is kept constant. Figure 3 illustrates the decrease of current with time at constant potentials using in each experiment a "fresh" indicator electrode of pure mercury in a $10^{-4}$ *M* solution of thallous ion. By graphical extrapolation, a plot of the "current at zero time," $i_0$, *vs.* potential was obtained, with a "half-wave potential at zero time," $(E_{1/2})_0$, of −0.503 v. and $(E_{3/4} - E_{1/4})_0$ equal to 0.058 v. In $5 \times 10^{-5}$ *M* aquo cadmium solution $(E_{1/2})_0$ and $(E_{3/4} - E_{1/4})_0$ were −0.601 and 0.029 v., respectively. (See values in Table II for comparison.)

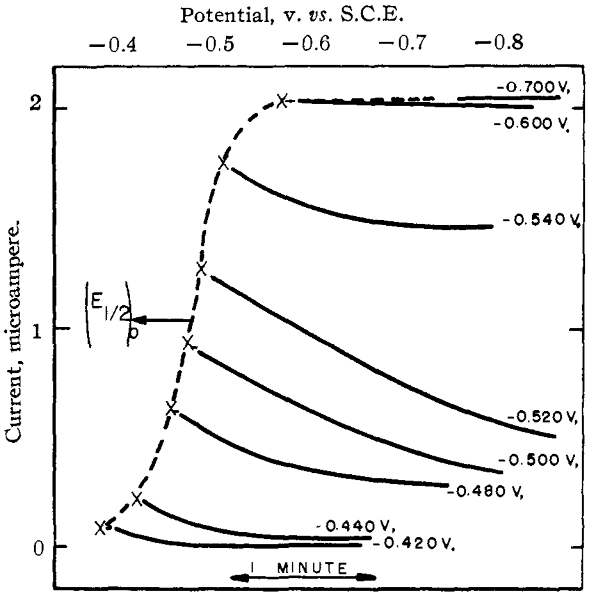

Fig. 3.—Current–time curves of $10^{-4}$ *M* $Tl^+$ in 0.1 *M* KCl. Starting point of each curve represents applied potential (top horizontal scale), as well as "zero time." Dotted curve represents plot of "current at zero time ($i_0$)" *vs.* potential. Currents are corrected for residual current and potentials for *iR* drop.

**Voltage–Time Curves at Constant Current.**—When the current at a point of the cathodic wave of thallous or cadmium ion is kept constant the potential of the CME becomes more negative with time. Voltage time curves recorded at a constant current of 1.03 μamp. in $10^{-4}$ and $2 \times 10^{-4}$ *M* thallous solutions and in $5 \times 10^{-5}$ and $10^{-4}$ *M* aquo cadmium solutions are shown in Fig. 4.

## Discussion

Equality of the limiting currents in the reduction of aquo mercurous, thallous and cadmium ions indicates that they are not diffusion controlled because the diffusion coefficients of the three species are $0.92 \times 10^{-5}$, $2.00 \times 10^{-5}$ and $0.72 \times 10^{-5}$ cm.$^2$ sec.$^{-1}$, respectively.[4,5] These limiting currents are controlled by the same expression as those at the convection platinum electrode.[1]

$$i_{\text{conv.}} = nFA\tau C_s = k_s C_s \qquad (2)$$

where *A* denotes the area of the indicator electrode expressed in sq. cm., $C_s$ the bulk concentration of the solution in moles/l. and $\tau$ the "convection coefficient."[1]

The equation of the wave corresponding to a reversible reduction of mercurous mercury

$$Hg_2^{++} + 2e \rightleftarrows 2Hg$$

---

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. I, Interscience Publishers, New York, N. Y., 1952, p. 52.

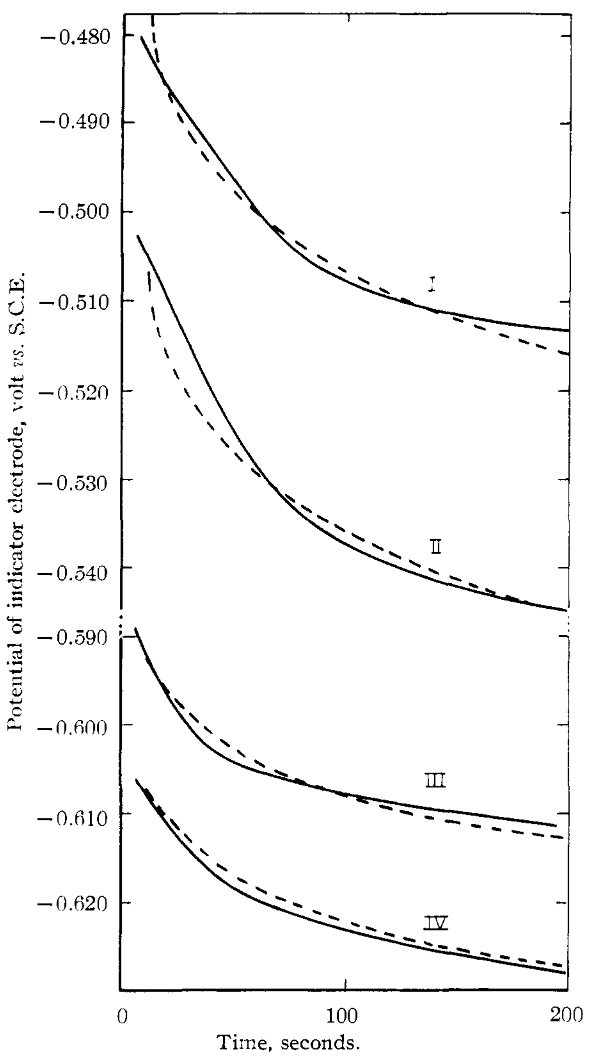

Fig. 4.—Voltage–time curves at constant current of 1.03 $\mu$amp. Continuous curves were recorded experimentally. Dotted curves are calculated from equation 12: I, 2 × $10^{-4}$ $M$ $Tl^+$ in 0.1 $M$ KCl; II, $10^{-4}$ $M$ $Tl^+$ in 0.1 $M$ KCl; III, $10^{-4}$ $M$ $Cd^{++}$ in 0.1 $M$ $KNO_3$; IV, 5 × $10^{-5}$ $M$ $Cd^{++}$ in 0.1 $M$ $KNO_3$.

at the CME is

$$E_{\text{c.e.}} = E^0 - \frac{RT}{nF} \ln \frac{k_s}{\gamma_s} + \frac{RT}{nF} \ln (i_{\text{conv}} - i) = K + \frac{RT}{nF} \ln (i_{\text{conv}} - i) \quad (3)$$

in which $E_{\text{c.e.}}$ is the potential of the convection electrode and $\gamma_s$ the activity coefficient of mercurous ion. The half-wave potential varies with concentration in the same way as at the dropping electrode

$$(E_{1/2})_{\text{c.e.}} = (E_{1/2})_{\text{d.e.}} = E^0 + \frac{RT}{nF} \ln \gamma_s + \frac{RT}{nF} \ln \frac{C_s}{2} = K' + \frac{RT}{nF} \ln C_s \quad (4)$$

Plots of $\log(i_{\text{conv}} - i)$ *vs.* $E_{\text{c.e.}}$ from c.v. curves of mercurous ion in 0.1 $M$ nitric acid yielded a straight line with a slope of (0.031 ± 0.001 v.) which is in satisfactory agreement for reversible two-electron transfer (eq. 3). The shift of the half-potential was 0.033 v. per tenfold dilution (Table I) as compared to 0.030 v. calculated from eq. 4. The zero current potentials were about 0.009 v. more negative than the thermodynamic equilibrium values (Table I). The discrepancy is attributed to liquid junction potentials.

At 0.01 $M$ amalgam electrodes the concentration of the amalgam during electrolysis of $10^{-4}$ $M$ ion solutions remains virtually constant and equations for the reversible cathodic c.v. curves and half-wave potentials are similar to eq. 3 and 4 from which they differ only in the constant terms. Consequently, plots of log ($i_{\text{conv}} - i$) *vs.* $E_{\text{c.e.}}$ should yield straight lines with a slope of 0.059 and 0.030 v. for the reversible electroreduction of thallium and cadmium, respectively, and the half-wave potentials should shift by the same values per tenfold change in concentration of the electroactive species. Experimentally, the logarithmic plots yielded a slope of $0.061_5$ v. for thallium and of 0.033 v. for cadmium and shifts of the half-wave potentials (Table I) of 0.061 and 0.030 v., respectively, in good agreement with eq. 3 and 4. The absolute value of the zero current potentials at the amalgam convection electrode (Table I) was 8 to 12 mv. more positive than the calculated thermodynamic equilibrium potentials, while the difference at the dropping electrode is of the same order in the opposite direction.[6]

Current–voltage waves of thallous and cadmium solutions yielded slopes considerably greater at pure mercury (Table II) than at the corresponding amalgam electrodes. At pure mercury the slopes decreased, and the half-wave potentials shifted to more positive values with increasing rates of change of applied potential, because of continuously increasing amalgam concentration at the interface mercury-solution. This effect also accounts for the decrease of the cathodic current with time at constant potential. A similar observation has been made by Lee, at the rotated mercury electrode.[7] Under his experimental conditions Lee postulated pronounced stirring of the mercury and homogeneous distribution of the amalgam throughout the mercury phase. With our convection electrode stirring of the mercury does not occur as is evident from the fact that the anodic current–voltage curves of thallium and cadmium amalgam are identical with and without stirring of the solution. The decrease of the limiting current with time is also unaffected by stirring of the solution, the current–time curve being controlled by linear diffusion in accordance with the expression[8]

$$(i_a)_t = 10^3 \times nFC_aA\sqrt{D_a/\pi t} = k_aC_a \quad (5)$$

where $D_a$ denotes the diffusion coefficient of the metal in the amalgam expressed in $\text{cm.}^2\ \text{sec.}^{-1}$. (The factor $10^3$ is introduced in order to correlate concentrations in moles per l. with the current expressed in $\mu$amp.). From eq. 1 and 5 it follows that

$$Q_{Tl}/Q_{Cd} = \sqrt{(D_a)_{Tl}/(D_a)_{Cd}} \quad (6)$$

The mean values of $Q$ for thallium and cadmium (Table III) yield a ratio of 0.80, which compares

---

(6) Reference 4, p. 198.

(7) T. S. Lee, This Journal, **74**, 5001 (1952).

(8) H. A. Laitinen and I. M. Kolthoff, *ibid.*, **61**, 3344 (1939).

with a value of 0.78 for $\sqrt{(D_a)_{Tl}/(D_a)_{Cd}}$ calculated from the diffusion coefficients of $0.99 \times 10^{-5}$ and $1.67 \times 10^{-5}$ cm.² sec.⁻¹ of thallium and cadmium, respectively.[9] Equations 1 and 5 also allow the evaluation of the effective area of the indicator electrode

$$A = Q\sqrt{\pi}/1000\ F\sqrt{D_a} \tag{7}$$

Substitution of the $Q$ and $D_a$ values of cadmium in eq. 7 yields 0.023 sq.cm. for $A$. From the bore of 0.15 cm. of the capillary cuvette the area of a planar circular section of 0.018 sq.cm. is calculated, and of a hemisphere protruding from it of 0.036 sq.cm. The area computed from eq. 7 is intermediate between these two values and indicates that our electrode surface has a slight convex curvature, deviating from a plane so little that the laws of linear diffusion (eq. 5) are still obeyed within experimental error.

Considering linear diffusion of the metal in the amalgam, an equation can be derived for the cathodic voltage–time curves at constant current (Fig. 4). Assuming reversible reduction the potential at $t$ seconds after start of the electrolysis is given by the expression

$$E_t = E_a^0 + \frac{RT}{nF}\ln\frac{\gamma_s}{\gamma_a} + \frac{RT}{nF}\ln\frac{(C_s^0)_t}{(C_a^0)_t} \tag{8}$$

where $(C^0{}_s)_t$ and $(C^0{}_a)_t$ denote concentrations at the electrode surface at time $t$ and $\gamma_a$ the activity coefficient of the metal in the amalgam. Under the experimental conditions, depletion by electrolysis of the solution was negligible at least for the first half-hour. Consequently the concentration of the electroactive ion at the interface at a given current can be written equal to $(i_{conv} - i)/k_s$. The number of moles of metal formed per unit time and unit electrode area (*i.e.*, the flux) is

$$f(0,t) = 10^6 i/nFA \tag{9}$$

where $i$ denotes the current expressed in microamperes. Since thallium is removed from the interface by linear diffusion in the amalgam, Fick's first law gives

$$f(0,t) = -D_a\frac{\partial C_a}{\partial x} \tag{10}$$

where $x$ represents the perpendicular distance from the interface. Equating 9 and 10, applying Fick's second law and solving[10] for $(C^0{}_a)_t$ we finally obtain

$$(C^0{}_a)_t = 2 \times 10^{-3}\, i\sqrt{t}/AnF\sqrt{\pi D_a} \tag{11}$$

where $(C^0{}_a)_t$ is expressed in moles/l. Substitution into (8) yields

$$E_t = E^0{}_a + \frac{RT}{nF}\ln\frac{\gamma_s}{\gamma_a} + \frac{RT}{nF}\ln\frac{(i_{conv} - i)/k_s}{i\sqrt{t}/500\ AnF\sqrt{\pi D_a}} = \text{const.} - \frac{RT}{2nF}\ln t \tag{12}$$

Plots of log $t$ *vs.* $E_t$ from experimental voltage–time curves yielded straight lines with slopes of 0.032 ± 0.002 for thallium and 0.015 ± 0.001 for cadmium, in good agreement with values of 0.030 and 0.015 v. predicted from eq. 12. In Fig. 4 the experimental voltage–time curves are compared with curves calculated from eq. 12. The agreement of ±0.002 v. between theoretical and experimental curves is considered satisfactory.

We have not succeeded yet in deriving a satisfactory expression for the current–time curves at constant potential (Fig. 3). The extrapolated values for zero time are very doubtful since no measurements have been made with an oscilloscope for very short periods of electrolysis. On theoretical grounds it is to be expected that the currents at zero time will actually be much greater than the graphically extrapolated values in Fig. 3.

Empirically it was found that the extrapolated "c.v. curves at zero time" yielded the same relation between $E$ and $i$ as is observed at the dropping electrode

$$E_{c.e.} = (E_{1/2})_0 - \frac{RT}{nF}\ln\frac{i_0}{i_{conv} - i_0} \tag{13}$$

The plots of log $i_0/(i_{conv} - i_0)$ for thallium and cadmium were straight lines with slopes of 0.062 and 0.033 v., respectively.

**Acknowledgment.**—This investigation was supported by a research grant from the National Cancer Institute, U. S. Public Health Service.

MINNEAPOLIS, MINNESOTA

---

[9] N. H. Furman and W. C. Cooper, THIS JOURNAL, **72**, 5667 (1950).

[10] See W. Jost, "Diffusion in Solids, Liquids, Gases," Academic Press, Inc., New York, N. Y., 1952, p. 16 ff.