dropping mercury electrode then for a given n its i_d could be predicted from a knowledge of the diffusion coefficient of the ester. Since it was found that the observed waves were always somewhat higher than would be predicted on the basis of Keilin's result of $n = 3$, we decided to re-examine the diffusion currents of nitrite and nitrate ion. Good agreement with Kolthoff, *et al.*,[3] was obtained on NO_3^-, $I = 13.3$ microamperes/millimole/liter mg.$^{2/3}$ sec.$^{-1/2}$ as against 13.8 found by Kolthoff.

For nitrite ion, on the other hand, results were always higher than those of Keilin and Otvos[4] with $I = 9.01$ as against 7.45 found by those authors. Their experimental procedure included the deaeration of the acidic nitrite solution with nitrogen. The error introduced by this procedure was estimated by Keilin and Otvos as due to the first-order decomposition of HONO to NO and NO_3^-. This excludes the direct loss of HONO which should be strongly dependent on the flow rate of nitrogen through the solution. The diffusion current of such a solution was therefore measured as a function of time and bubbling rate (Table IX).

TABLE IX

PASSING N_2 THROUGH 0.448 mM $NaNO_2$ IN 0.1 M KCl, 0.01 M HCl, 0.2 mM UO_2Cl_2

t, min.	i_d, μa.	$\frac{\Delta i_d}{i_d} \times 100$	ml. N_2 passed through
0	7.62	..	0
15	7.56	0.8	0
25	6.86	9.3	530
40	5.94	13.4	855
60	5.54	6.7	520
75	5.44	1.8	0
155	4.34	20.2	1120

The % decrease of i_d (column 3) is seen to be roughly proportional to the amount of N_2 passed through the cell and almost independent of the time interval. This suggests that the higher value of I as obtained by us is correct, but leads to $n = 3.4$. Preliminary coulometric experiments on the reduction of NO_3^- and NO_2^- at a quiescent mercury cathode have so far been unsuccessful and the uranyl-catalyzed nitrate and nitrite wave may also turn out to be a catalytic reduction of water or hydronium ion. Further work will be necessary to clarify this question.

ABERDEEN PROVING GROUND, MD.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Electrochemical Phenomena at a Rotating Mercury Electrode. I. Reduction of Metal Ions

BY T. S. LEE

RECEIVED DECEMBER 11, 1951

A new type of polarized electrode is described. The diffusion current of metal ions was found to be strictly proportional to concentration in the range 10^{-4} to 10^{-7} M. In the same concentration range the half-wave potential of a given metal ion was found to be independent of concentration. Equations were derived for (1) the decrease of current with time at constant potential, (2) the dependence of current on potential, and (3) the relation of half-wave potentials to polarographic half-wave potentials. The theoretical equations were tested and were verified within experimental limits of error. The rotating mercury electrode is useful for the analysis of electro-reducible substances at very low concentrations in aqueous solutions.

The value of the *dropping mercury* electrode, as compared with other polarized electrodes, in analysis and in physico-chemical studies is due, in a large measure, to the following facts[1]: (1) electrochemical reactions at the dropping mercury electrode are highly reproducible, and, in the case of metal ions, usually reversible, and (2) the exceptionally high overvoltage of hydrogen on mercury permits the reduction of substances that are, thermodynamically, more difficult to reduce than the solvent, water or alcohol. The *rotating platinum* electrode (or the stationary platinum electrode in a stirred solution), which is also of considerable importance in analysis,[2] has the following advantages: (1) it yields a high diffusion current for low concentration of reducible or oxidizable substances, and (2) the current does not fluctuate as does the current of the dropping mercury electrode. A *rotating mercury* electrode has not, apparently, been constructed previously, but the idea of combining the advantages of the dropping mercury and rotating platinum electrodes is probably familiar to many of those who are interested in polarography, voltammetry, amperometric titrations, and coulometric determinations. The rotating mercury electrode described below does, in fact, possess all of the advantages mentioned, but certain limitations as well.

Experimental

Electrode.—The details of the construction of the electrode and of the technique of analytical applications are described elsewhere.[3] The brief description given here is chiefly for the purpose of clarifying the discussion of results and theory. Figure 1 shows the electrode: a round plastic cup (one inch in diameter) with an annular groove on the inside edge. One-tenth ml. of mercury was put in the groove before each experiment. The centrifugal force on the mercury was five times that of gravity when the speed of rotation was 1200 r.p.m. Electrical contact with the mercury was made by platinum, gold or silver wire, the outer part of

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(1) (a) J. Heyrovsky, "Polarographie," Springer-Verlag, Vienna, 1941, p. 11; (b) J. Heyrovsky, "Polarographisches Praktikum" in "Anleitungen für die chemische Laboratoriumspraxis," Vol. IV, Springer-Verlag, Berlin, 1948, p. 1; (c) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, Chap. IX and XII; (d) M. v. Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter and Co., Berlin, 1950, p. 6; (e) O. H. Müller, "Polarographic Method of Analysis," Chemical Education Publishing Co., Easton, Pa., p. 29.

(2) (a) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941); (b) I. M. Kolthoff and D. L. Leussing, *Z. anorg. Chem.*, **262**, 160 (1950).

(3) T. S. Lee, *Anal. Chem.*, in press.

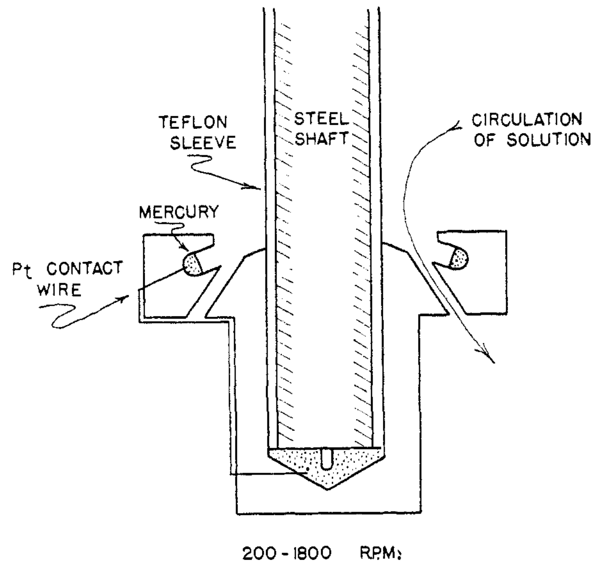

Fig. 1.—Rotating mercury electrode (constructed of Bakelite).

the wire being insulated from the solution by ceresin wax.[2a] Thus, the electrode presented to the solution a surface of mercury of constant area; no other metal was exposed to the solution.

The shaft of the electrode was provided with precision ball bearings and the electrode assembly was supported on a heavy stand to eliminate vibration due to rotation. Electrical contact to the shaft was made by copper slip rings and carbon brushes.

There were eight large holes in the cup of the electrode through which solution circulated. Surface films of oxide or other impurities were removed from the mercury by application of cathodic or anodic potentials for a short time prior to each experiment.

Cell.—The cell consisted of the mercury electrode and a reference half-cell, either a saturated calomel electrode or a silver–silver chloride electrode.[4] The cell vessel was cylindrical and had a capacity of 200 ml. The vessel was provided with a Lucite top through which the shaft of the electrode extended and which was nearly air-tight. The cell was also equipped with a side arm for the reference calomel electrode and a fritted glass gas dispersion tube through which nitrogen was passed. The oxygen concentration in the solution was reduced to less than 10^{-7} M by 2 or 3 minutes bubbling. Nitrogen was bubbled through the solution continually during current and potential measurements.

The resistance of the cell was about 400 ohms if the electrolyte was 0.1 M potassium chloride and if the calomel electrode and salt bridge were used, and 60 ohms if an internal silver–silver chloride electrode was used. All measurements were made with the cell vessel in a water-bath at 25 ± 0.1°.

Instrumentation.—Current–voltage waves were recorded by a Sargent XXI Polarograph,[5] with damping switch in position 1 and chart speed 2 inches/min. An e.m.f. was applied to the cell either by means of the bridge of the polarograph or by a 10-rotation Helipot (slidewire potentiometer with linearity of ±0.1%). The polarograph bridge and Helipot were used only for interpolation of e.m.f.'s; measurements accurate to ±0.2 millivolt were made in every experiment at appropriate span intervals with a Leeds and Northrup Student Potentiometer. For experiments in which the applied e.m.f. changed with time the Helipot was linked to the chart driving mechanism of an Esterline–Angus recording milliammeter.

The electrical currents reported were corrected for residual currents, except in Figs. 2 and 9. Applied potentials are reported as volts *vs.* the saturated calomel electrode regardless of which reference half-cell was used. (The potential of the silver–silver chloride electrode was measured against the S.C.E. at the beginning and end of each experiment.)

Chemicals.—Distilled water was purified by redistillation through a still provided with a pure tin condenser. The other chemicals used were all of reagent grade quality but were not further purified. Tank nitrogen, specified as 99.99% pure, was obtained from Linde Air Products Co. For some experiments this nitrogen was purified by bubbling it through a tower containing 20 mesh amalgamated zinc and 0.5 M chromous chloride, 0.5 M hydrochloric acid solution. No difference between the purified and unpurified gas could be detected.

Results and Discussion

Typical current–voltage waves of the rotating mercury electrode (R.M.E.) are shown in Fig. 2. The waves were well-defined, even if the concentration of electro-reducible ion was as low as 10^{-7} M. The half-wave potential at this concentration was the same as at 10^{-4} M. The current of the R.M.E. was not steady but fluctuated slightly. The fluctuations, which are barely discernible in Fig. 2, were undoubtedly due to motion of the mercury in the cup, but the exact explanation of their origin is unknown. The record of the oscillations could be eliminated by electrical damping, and, moreover, the needle of a micro-ammeter showed no appreciable fluctuation when connected to the cell. The small increase of current with potential, observable at high recording sensitivity (Fig. 2), was caused by residual current (see below). The bump that appears in the upper curve of Fig. 2 at −0.52 v. is an anomaly. Although such bumps occur only rarely in the current–voltage curves, they are a nuisance. Their cause is not known.

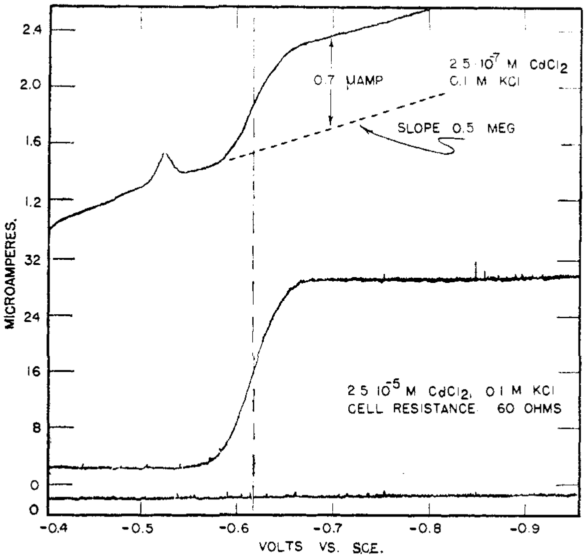

Fig. 2.—Tracing of chart record of reduction of cadmium chloride at the R.M.E.

The proportionality of diffusion current to concentration was demonstrated by measuring the current after successive additions of a standard solution to the cell vessel. The linear relation between current and concentration was found to extend from concentrations of 10^{-7} to 10^{-4} M for the three metal ions studied: lead, cadmium and copper (supporting electrolyte 0.02 M in each experiment). The average deviation from linearity in this concentration range was about ±1%. In the same concentration range the half-wave

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[4] O. Redlich and L. F. Maranville, *J. Chem. Ed.*, **20**, 10 (1943).

[5] J. J. Lingane, *Anal. Chem.*, **18**, 734 (1946).

potential was found to be essentially constant as shown in Table I. The small deviations observed at very low concentrations may be due to the slowness in response of the recorder at high sensitivity.

TABLE I

HALF-WAVE POTENTIAL OF CADMIUM IN 0.1 *M* KCl[a]

Approx. concn., *M*	i_d, μamp.	Half-wave potential *vs.* S.C.E., v.
2.5×10^{-7}	0.3	0.619
5×10^{-7}	0.6	.616
10^{-6}	1	.613
2.5×10^{-6}	3	.613
5×10^{-6} [b]	5	.612
10^{-5}	10	.612
2.5×10^{-5}	26	.611
5×10^{-5}	52	.612
10^{-4}	104	.614
400-fold change		Av. dev. ±0.002 v.

[a] The "limiting slope" for this electrode was found to be -2.2 min.$^{-1}$. [b] In this experiment and those following a silver–silver chloride electrode was used as the reference electrode in order that the *iR* drop across the cell would be small (see Experimental).

It should be noted here that the half-wave potential, although independent of concentration of reducible ion, does depend to some extent on the geometry of the electrode, the speed of rotation, and the amount of mercury in the cup (see below).

The high current of the R.M.E., as compared with the D.M.E., is due primarily to its larger area and only secondarily to a higher rate of diffusion. This is evident from a consideration of the following values for typical dropping mercury, rotating platinum and rotating mercury electrodes: area, 0.02, 0.2 and 1.0 cm.^{2}, respectively; "effective thickness of diffusion layer,"[6] 0.042, 0.003 and 0.010 mm. Thus the area of the R.M.E. is fifty times larger than the average area of the D.M.E.; the "effective thickness of the diffusion layer" is one-fourth that of the D.M.E. These two factors, operating together, give the R.M.E. a sensitivity 200 times greater than that of a typical D.M.E.

Current at Constant Applied Potential.—There is an interesting qualitative difference between the R.M.E. and the D.M.E. During the reduction of a metal ion at the R.M.E. the metal accumulates in the mercury, whereas, in reductions at the D.M.E., renewal of the drop occurs before an appreciable amount of metal has accumulated. The accumulation of metal tends to decrease the cathodic current with time at constant potential. The decrease is, however, negligible in the diffusion current region, and, consequently, diffusion currents of the R.M.E. (and also of the D.M.E.) do not decrease appreciably with time.

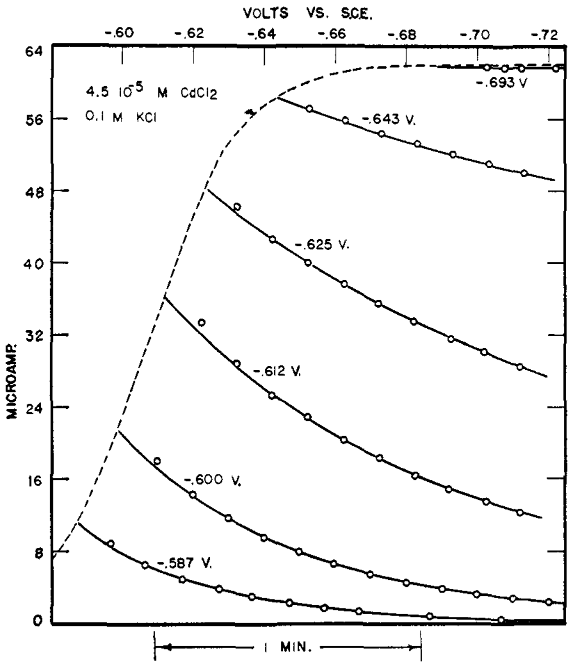

Fig. 3.—Plot of current *vs.* time at constant potential. Note that the starting point of each curve represents applied potential (top horiontal scale) as well as "zero time." Consequently, the dashed curve is a plot of current at "zero time" *vs.* potential.

The decrease of current with time is illustrated in Fig. 3. A potential of −0.54 v. *vs.* the saturated calomel electrode was applied to a R.M.E. in 4.5×10^{-5} *M* cadmium chloride, 0.1 *M* potassium chloride solution. At this potential cadmium ion was not reduced and no current flowed. The potential was suddenly switched, by means of a toggle switch, to −0.587 v. and the lowest curve of Fig. 3 was recorded. A cathodic current of about 10 μamp. was observed initially, but the current decreased to zero in a few minutes. The interpretation is that, a few minutes after application of −0.587 v., the electrochemical equilibrium concentration of cadmium in mercury was attained, and, consequently, the current ceased flowing. The applied potential was switched again to −0.54 v., whereupon an *anodic* current, due to the oxidation of metallic cadmium to cadmium ion, was observed (not shown in Fig. 3). After a few minutes the current was again zero, indicating that the cadmium had been completely removed from the mercury. The potential was then switched to −0.600 v. and the next curve recorded, and so on. In the region of potentials at which diffusion currents are obtained the decrease of current with time is negligible, as can be seen from the experimental points at −0.693 v. of Fig. 3. On theoretical grounds it is calculated that at a potential 0.15 v. more negative than the half-wave potential the decrease of current due to accumulation of cadmium in the mercury of the R.M.E. of Fig. 3 is only 0.002% per min., and at more negative potentials the rate is even smaller.

The well-known equation relating the potential of the D.M.E. to current is, for the reduction of a metal ion to a metal soluble in mercury[7]

$$\pi = (\pi_{1/2})_{\text{D.M.E.}} + \frac{RT}{nF} \ln \frac{i_d' - i}{i} \qquad (1)$$

---

(6) The "effective thickness of the diffusion layer," δ, is defined by the equation $\delta = nFADC'/i'_d$, where *F* is the Faraday constant, *A* the area of the electrode, *D* the diffusion coefficient of the metal ion, *n* its valence, *C'* its concentration, and i'_d the cathodic diffusion current. See J. A. V. Butler, "Electrocapillarity," Chem. Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1940, Chap. VII; I. M. Kolthoff and J. J. Lingane, ref. 1c, p. 435.

(7) For discussion of equation (1) see appropriate pages of reference 1.

where π represents the potential of the electrode, i is the current, i_d is the diffusion current, R the gas constant, T the absolute temperature, n the number of electrons required for the reduction of one ion and F the faraday constant. The superscript prime denotes the ion in aqueous solution. The superscript double prime, used in equations that follow, denotes the metal (*e.g.*, cadmium) in mercury. The postulated equation for the R.M.E. is

$$\pi = (\pi_{1/2})_0 + \frac{RT}{nF} \ln \frac{i_d' - i}{i + k''C''} \tag{2}$$

The additional term in the denominator of equation (2) provides for the accumulation of metal in the mercury, and is equal to the product of k'', the "diffusion constant[8]" for the diffusion of metal in mercury, and C'', the concentration of metal in mercury. The latter is given by the equation

$$C'' = \frac{1}{VnF} \int_0^t i\mathrm{d}t \tag{3}$$

where V represents the volume of mercury. Combination of equations (3) and (2), and differentiation (at constant potential) of the resulting expression, yields equation (4).

$$-\frac{\mathrm{d} \log i}{\mathrm{d}t} = \frac{1}{(1 + T)} \frac{k''}{2.303\, VnF} \tag{4}$$

where $T = 10^{-v}$, and

$$v = [\pi - (\pi_{1/2})_0]n/0.0591 \text{ at } 25° \tag{5}$$

According to equation (4) a plot of logarithm of current at constant potential *vs.* time yields a straight line, the slope of which is dependent on potential. In Fig. 4 the data of Fig. 3 are replotted with a logarithmic scale. The experimental points lie on straight lines in accordance with equation (4).

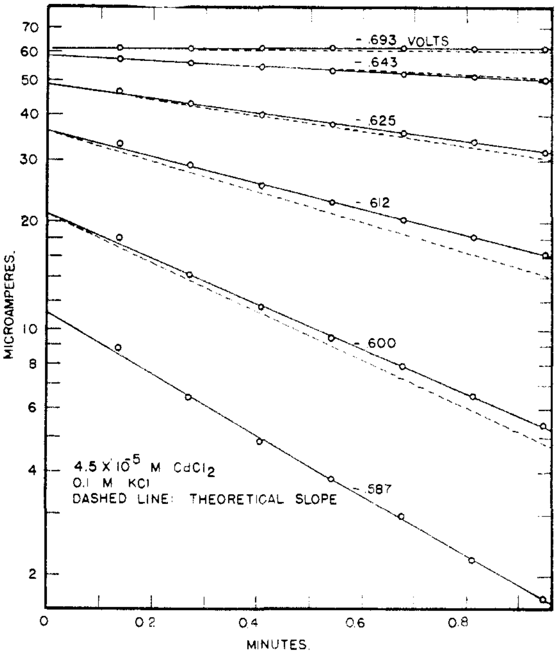

Fig. 4.—Data of Fig. 3 plotted with logarithmic scale. Limiting slope, calculated from line at −0.587 v. by equation (4), was −1.03 min.$^{-1}$.

If the lines of Fig. 4 are extrapolated to "zero time," the intercept represents the hypothetical current that would be obtained if no cadmium had accumulated in the mercury (*i.e.*, at "zero time"). The intercept current should therefore conform to equation (2) with C'' equal to zero. Under these conditions the wave of the R.M.E. is entirely analogous to that for the D.M.E. (see equation 1). In Fig. 5 the data of Fig. 4 are again replotted. The logarithm of the quantity $[(i_d)_0 - i_0]/i_0$, where the subscript zero represents "zero time," is plotted against applied potential. Within experimental error the extrapolated values, represented by circles, fall on a straight line which was drawn with the theoretical slope $nF/2.30\ RT$. The intersection of the line with the horizontal axis represents the "half-wave potential at zero time," $(\pi_{1/2})_0$. It is to be noted that the value of $(\pi_{1/2})_0$ of −0.608, obtained from Fig. 5 is an experimental value obtained by suitable plotting of the data of Fig. 3, and is not dependent on the assumptions involved in the derivation of equations (2), (3) and (4).

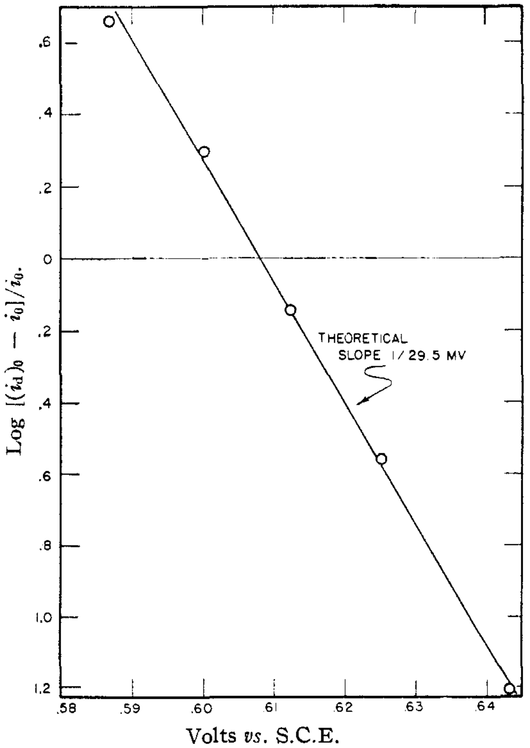

Fig. 5.—Intercept current of Fig. 4 plotted against applied potential. The value of $(\pi_{1/2})_0$, obtained from intersection of horizontal axis and heavy line, is −0.608 v.

The experimental value of $(\pi_{1/2})_0$ of cadmium was used in further testing the validity of equation (4). Equation (4) cannot be used to calculate the absolute values of the slopes of the lines of Fig. 4 because it is not possible to calculate k''. This constant depends on the speed of rotation, geometry of the electrode and turbulence, and is not

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[8] The constant, k'', is defined by the equation $k'' = -i_d''/C''$, where i_d'' is the anodic diffusion current and C'' is the concentration of cadmium in the body of the mercury (*i.e.*, everywhere except in the diffusion layer). Note that k'' is a positive quantity and that i_d'' is, by convention, negative. See I. M. Kolthoff and J. J. Lingane, ref. 1c, p. 143, and other monographs of reference 1.

amenable to theoretical treatment. However, equation (4) can be used to calculate the *relative* slopes at different potentials. The calculated slopes, based on the slope at −0.587 v., are shown as dashed lines in Fig. 4. Agreement with theory is satisfactory, thus verifying the factor $1/(1 + T)$ of equation (4).

If T is negligible compared with unity, that is, if the applied potential is at least 0.1 v. more positive than the half-wave potential, the slope is practically independent of potential and will be referred to as the "limiting slope."

$$-\text{ lim. slope} = k''/2.303\,VnF \qquad (4A)$$

The "limiting slope" of the reduction of a given metal ion at a given R.M.E. is an important characteristic of the electrode. In practice it is determined by plotting the logarithm of the *anodic* diffusion current (at constant potential) against time, as will be described in a subsequent communication. It will also be shown that the limiting slope obtained from the anodic current is the same as that obtained from the cathodic current.

Current–Voltage Curves.—It is of practical interest to ask, what is the shape of the current–voltage wave obtained with an automatic polarograph? This instrument applies to the cell an e.m.f. that changes at a constant rate. Equation (2) can be rewritten

$$v_e = \ln \frac{i_d' - i}{i + k''C''} = \ln \frac{i_d' - i}{i + \dfrac{k''}{VnF}\displaystyle\int_0^t i\,dt} \qquad (6) \text{ and } (7)$$

where the subscript e refers to natural logarithms, and v_e is equal to $2.303\,v$ (see equation 5). Equation (7) is rewritten

$$v_e = \ln \frac{i_d' - i}{i - m \displaystyle\int_{v_e}^{v_e} i\,dv_e} \qquad (8)$$

The quantity m is defined as

$$m = -\frac{k''RT}{rVn^2F^2} = -2.661 \times 10^{-7}\,\frac{\text{volt-equiv.}}{\text{coulomb}} \times \frac{k''}{rVn^2} \qquad (9)$$

where r is the rate at which potential is changed. Note that r is negative and m is positive if the negative (reducing) potential is increased with time. Note also that m, as well as v, v_e and T, is dimensionless. Differentiation of equation (8) gives the differential equation

$$(T + 1)\mathrm{d}i + (mi/T + i - i_d')\mathrm{d}T = 0 \qquad (10)$$

where

$$T = e^{-v_e} = 10^{-v}$$

By suitable substitutions equation (10) can be changed to a linear differential equation with the solution[9]

$$\frac{i}{i_d'} = \frac{(T+1)^{m-1}}{T^m}\left[\int_{T_0}^{T} (1 + 1/T)^{-m}\,\mathrm{d}T + \frac{T_0^{m+1}}{(T_0 + 1)^m}\right] \qquad (11)$$

where subscript zero indicates initial. If the initial potential is such that T is much greater than unity, that is, at a potential at least 0.2 more positive than the half-wave potential, the last term of equation (11) can be neglected and the equation can be written in the form

$$i/i_d' = XI \qquad (12)$$

where X is the factor outside the brackets of equation (11) and I is the definite integral. The integral is a transcendental function that has a closed algebraic equivalent only for integral and half-integral values of m. The integral has, however, been evaluated from suitable infinite, convergent series, and values of i/i_d have been computed and tabulated[3] for various values of m. From the tables the theoretical shape of the current–voltage wave can readily be found for any given experimental conditions.

The results of an experimental test of equation (12) are shown in Fig. 6. Four experimental current–voltage waves, each resulting from a different rate of change of applied potential, are indicated by the circles. The theoretical curves, calculated from equation (11), are indicated by solid lines. The value of m was found as described below and the value of $(\pi_{1/2})_0$ was assumed to be −0.606 v. (*cf.* value −0.608 v. obtained from data of Fig. 5). The diameter of the circles corresponds to an experimental uncertainty of 3 or 4 mv., and within this accuracy the theoretical equation (11) agrees satisfactorily with experiment.

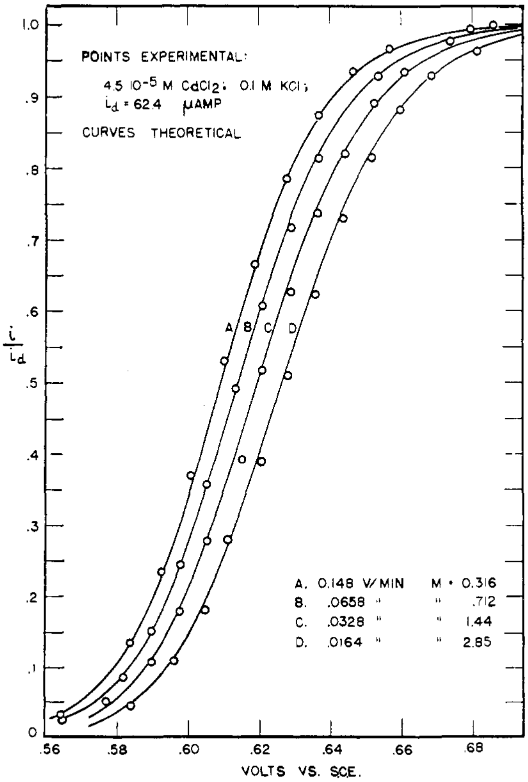

Fig. 6.—Current–voltage curves of cadmium chloride. Limiting slope of this R.M.E. was −1.58 min.⁻¹. Value of $(\pi_{1/2})_0$ was assumed to be −0.606 v.

Evaluation and Significance of *m*.—It is seen from equation (11) that, at a given temperature,

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[9] The substitution $W = i(T + 1)$ transforms equation (10) into a linear differential equation. The constant of integration is evaluated by letting $T = T_0$. Under this condition no metal accumulates in the mercury, and equation (1) is applicable. Equation (1), in terms of T, is

$$i/i_d' = T/(T + 1)$$

the shape[10] of the wave depends only on the number of electrons involved in the reduction of the metal ion and on the value of m. The latter is a parameter of the wave and its value depends on the geometry of the electrode, the speed of rotation, the diffusion characteristics of the metal to which the metal ion is reduced, the volume of mercury, and the rate of change of applied potential. The value of m can be calculated from the experimentally determined limiting slope of the plot of logarithm of current *vs.* time at constant potential

$$m = \frac{0.0591\ (\text{lim. slope})}{nr} \text{ at } 25° \qquad (13)$$

Equation (13) is easily derived by combining equations (9) and (4A). The experimental determination of the limiting slope for a given R.M.E. and a given reducible ion requires only a few minutes, and is accomplished merely by applying a reducing potential to the electrode, switching to a more positive potential, and recording the resulting anodic current.[3]

The ordinary polarographic (D.M.E.) wave, represented by equation (1), is identical in shape with the theoretical R.M.E. wave if m is equal to zero. This theoretical wave is not shown in Fig. 6 but would lie close to curve A for which m is about 0.3. From equation (11) and Fig. 6 it appears that the wave is shifted to more negative (more reducing) potentials if the value of m is increased; that is, if the rate of change of potential is decreased. The theoretical shift is illustrated in Fig. 7.

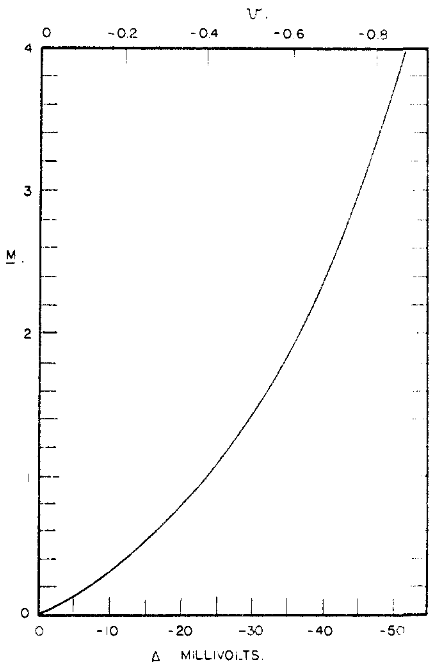

Fig. 7.—Plot of [$\pi_{1/2} - (\pi_{1/2})_0$] *vs.* m (vertical scale) for reduction of a monovalent metal ion. If valence of metal is n, the numbers given on the horizontal scale must be divided by n.

The "spread" of the wave is also dependent on m and increases if m is increased. This is shown in Fig. 8. The spread is measured as "index potential" after Michaelis[11] and is explained by the insert diagram. It is of practical interest to note that the spread of the R.M.E. wave is only slightly greater than the spread of the polarographic wave, even if the rate of change of potential of the R.M.E. is as small as 16 millivolts per min. (Fig. 6). At rates ordinarily employed in polarography the shape of the R.M.E. wave can, for most purposes, be assumed to be the same as the shape of the polarographic wave.

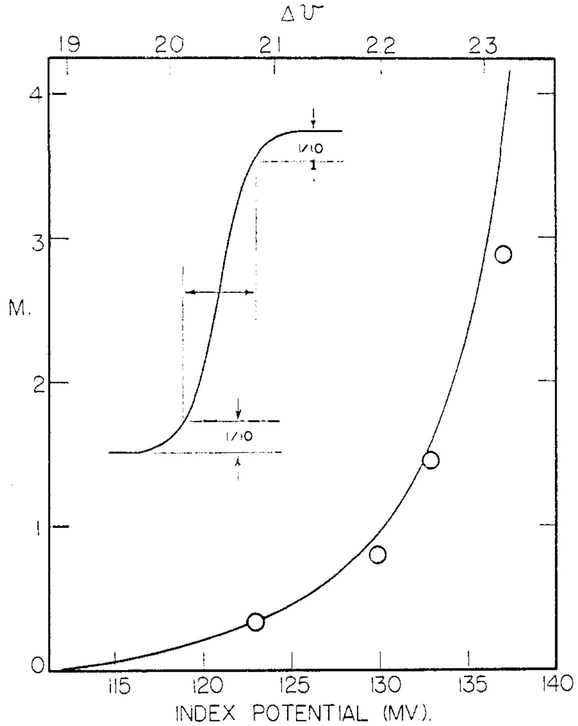

Fig. 8.—Plot of index potential ($\pi_{1/10} - \pi_{9/10}$) *vs.* m for reduction of a monovalent metal ion. If valence of metal is n, numbers on horizontal scale must be divided by n.

It will be noted that the equations derived above apply only to the reduction of metals that are "soluble" in mercury. Under practical conditions of recording the current–voltage curve, the concentration of metal in the mercury of the R.M.E. is usually less than 10^{-4} M. The solubilities of all of the common metals except chromium and iron exceed that value, and, consequently, equations (2)–(12) are theoretically applicable except to those two metals.

The equation of the wave of a substance, the oxidized and reduced forms of which are both soluble in water, would be expected to be the same for the R.M.E. and the D.M.E., since no accumulation of reduction product in the mercury occurs. This expectation was verified for the reduction of sulfur dioxide in 0.05 M hydrochloric acid. The reduction at the D.M.E. is reversible and requires two electrons per mole of sulfur dioxide (reduction product, sulfoxylic acid).[12] The R.M.E. wave corresponded within experimental error to equation (1) with n equal to two.

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[10] The phrase "shape of the wave," as used here, refers to the plot of i/i_d', *vs.* potential rather than current *vs.* potential.

[11] L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 460 (1938).

[12] I. M. Kolthoff and C. S. Miller, This Journal, **63**, 2818 (1941).

Half-wave Potential.—It has been shown that the half-wave potential of the R.M.E. is independent of concentration and dependent on m. It might seem on first thought that the half-wave potential, $(\pi_{1/2})_0$, of a hypothetical electrode for which m were zero, would be identical with the polarographic half-wave potential, $(\pi_{1/2})_{\text{D.M.E.}}$ However, $(\pi_{1/2})_0$, also called the half-wave potential at zero time, was found to be about -0.607 v. (experiments of Fig. 5 and 6) for the reduction of cadmium ion in 0.1 M potassium chloride. The corresponding polarographic half-wave potential is about -0.600 v.[13] The difference in the two values is undoubtedly due to differences in diffusion conditions at the two electrodes.

The D.M.E. half-wave potential of the reduction of a metal ion to a metal soluble in mercury is given by the equation[14]

$$(\pi_{1/2})_{\text{D.M.E.}} = \pi_{\text{a}} + \frac{RT}{nF}\ln\frac{\gamma'}{\gamma''}(k''/k')_{\text{D.M.E.}} \quad (14)$$

where π^0_{a} is the standar potential of the amalgam electrode, γ' is the molarity activity coefficient of the metal ion in the aqueous phase, γ'' is the molarity activity coefficient of the metal in mercury, and the other symbols are as defined previously. Comparison of equations (1) and (2) gives the corresponding equation for the R.M.E.

$$(\pi_{1/2})_0 = \pi^0_{\text{a}} + \frac{RT}{nF}\ln\frac{\gamma'}{\gamma''}(k''/k')_{\text{R.M.E.}} \quad (15)$$

Combination of equations (14) and (15) yields the relation

$$(\pi_{1/2})_0 - (\pi_{1/2})_{\text{D.M.E.}} = \frac{RT}{nF}\ln\frac{(k''/k')_{\text{R.M.E.}}}{(k''/k')_{\text{D.M.E.}}} \quad (16)$$

Equation (16) was applied to the reduction of cadmium ion. The ratio of k's for the D.M.E. is equal to I''/I' where I is the "diffusion current constant."[13b] This ratio is equal to 1.40 for cadmium in 0.1 M potassium chloride.[13b,15] The corresponding ratio for the R.M.E. is found from equation (4A) to be

$$\left(\frac{k''}{k'}\right)_{\text{R.M.E.}} = -\frac{(\text{lim. slope})nFV\,2.303}{i'_{\text{d}}/C'} \quad (17)$$

Substitution in equation (17) of the experimental values of the electrode of Fig. 4 yields a value of 0.72 for the ratio of k's. The experimental result that $(k''/k')_{\text{R.M.E.}}$ is smaller than $(k''/k')_{\text{D.M.E.}}$ is reasonable. Mercury has a higher viscosity than water; therefore, the velocity gradient of the mercury of the R.M.E. is less than the velocity gradient of the water. Consequently, $(\delta''/\delta')_{\text{R.M.E.}}$ is greater than $(\delta''/\delta')_{\text{D.M.E.}}$ where δ is the effective thickness of the diffusion layer,[6] and it follows that $(k''/k')_{\text{R.M.E.}}$ is less than $(k''/k')_{\text{D.M.E.}}$ For this reason it is probable that R.M.E. half-wave potentials (at zero time) of all metal ions are slightly more negative than the corresponding polarographic (D.M.E.) half-wave potentials.

The difference, $(\pi_{1/2})_0 - (\pi_{1/2})_{\text{D.M.E.}}$, for cadmium is calculated from equation (16) to be -8.5 mv. The observed difference is 6–8 mv. Agreement of theory with experiment is considered satisfactory although a more exacting experimental test, including study of other ions, would be desirable.

It is predicted that $(\pi_{1/2})_0$ of a given metal ion is practically independent of volume of mercury and speed of rotation because the ratio $(k''/k')_{\text{R.M.E.}}$, rather than either k'' or k' independently, appears in equation (16). Furthermore, the difference between $(\pi_{1/2})_0$ and $(\pi_{1/2})_{\text{D.M.E.}}$ would be expected to be nearly, but not entirely, independent of the metal ion being reduced.

In practice $(\pi_{1/2})_0$ is found from the observed half-wave potential, $\pi_{1/2}$, and from Fig. 8, which shows the dependence of $\pi_{1/2}$ on m. For example, in the experiments of Table I the observed $\pi_{1/2}$ of cadmium was -0.613 volt. The observed limiting slope of the electrode was -2.2 min.$^{-1}$, and the rate of change of applied potential was -0.148 volt/min. From equation (13) the value of m is found to be $+0.44$, and from Fig. 7 the shift in half-wave potential is found to be 7 millivolts (note that cadmium ion is divalent). The calculated value of $(\pi_{1/2})_0$ is therefore -0.613, $+0.007$ or -0.606 volt. This value is in satisfactory agreement with the values reported above.

Residual Current.—The residual current, that is, the current that flows in the absence of any solute except the supporting electrolyte (*e.g.*, potassium chloride), is a troublesome feature of the R.M.E. although it can be minimized by proper construction of the electrode. Theoretically, the R.M.E., unlike the D.M.E., has a negligible condenser current[16] because the amount of mercury in the cup is constant and is not continuously renewed. Actually, a residual current, the cause of which is not known, is observed in region B of Fig. 9. The current is proportional to applied e.m.f., but the slope varies from electrode to electrode and depends partly on the care taken in covering the contact wire with wax. The slope usually corresponds to about 0.2 to 0.5 megohm (see also Fig. 2).

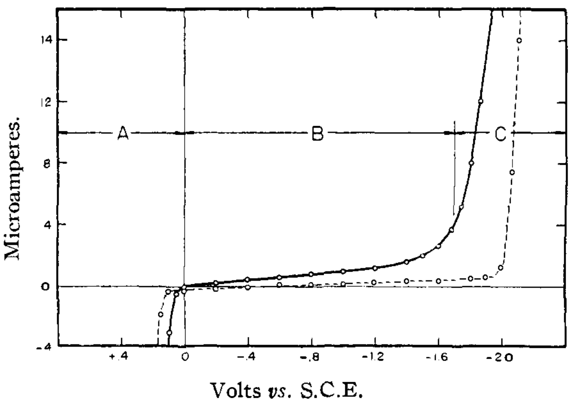

Fig. 9.—Residual current of 0.02 M potassium chloride solution: solid line, R.M.E.; dashed line, D.M.E.

Theoretically, the *range* of potentials available for study with the R.M.E. (*i.e.*, region B of Fig. 9)

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[13] (a) I. M. Kolthoff and J. J. Lingane, ref. 1c, p. 482, reported the value -0.599 v.; (b) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943), reported -0.60 v.; (c) a value of -0.600 v. (D.M.E.) was found in this Laboratory.

[14] I. M. Kolthoff and J. J. Lingane, ref. 1c, p. 142. See also other monographs of reference 1.

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

[16] I. M. Kolthoff and J. J. Lingane, ref. 1c, p. 105. See also other monographs of reference 1.

is more limited than the range of the D.M.E. because of the greater sensitivity of the former electrode. For example, the reduction of 0.1 *M* potassium ion at the R.M.E. would be expected to begin at a potential about 140 mv. *less* negative than the potential of the same reduction at the D.M.E. because the R.M.E. is 200 times more sensitive than the D.M.E. Likewise, the anodic dissolution of mercury at the R.M.E. would occur at a *more* negative potential than at the D.M.E. The range of potentials of the R.M.E. would therefore be expected to be less by several tenths of a volt. In practice it was found that the range was even more restricted, and that the residual current became large, presumably due to the reduction of water, at potentials more negative than -1.2 v. *vs.* S.C.E. unless (1) the surface of the groove of the electrode was highly polished, and (2) vibration of the electrode was minimized. In addition it was found that the range B was increased if the chemical and physical nature of the surface of the groove was such that the interfacial tension between plastic and mercury was as small as possible and the interfacial tension between plastic and electrolyte was as large as possible.

The residual current (Fig. 9) of the R.M.E., at its present stage of development, is such that analysis for the alkaline earth ions and the alkali ions is not possible.[17] Aluminum ion can be reduced but the analysis for aluminum at low concentrations is not practical. Most of the other metal ions that can be determined with the D.M.E. can probably be determined with the R.M.E., although this expectation has not yet been put to an exhaustive test.

Applications.[3]—The current-voltage curves of the R.M.E. can be used for the qualitative and quantitative analysis of electro-reducible substances at concentrations as low as 10^{-7} *M*. Metal ions at concentrations down to 5×10^{-9} *M* can be determined by a combination of coulometric and voltammetric techniques. The R.M.E. is also useful for amperometric titrations and "derivative" analysis.[18]

Acknowledgment.—The author is indebted to Professor I. M. Kolthoff, University of Minnesota, for interesting discussions and valuable suggestions.

Part of this study was aided by a grant from the Shell Oil Company.

[17] The surface of the groove of the R.M.E. of Fig. 9 was coated with a thin layer of "Lubriseal," a high molecular weight saturated hydrocarbon. See reference 3.

[18] O. H. Müller, ref. 1e, p. 132.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Electrode Potentials in Liquid Hydrogen Fluoride

BY GEORGE G. KOERBER[1] AND THOMAS DE VRIES

RECEIVED MAY 22, 1952

The values of the electromotive force of cells of the type $M,MF_2(s)/HF(NaF)/Hg_2F_2(s)/Hg$ where M represents cadmium, copper or lead were found at 10 and 0°. These were used to evaluate the standard free energies of formation of mercurous, cupric and lead fluorides. A study of the vapor pressures of the systems mercurous fluoride–hydrogen fluoride, cadmium fluoride–hydrogen fluoride, and lead fluoride–hydrogen fluoride was made at 0°. Lead fluoride was found to form an addition compound with hydrogen fluoride with the formula $PbF_2 \cdot 2^1/_2HF$. The cell $Hg,Hg_2F_2(s)/NaF(\text{in } HF)//NaF,H_3OF,AgF\ (\text{in } HF)/Ag$ was studied at 0° over a range of concentrations of the electrolytes. The data from this were used to calculate activity coefficients of silver fluoride in liquid hydrogen fluoride. An ion size parameter of 1.9 Å. was found for silver fluoride in the solutions studied. The standard free energy of formation of $AgF \cdot HF$ from silver, fluorine and hydrogen fluoride was calculated.

It has been known for a long time that liquid hydrogen fluoride is a good ionizing solvent medium. With the exception of the work by O. T. Krefft,[2] who evaluated the standard free energy of formation of liquid hydrogen fluoride at 0° by measuring the potential of the cell $H_2(Pt)/HF(KF)/F_2(Pt)$, the use of electrode potentials in liquid hydrogen fluoride as a means of studying the thermodynamics of solutions in hydrogen fluoride, and of evaluating thermodynamic properties of metal fluorides has been neglected.

In this research, cells of the type $M,MF_2(s)/HF(NaF)/Hg_2F_2(s),Hg$ where M represents cadmium, copper and lead, were measured in order to evaluate the standard free energies of formation of the metal fluorides and the cell $Hg,Hg_2F_2(s)/NaF(\text{in } HF)//NaF,H_3OF,AgF(\text{in } HF)/Ag$ was studied in order to investigate the thermodynamics of solutions in hydrogen fluoride. Vapor pressure measurements were made of the systems metal fluoride–hydrogen fluoride in order to determine whether any of the metal fluorides formed addition compounds with hydrogen fluoride.

Experimental

Materials.—Harshaw "Anhydrous" hydrogen fluoride of a purity of 99.5% was used directly from the cylinder. The water content of this material was less than 0.2%.

Lead, cadmium and mercurous fluorides were prepared by treating the carbonates with hydrofluoric acid, Baker Reagent Grade. Cupric fluoride was prepared by passing hydrogen fluoride over the basic carbonate at 200°.

Copper and cadmium amalgams were prepared by electrolysis and lead amalgam was prepared by mixing the proper proportions of spectroscopically pure lead and triple distilled mercury. Two-phase amalgams were used throughout this research.

Silver oxide was prepared by precipitation of the oxide from a solution of silver nitrate with potassium hydroxide.

Silver and lead stick electrodes were made by inserting silver wire or lead sticks into Teflon plugs that screwed into the base of the cell. These were made reversible by etching

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[1] Abstract from the Ph.D. dissertation of George G. Koerber whose present address is Bell Telephone Laboratories, Murray Hill, New Jersey.

[2] O. T. Krefft, "Inaug. Diss.," Greifswald Institut für Physikalische Chemie, Greifswald, Germany, 1939.