differed in stoichiometry with respect to hydrogen ion from the analogous U(V) reaction.[24] On the other hand, one of the paths for the Np(IV)–Np(V) exchange reaction had the stoichiometry of the U(V) disproportionation.

$$-\frac{d[NpO_2^+]}{dt} = k_1''[NpO_2^+]^2[H^+] \qquad (19)$$

It was found further that the energetics for the overall equilibrium was not in accord with the energetics for the two reactions, (19) and (17). It appears likely from the present observations that the explanation for the disparities is that multiple reaction paths are involved. With this possibility in mind the data for the Np(IV)–Np(VI) reaction were re-examined. Least squares analysis showed that the hydrogen ion dependence was $[H^+]^{-2.08 \pm 0.06}$ (95% confidence level). From this it is possible to write a kinetic expression involving two hydrogen ion dependent paths as

$$k_{obsd} = k_1[H^+]^{-2} + k_2[H^+]^{-3} \qquad (20)$$

with $k_1 = 2.59$ and $k_2 = 0.074$. Although it is clear that the predominant reaction involves only two hydrogen ions these computations lend some support to the hypothesis that more than a single reaction path is involved in perchlorate solution.

LEMONT, ILLINOIS

[24] D. M. H. Kern and E. F. Orlemann, THIS JOURNAL, 71, 2102 (1949).

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

Anodic Stripping Voltammetry with Mercury Electrodes—Potential-step and Current-step Methods

BY GLEB MAMANTOV,[1a] PAOLO PAPOFF[1b] AND PAUL DELAHAY

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An amalgam forming metal is deposited on a stationary mercury electrode and then is anodically oxidized. Anodic stripping is carried out either by sudden switching of potential (potential-step method) or by passing a constant current through the cell (current-step method). A theoretical analysis is developed for both methods for conditions of semi-infinite linear diffusion. The following derivations are given: equations for current–time, current-potential and potential–time curves; diffusion current and transition time for the stripping process; sensitivity gain. Detailed experimental results are discussed for the anodic stripping of cadmium from a hanging mercury drop, and theory and experiment are compared. Sensitivity gains with respect to voltammetry with stirred solution can be larger than 100. Application to concentrations as low as 10^{-7}–10^{-9} molar appears feasible. The two methods are compared with anodic stripping at continuously varying potential (Nikelly and Cooke).

Anodic stripping methods which have been known for years[2] recently have been applied again to the analysis of traces of metals.[3–5] The metal to be determined in a solution is first deposited on a solid[3,5] or amalgamated[4] electrode, and then is stripped from this electrode by anodic oxidation. The amount of metal ion in solution is determined from the quantity of electricity consumed in the stripping process. Nikelly and Cooke[6] recently modified the method and used a mercury pool electrode for deposition of the metal to be analyzed. They reoxidized the metal at continuously varying potential and obtained current–potential curves not unlike those of oscillographic polarography. These curves exhibit a peak from the height of which the concentration of metal is deduced directly. The method of Nikelly and Cooke is a voltammetric procedure whereas previous methods belong to coulometry. These authors coined the expression "anodic stripping polarography" for their method, but we prefer to call it "anodic stripping voltammetry," thus reserving the term "polarography" for methods involving the use of the dropping mercury electrode.[7]

In addition to the method of Nikelly and Cooke, two other simple methods can be conceived: (a) the "potential-step" method in which the metal is oxidized by sudden variation of potential to a more anodic value; and (b) the "current-step" method in which the stripping process is carried out at constant current. These methods are discussed and compared in this paper for the case of stationary mercury electrodes.

Potential-step Method

Diffusion Stripping Current.—A metal M is deposited at constant potential on a stationary mercury electrode in stirred solution. The conditions are such that the electrolysis current is constant; *i.e.*, the volume of solution is so large and the plating time so short that depletion of ions M^{+n} in solution can be neglected. Electrolysis is carried out at a potential corresponding to the limiting current range. Mercury is not stirred, and M is supposed to diffuse in the bulk of mercury under conditions of semi-infinite linear diffusion. After τ seconds, the potential is changed abruptly to a sufficiently anodic value at which metal M is oxidized at a rate that is solely diffusion controlled. The resulting *diffusion stripping current* will now be derived. This current is obtained by deriving the flux of metal M at the electrode surface, *e.g.*, by solving

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[2] C. Zbinden, *Bull. soc. chim. biol.*, **13**, 35 (1931).

[3] S. S. Lord, Jr., R. C. O'Neill and L. B. Rogers, *Anal. Chem.*, **24**, 209 (1952).

[4] K. W. Gardiner and L. B. Rogers, *ibid.*, **25**, 1393 (1953).

[5] M. M. Nicholson, THIS JOURNAL, **79**, 7 (1957).

[6] J. G. Nikelly and W. D. Cooke, paper presented at the International Congress of Pure and Applied Chemistry, Lisbon, September 9–16, 1956.

[7] See P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 11.

Fick's equation for the following initial and boundary conditions.

The initial condition expresses the concentration of M in mercury at time τ, *i.e.*, at the instant of switching of potential. This concentration is[8]

$$C_M(x,0) = \frac{i_p}{nFAD_M}\left[2\left(\frac{D_M\tau}{\pi}\right)^{1/2}\exp\left(-\frac{x^2}{4D_M\tau}\right) - x\,\mathrm{erfc}\left(\frac{x}{2D_M^{1/2}\,\tau^{1/2}}\right)\right] \quad (1)$$

There, x is the distance from the electrode surface in the mercury, i_p the plating current during deposition of M on mercury, D_M the diffusion coefficient of M in mercury, n the number of electrons for the discharge of M^{+n}, F the faraday, A the electrode area, and "erfc" represents the error function complement. We write $C_M(x,0)$ to indicate that the origin of time in the following derivation is taken at the beginning of the stripping process.

As boundary condition we prescribe that M is immediately oxidized to M^{+n} as it reaches the electrode surface. Hence, $C_M(0,t) = 0$ for $t > 0$. Finally, $C_M(x,t) \rightarrow 0$ for $x \rightarrow \infty$ and for $t \geqslant 0$.

This boundary value problem is quite similar to the one previously studied in this Laboratory for two consecutive electrode reactions in voltammetry at constant current.[9] The result is[10]

$$-\frac{i_{s,d}}{i_p} = \frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2} - \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau - t}{\tau + t} \quad (2)$$

where $i_{s,d}$ is the diffusion stripping current. According to polarographic practice, the anodic current $i_{s,d}$ is negative and the cathodic current i_p is positive in (2).

Variations of $-i_{s,d}/i_p$ with t/τ are shown in Fig. 1 (solid curves). It is seen from this diagram that the ratio $-i_{s,d}/i_p$ is much larger than unity provided that t/τ is sufficiently small. One has[11] $i_{s,d}/i_p \rightarrow \infty$ for $t/\tau \rightarrow 0$, and $-i_{s,d}/i_p \rightarrow 0$ for $t/\tau \rightarrow \infty$.

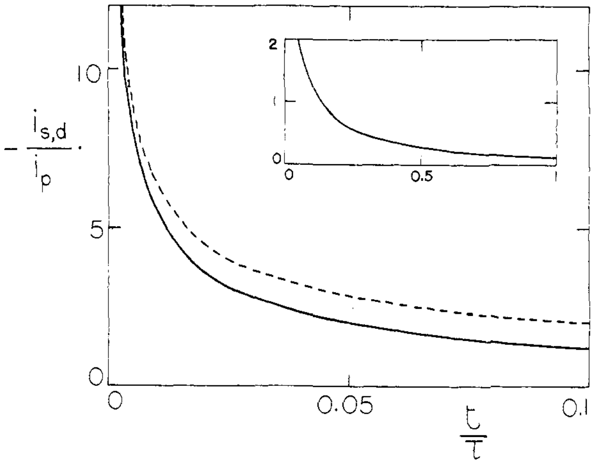

Fig. 1.—Variations of $-i_{s,d}/i_p$ with t/τ for the plane electrode in the potential-step method. Solid curve represents exact solution in equation 2; dashed curve corresponds to the approximate solution $-i_{s,d}/i_p = (2/\pi)(\tau/t)^{1/2}$.

Tracings of experimental curves $i_{s,d}$ against t are shown in Fig. 2 for the anodic stripping of cadmium for different pre-electrolysis times. For reasons discussed in the Experimental part, these curves were recorded with a hanging mercury drop and not with a mercury pool. Furthermore, the mechanical stirrer was stopped at the end of pre-electrolysis and 4 seconds were allowed to elapse before the recording of the current–time stripping curves. Deformation of the drop during stripping was avoided in this fashion, and results were more reliable. These conditions do not correspond to the foregoing theoretical analysis, which should be regarded primarily as a guide for a judicious choice of experimental conditions. Note that the experimental curves have the same general shape as the theoretical curve of Fig. 1 (see also below).

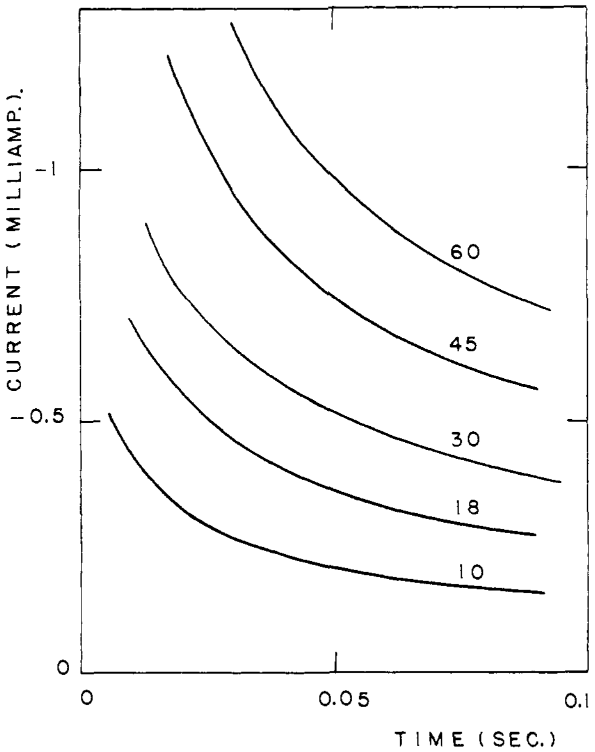

Fig. 2.—Tracings of current–time curves for the anodic stripping of cadmium in 1 *M* potassium chloride at −0.25 volt (*versus* S.C.E.). Numbers on curves are pre-electrolysis times in seconds. Time interval between pre-electrolysis and stripping, 4 seconds.

The term $(2/\pi)(\tau/t)^{1/2}$ in equation 2, which is determinative for short and very long times (dashed curve in Fig. 1), is the ratio $-i_{s,d}/i_p$ one would calculate by assuming that the concentration $C_M(x,0)$ at the instant of switching of potential is independent of x and equal to the concentration at $x = 0$. Thus, one deduces from (1) for $t = 0$ (*i.e.*, after τ seconds of pre-electrolysis)

$$C_M(0,0) = 2\left(\frac{D_M\tau}{\pi}\right)^{1/2}\frac{i_p}{nFAD_M} \quad (3)$$

By introducing this concentration in the Ilkovic equation, as written for the plane electrode, there follows the approximate relationship $-i_{s,d}/i_p = (2/\pi)(\tau/t)^{1/2}$. The resulting approximation is

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[8] (a) Z. Karaoglanoff, *Z. Elektrochem.*, **12**, 5 (1906); (b) see ref. 7, p. 180.

[9] T. Berzins and P. Delahay, THIS JOURNAL, **75**, 4205 (1953).

[10] The detailed and rather involved derivation is given in Mamantov's Ph.D. dissertation, June, 1957.

[11] Note that $\sin^{-1}(-1) = -\pi/2$.

quite satisfactory for short times, *i.e.*, for $t/\tau < 0.01$. For larger values of t/τ, the effect of the non-uniform initial concentration distribution is very pronounced (Fig. 1) at least until t/τ is much larger than unity. The term $(2/\pi)(\tau/t)^{1/2}$ is again determinative for $t/\tau >> 1$ because the last two terms in (2) cancel: the argument of the term in $\sin^{-1}$ is then approximately equal to -1.

It follows from these considerations that a plot of $i_{s,d}$ against $1/t^{1/2}$ should be linear for $t/\tau < 0.01$. This is indeed the case (Fig. 3) even for the conditions prevailing in the recording of the curves of Fig. 2 (spherical electrode, time interval between pre-electrolysis and anodic stripping). Note that the extrapolated segments of the lines of Fig. 3 pass through the origin.

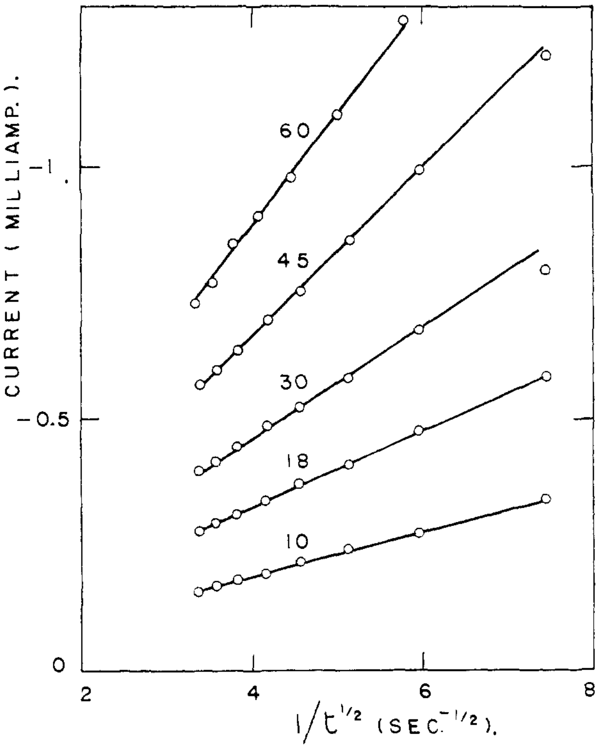

Fig. 3.—Plot of diffusion stripping against $1/t^{1/2}$. Data are from Fig. 2.

It is of interest to calculate the recovery of metal M during stripping. The recovery, which is defined as the ratio $[-\int_0^t i_{s,d}\,dt]/i_p\,\tau$, is obtained by integrating $i_{s,d}$ from 0 to t. Integration is performed by expanding $\sin^{-1}[(\tau - t)/(\tau + t)]$ in series[12] and by retaining only the first term. The resulting approximation is fairly good since the argument is practically equal to unity for $t/\tau << 1$ and the term in $\sin^{-1}$ is quite unimportant. Variations of the recovery with t/τ are shown in Fig. 4. It is seen from this diagram that the recovery is small (< 10%) for $t/\tau < 0.01$. For long times, the recovery is surprisingly good; it approaches unity for $t/\tau \rightarrow \infty$.

Sensitivity Gain.—The gain in sensitivity can be expressed in two ways: (a) as the ratio $-i_{s,d}/i_p$ of equation 2; or (b) as the gain $-i_{s,d}/i_d$ where i_d is the diffusion current measured directly with the analyzed solution (*e.g.*, without pre-electrolysis) and for the same time t as $i_{s,d}$. Both methods will be discussed.

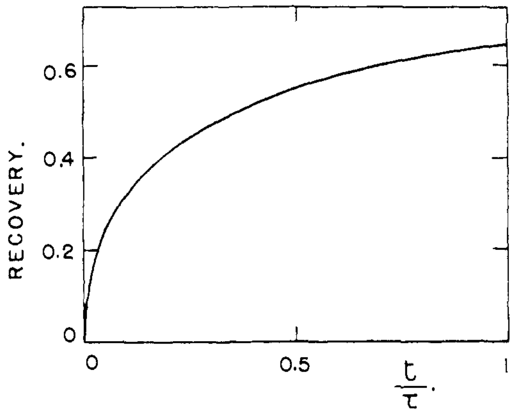

Fig. 4.—Recovery as a function of t/τ in the potential-step method.

The gain in sensitivity, as expressed by equation 2, corresponds to the comparison between the stripping method and voltammetry with a stationary electrode in stirred solution. It follows from the discussion of equation 2 that the gain for $t/\tau << 1$ is approximately $(2/\pi)(\tau/t)^{1/2}$. The ratio $(\tau/t)^{1/2}$ should be as large as possible, but there are two limitations: (a) convection interferes with diffusion when τ is too long thus causing unreliability; and (b) the charging (or discharging) of the double layer interferes with the stripping current when t is too short. Obviously, one should have $i_{s,d} >> i_c$ where i_c is the charging current of the double layer. If one makes the rather coarse assumption that the differential capacity c of the double layer is constant in the interval ΔV of potential during switching of potential, one has $i_c = (\Delta V/R)\exp(-t/Rc)$, R being the total resistance of the cell circuit. The condition $i_{s,d} >> i_c$ now becomes (using the simplified form of equation 2)

$$\frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2} i_p >> \frac{\Delta V}{R}\exp\left(-\frac{t}{Rc}\right) \qquad (4)$$

If an electrode area of 0.03 cm.^{2} (see Experimental) is utilized, c is of the order of 1 microfarad, and the time constant Rc should be less than 10^{-3} second for a cell having not too high a resistance ($R \leqslant 1000$ ohms). If $t = 0.01$ sec., $R = 1000$ ohms, $\Delta V = 0.5$ volt, and $\tau = 100$ sec., condition (4) becomes $i_p >> 5 \times 10^{-10}$ amp. This condition is fulfilled easily with an electrode of 0.03 cm.^{2} even for very dilute solutions. Hence, the capacity current could be neglected for $t \geqslant 0.01$ sec. Actually, there are traces of impurities adsorbed on the electrode, and the switching of potential generally causes a variation in the surface concentration of these impurities. Variations of surface concentrations are quite slow,[13] and the capacity current may not die out for times appreciably longer that $t = 0.01$ sec. Removal of traces of adsorbable organic substances, possibly

(12) $\sin^{-1} y = y + \frac{y^3}{6} + \frac{1 \times 3}{2 \times 4} \times \frac{y^5}{5} \ldots\ldots$

(13) P. Delahay and I. Trachtenberg, This Journal, in press.

by chromatography,[14] is recommended. At any rate, experimental gains of the order of 100 are possible. Since voltammetry with stirred solution is applicable to concentrations as low as 10^{-6} to 10^{-7} molar,[15,16] application of the potential-step stripping method to solutions even as dilute as 10^{-8} molar appears feasible.

Experimental gains are given in Table I for conditions similar to those of Fig. 2 (hanging mercury drop, 4 second interval between pre-electrolysis and anodic stripping). Gains of the order of 100 were obtained for the longest plating time (180 sec.). Experimental and theoretical gains which are in fairly good agreement for short pre-electrolysis times (τ = 10 sec.), are quite different for the larger values of τ. There are two main reasons for this discrepancy. Firstly, convection of metal M in mercury causes a loss of metal in the layer adjacent to the mercury surface, and this tends to decrease the gain. Conversely, diffusion of M in a small mercury sphere (perhaps 1 mm. in diameter) is slower than for semi-infinite linear diffusion, and metal M diffuses away from the mercury surface more slowly in a hanging mercury drop than in a mercury pool. This results in an increase in gain, which becomes more pronounced as τ is made larger. It is seen from Table I that the effect of the sphericity of the electrode outweighs the influence of convection. An evaluation of these two sources of discrepancy would require the derivation of the diffusion stripping current for a spherical electrode. This involved derivation was not attempted since the main purpose of this theoretical analysis was to determine the most important factors which ought to be considered in analytical applications. The theoretically derived general conclusions are confirmed by experiment.

TABLE I

EXPERIMENTAL GAIN FOR HANGING MERCURY DROP *versus* CALCULATED GAIN FOR PLANE ELECTRODE—ANODIC STRIPPING OF CADMIUM

τ, sec.	$t \times 10^{-2}$, sec.	$i_{s,d}$,[a] ma.	$-i_{s,d}/i_p$ Exptl.	Calcd.
180	3	4.62	136	48.4
180	6	3.18	93.5	34
180	9	2.49	73	27.5
60	3	1.29	50	27.5
60	6	0.90	35	19.1
60	9	.73	28	15.5
30	2.8	.68	26	19.8
30	5.8	.49	18.8	13.3
30	8.8	.40	15.4	10.8
10	2.8	.274	10.5	11.0
10	5.8	.196	7.54	7.40
10	8.8	.160	6.16	5.80

[a] The pre-electrolysis current was 26 microamp. except for τ = 180 sec. for which it was 34 microamp.

The second method of expressing the sensitivity gain is to compare $i_{s,d}$ with the diffusion current i_d measured at time t in direct voltammetry without pre-electrolysis. The current i_d is given by the Ilkovic equation written for the plane electrode. The gain calculated by the simplified form of equation 2 and by replacing i_p by its value, $i_p = nFADD_{M+n}C^0/\delta$ (C^0 bulk concentration of M^{+n}, δ diffusion layer thickness), is $(2/\pi^{1/2})(D^{1/2}\tau^{1/2}/\delta)$.

One has $i_{s,d}/i_d \approx 40$ for data of the following orders of magnitude: $D = 10^{-5}$ cm.^{2} sec.$^{-1}$, τ = 100 sec., and $\delta = 10^{-3}$ cm. (an approximate value of the conditions in the experimental study[17]). The anodic stripping method is thus more sensitive than the direct method. Actually, we found that direct voltammetry is not satisfactory at low concentrations (below 10^{-5} molar) because of interference by adsorbed impurities on the electrode (oxide film on mercury). This difficulty is greatly minimized in stripping voltammetry because of pre-electrolysis.

Current–Potential Curves.—The potential after pre-electrolysis is now switched to a value at which the concentration of metal M at the electrode surface is larger than zero during stripping. A set of current–time curves[18] (Fig. 5) is obtained for different stripping potentials. By measuring the current on each of these curves at a given time, one can construct a current–potential curve for that particular stripping time. These curves will now be discussed on the assumption that the Nernst equation is applicable. It first will be assumed that the solution is stirred during stripping and that there is no time interval between pre-electrolysis and stripping.

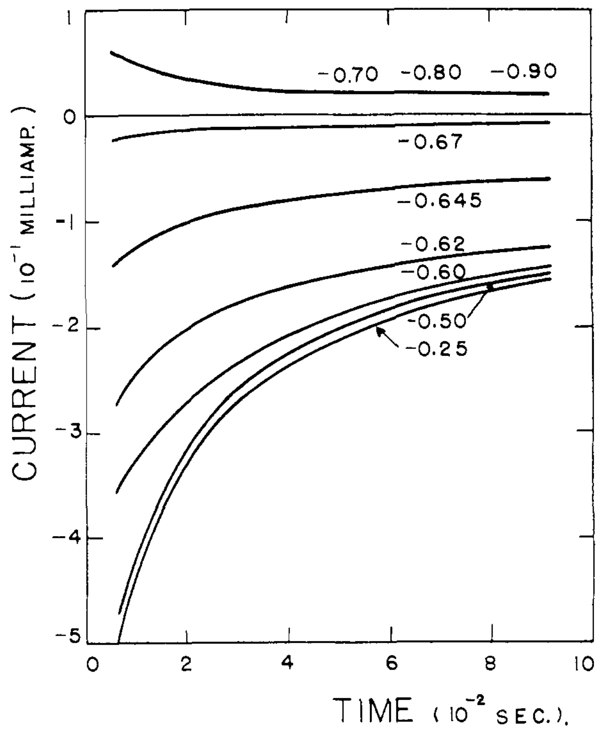

Fig. 5.—Tracings of current–time curves for the anodic stripping potentials (in volts *versus* S.C.E.). Pre-electrolysis time, 10 seconds; time interval between pre-electrolysis and stripping, 4 seconds.

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(14) As far as we know, chromatography was first used in the purification of electrolytes in electrochemical studies by P. J. Hillson, *Trans. Faraday Soc.*, **50**, 385 (1954).

(15) T. S. Lee, THIS JOURNAL, **74**, 5001 (1952).

(16) J. G. Nikelly and W. D. Cooke, *Anal. Chem.*, **28**, 243 (1956).

(17) Data were: $i_p \approx 3 \times 10^{-5}$ amp., $n = 2$. $A \approx 3 \times 10^{-2}$ cm.^{2}, $D = 10^{-5}$ cm.^{2} sec.$^{-1}$, $C^0 = 5 \times 10^{-7}$ mole cm.$^{-3}$.

(18) Note that the curves for −0.90, −0.80 and −0.70 volt in Fig. 5 correspond to the limiting current range for pre-electrolysis. The current decreases progressively because of concentration polarization. Thus, the electrolysis circuit was open after pre-electrolysis and closed again after the interval of 4 seconds, the solution being not stirred after pre-electrolysis.

To derive the equation of the i_s *versus* t curves for any potential we could use again the initial condition (1) for M and prescribe that the ratio $C_{M^{+n}}/C_M$ at $x = 0$ is equal to a constant readily given by the Nernst equation. Another boundary condition would be obtained by prescribing that the sum of the fluxes of M and M^{+n} at $x = 0$ is equal to zero. The approach is the same as in the rigorous derivation of reversible polarographic waves,[19] but the algebra is far more involved—in fact, too involved for the result to be achieved. It is much easier to assume that C_M is independent of x at $t = 0$ and has the value given by equation 3. This approximation is very good for $t/\tau \leqslant 0.01$ (see above) but is poor for $t/\tau > 0.1$. The concentrations $C_{M^{+n}}(0,t)$ and $C_M(0,t)$ are calculated as follows.

The concentration $C_{M^{+n}}(0,t)$ during stripping is deduced from the condition that the sum of the fluxes of M and M^{+n} at $x = 0$ is equal to zero. On the basis of the Nernst diffusion layer treatment, the flux of M^{+n} during stripping which is equal to i_s/nFA is $D_{M^{+n}}[C_{M^{+n}}(0,t) - C^0]/\delta$, δ being the diffusion layer thickness, and C^0 the bulk concentration of M^{+n}. The thickness δ can be evaluated from $i_p = nFA \cdot D_{M^{+n}}C^0/\delta$. Hence

$$C_{M^{+n}}(0,t) = C^0\left[1 - \frac{i_s}{i_p}\right] \qquad (5)$$

The concentration $C_M(0,t)$ is derived by noting that, as in polarography theory, i_s is proportional to the difference $[C_M(0,0) - C_M(0,t)$, the proportionality factor being deduced from the Ilkovic equation written for the plane electrode. By using for $C_M(0,0)$ the value given in (3) there follows after simple transformations

$$C_M(0,t) = C_M(0,0)\left[1 - \frac{i_s}{i_{s,d}}\right] \qquad (6)$$

By introducing the C's from (5) and (6) in the Nernst equation one obtains after rearrangement of terms (the F's are activity coefficients)

$$E = E + \frac{RT}{nF}\ln\frac{f_{M^{+n}}}{f_M}\frac{nFAD_M{}^{1/2}C^0}{\pi^{1/2}i_p}\frac{1}{t^{1/2}} - \frac{RT}{nF}\ln\frac{i_s - i_{s,d}}{i_p - i_s} \qquad (7)$$

As in the foregoing treatment, anodic stripping currents are negative in equations 5 to 7, and the cathodic current i_p is positive. The half-wave potential, which is equal to the sum of the first two terms on the right-hand side of (7), is shifted toward less anodic potentials as the time t increases. The half-wave potential corresponds to $i_s = (i_{s,d} + i_p)/2$ and is the point of inflection of the current–potential curve (set $d^2E/di^2 = 0$). The potential at $i = 0$ is independent of time. Its value is obtained by setting $i_s = 0$ in (7) and by noting that $-i_{s,d}/i_p$ is set equal to $(2/\pi)(\tau/t)^{1/2}$ in this simplified treatment.

Equation 7 still holds as a simplified formula for the case in which stirring is stopped after pre-electrolysis and a time interval elapses before anodic stripping, but the half-wave potential has now the value $E^0 + (RT/nF)\ln(f_{M^{+n}}/f_M)(D_M/D_{M^{+n}})^{1/2}$ and is independent of time. This is the value derived in the theory of reversible polarographic waves.

Current–potential curves deduced from the data of Fig. 5 are plotted in Fig. 6 for different values of t. The half-wave potential is independent of time and has the same value (−0.64 volt *versus* S.C.E.) as the polarographic half-wave potential. The foregoing approximate analysis is thus quite satisfactory for the stripping times involved here.

Current-step Method

Transition Time and Sensitivity Gain.—The conditions are the same as in the potential-step method except that anodic stripping is carried out at constant current. The potential of the amalgam electrode is followed during anodic stripping, and a potential–time curve is recorded. This curve exhibits a rapid variation of potential at the transition time τ_s, *i.e.*, at the time at which $C_M(0, \tau_s) = 0$ (Fig. 7). The ratio τ_s/τ, of the transition time τ_s to the pre-electrolysis time τ, was calculated in a previous paper[9]

$$\frac{\tau_s}{\tau} = \frac{1}{\left(1 - \frac{i_s}{i_p}\right)^2 - 1} \qquad (8)$$

with i_p positive and i_s negative. Experimental and calculated values of τ_s/τ are compared in Table II for the anodic stripping of cadmium from a hanging amalgam drop. The agreement is relatively good in view of the two sources of discrepancy, sphericity of the electrode and loss of metal in mercury by convection. The effect of sphericity becomes more pronounced as the electrolysis is prolonged (compare data for $\tau = 10$ sec. and $\tau = 75$ sec.).

TABLE II

EXPERIMENTAL RATIO τ_s/τ FOR HANGING MERCURY DROP *versus* CALCULATED GAIN FOR A PLANE ELECTRODE—ANODIC STRIPPING OF CADMIUM

i_s,[a] µa.	τ, sec.	τ_s, sec.	τ_s/τ Exptl.	τ_s/τ Calcd.
9.9	10	17.5	1.75	2.18
19.6	10	8.5	0.85	1.02
49.4	10	2.4	.24	0.32
49.4	25	7.8	.31	.32
49.4	50	16.0	.32	.32
49.4	75	27.2	.36	.32

[a] Pre-electrolysis current, 48 microamperes; electrode area, 3.16×10^{-2} cm.^{2}.

The sensitivity gain can be expressed by comparing τ_s with the transition time τ_d that would be observed in direct electrolysis at current i_s without pre-electrolysis. Since $\tau_d{}^{1/2}$ is proportional to the bulk concentration of reducible substance, the ratio $(\tau_s/\tau_d)^{1/2}$, and not τ_s/τ_d, should be considered to express the gain in sensitivity. The gain is $(\tau/\tau_d)^{1/2}[(1 - i_s/i_p)^2 - 1]^{-1/2}$. For the data of Table II ($\tau = 10$ sec., $\tau_s = 17.5$ sec.), one evaluates a gain, $(\tau_s/\tau_d)^{1/2}$, of approximately 6 over the direct method.[20] Actually, the direct method is not applied easily at low concentrations (adsorbed impurities, capacity effect), and the stripping method is more advantageous than this simple calculation of the gain would indicate.

Potential–Time Curves.—As in the potential-step method, we consider only the case in which the Nernst equation is applicable. By introducing the value of the concentration previously derived[9]

$$C_M(0,t) = \frac{2[i_p(\tau + t)^{1/2} - (i_p - i_s)t^{1/2}]}{\pi^{1/2}\, nFAD_M{}^{1/2}} \qquad (9)$$

and $C_{M+N}(0,t)$ from equation **5** in the Nernst equation there follows after simple transformations (no time interval between pre-electrolysis and stripping)

$$E = E^0 + \frac{RT}{nF}\ln\frac{f_{M^{+n}}}{f_M}\frac{\pi^{1/2}\, nFAD_M{}^{1/2}\, C^0}{2i_p} - \frac{RT}{nF}\ln\left[(\tau + t)^{1/2}\frac{i_p}{i_p - i_s} - t^{1/2}\right] \qquad (10)$$

Potential–time curves do not have a point of inflection, and the potential becomes progressively more anodic as the electrolysis proceeds (Fig. 7). The potential at $t = 0$ is readily deduced from (10); it depends on pre-electrolysis time and current. It follows from (10) that a plot of log $[(\tau + t)^{1/2}[i_p/i_p - i_s)] - t^{1/2}]$ against E should have the reciprocal slope of $0.059/n$ at 25°.

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(19) See ref. 7, pp. 52–57. Note that this derivation is different from the one usually given in the polarographic literature.

(20) On the basis of the evaluated value $\tau_d \approx 0.5$ sec.

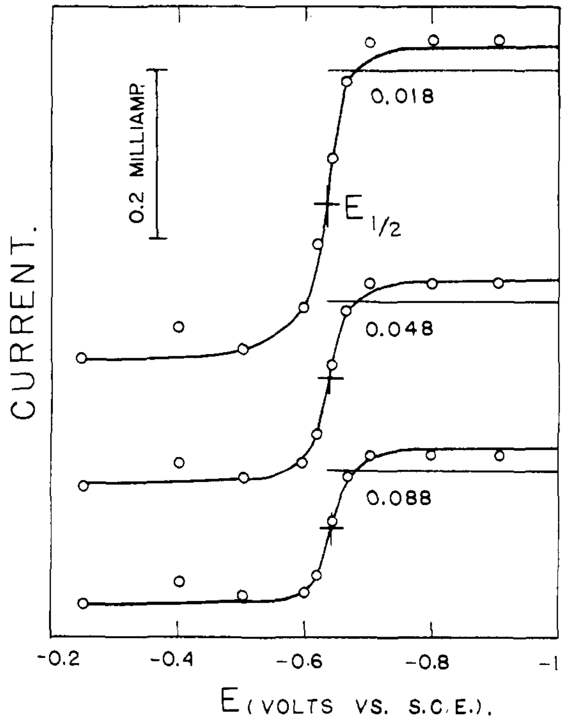

Fig. 6.—Current–potential curves from the data of Fig. 5. Numbers on curves are the times in seconds at which current was measured.

Potential–time curves for the case in which stirring is stopped after pre-electrolysis can be analyzed readily in an approximate fashion on the basis of previous results for voltammetry at constant current (g).

Application to Analysis

The two methods studied in this paper and the method of Nikelly and Cooke[6] (anodic stripping with continuously varying potential) are of interest in the analysis of traces of amalgam forming metals in the concentration range in which direct voltammetry and polarography fail. Hence, anodic stripping methods have a practical value for concentrations below 10^{-6} molar.[21] The sensitivity gain that is achieved results from concentration of the metal to be analyzed in a thin layer at the surface of the mercury electrode. Rather high gains are possible because the metal is deposited in stirred solution at a much higher rate than it diffuses into the bulk of mercury. In this respect, anodic stripping methods can be compared to extraction.[22] It should be emphasized that the gain does not result so much from an increase in current to be measured *per se* (very low currents are quite easy to measure) but rather from an enhancement of current under conditions in which the capacity current is not particularly increased.

A comparison of the gains obtained by the three anodic stripping methods would require actual application to trace analysis, and only the tentative conclusion that the potential-step method is the most sensitive will be made here.[23]

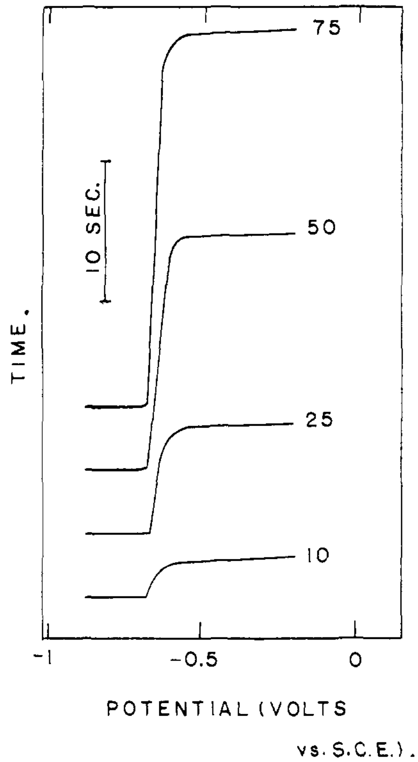

Fig. 7.—Tracings of potential–time curves for the anodic stripping of cadmium in 1 *M* potassium chloride at 1.56×10^{-3} amp.cm.$^{-2}$. Numbers on curves are pre-electrolysis times in seconds. Time interval between pre-electrolysis and stripping, 4 seconds.

An obvious application of anodic stripping methods would be amperometric titrations at concentrations below 10^{-6} molar.

Experimental

A cell with hanging mercury drop[24] of the type previously used in this Laboratory[25] was utilized. A mercury drop falling from a conventional dropping mercury electrode was caught in a small glass spoon and then hung (by rotation of the spoon) on a small gold-plated platinum wire (perhaps 0.1 mm. long) sealed in a glass tube with fine tip. The cell also was provided with a constant speed stirrer of the propeller type. The blades of the propeller were below the tip of the dropping mercury electrode and the hanging drop to avoid the projection of mercury drops on the hanging drop. The stopper was made of plastic and was carefully machined to fit the ground glass collar of the cell. Accuracy in the spacing of the electrodes and spoon was far more easily achieved with a plastic stopper than with a ground glass stopper. A saturated calomel electrode was prepared in the other arm of the cell, and the cell had the usual nitrogen inlet.

It was found that the solution could be rather vigorously

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(21) For a review of voltammetric and polarographic methods for trace analysis see P. Delahay in "Symposium on Trace Analysis," J. H. Yoe and H. J. Koch, Eds., John Wiley and Sons, New York, N. Y., in preparation, 1955.

(22) Comparison also should be made with the method of N. H. Furman, C. E. Bricker and B. McDuffie, *J. Wash. Acad. Sci.*, **38**, 159 (1948), in which the metal to be analyzed is plated on mercury and is subsequently dissolved in acid after removal of mercury by distillation. See also A. Hickling, J. Maxwell and J. V. Shennan, *Anal. Chim. Acta*, **14**, 287 (1956).

(23) The sensitivity gain of the method of Nikelly and Cooke can be evaluated by noting that the Randles–Sevcik treatment of oscillographic polarography is applicable as a first approximation when the stirrer is stopped before anodic stripping.

(24) First used, as far as we know, by H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

(25) (a) T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955); (b) W. Vielstich and P. Delahay, *ibid.*, in press.

stirred without the dislodging of the hanging drop, and pre-electrolysis limiting currents were relatively large (diffusion layer thickness of the order of 10^{-3} cm.). Because of vigorous stirring, the pre-electrolysis current dropped within 1–2 seconds to an average constant value upon switching on. The area of the hanging drop was reproducible with an error smaller than 1% (a conservative estimate) in a given medium.[26]

The stirring achieved with the rotated propeller stirrer was not uniform, and rapid fluctuations of the pre-electrolysis current about a constant average value were observed. Non-uniform stirring also caused deformation of the hanging drop, and consequently the stirrer was stopped at the end of pre-electrolysis. A time interval of 4 seconds was allowed to elapse before anodic stripping. The small loss in sensitivity gain was more than compensated by improvement in accuracy.

A cell in which the hanging drop was suspended on a rotating glass tube with gold-plated platinum tip also was used but was not studied in detail. This type of electrode might well be more advantageous than the combination of hanging drop and stirrer.

Instrumentation for the control of the potential of the hanging drop and the stripping current (current-step method) was conventional. Pre-electrolysis was carried out at −1 volt (*versus* S.C.E.) in all the experiments. Time intervals during pre-electrolysis and between stripping and pre-electrolysis were controlled manually with an electric timer. The utilization of time relays would be advantageous and would require only simple instrumentation. Recordings were made with a Tektronix cathode-ray oscilloscope, model 531, with preamplifier 53D.

Solution composition: 0.5 mM Cd^{++} in 1 M potassium chloride; oxygen removal by nitrogen. The temperature was approximately 25°; it did not vary by more than 1–2 degrees in a series of determinations.

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[26] The reproducibility would be improved by polarizing the dropping mercury electrode at a constant potential (not so cathodic as to cause any appreciable metal deposition) instead of letting the electrode acquire the mixed potential corresponding to the condition that the algebraic sum of faradaic and capacity currents is equal to zero.

[CONTRIBUTION FROM THE UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY, CALCUTTA, INDIA]

The Silver–Silver Chloride Electrode in Formic and Acetic Acids as Solvents

BY L. M. MUKHERJEE[1]

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This paper explains the observed behavior of the Ag/AgCl electrode in formic and acetic acids, as solvents, in terms of the dielectric constant and autoprotolysis constant of each medium.

Introduction

Suitable reference electrodes are not easily obtainable for use in formic and acetic acid solutions. Cells employed in previous studies[2,3] of acids and bases in acetic acid, for instance, seem to consist essentially of an aqueous calomel reference electrode in conjunction with chloranil or glass electrode, both with and without salt bridge. To eliminate the difficulties encountered with the use of the calomel electrode, Fritz[4] and Glenn[5] recommended the Ag/AgCl electrode as a reference standard in acetic acid. Accordingly, the purpose of the present investigation is to determine the standard potential of the Ag/AgCl electrode (relative to hydrogen electrode as zero) in both formic and acetic acids with a view to test its performance as a reference electrode and also to explain the observed E^0 values in terms of the properties of the solvents themselves.

Experimental

Cells of the following type were studied in both the solvents

$$\text{Pt, } H_2\text{; } HCl_{\text{non-aq}}\text{; } AgCl/Ag$$

$$E_{\text{obs}} = E^0 - \frac{2RT}{F} \ln a^0{\pm}_{\text{HCl}}$$

The observed e.m.f.'s were extrapolated to obtain the standard potential $E°$ of the silver–silver chloride electrode by the procedure outlined by Harned,[6] taking into account the Gronwall–LaMer–Sandved extended terms. Due to incomplete ionization of HCl in formic acid and acetic acid, the extrapolation formula has been modified in each case by replacing the concentration C by $\alpha . C$ (= $\sqrt{KC}$) where α and K represent, respectively, the degree of dissociation, and the dissociation constant of HCl as obtained from the previous conductance data in the particular medium. The values of the dissociation constant of HCl in formic and acetic acids used in the present case refer, respectively, to the work of Schlesinger and Martin[7] and of Kolthoff and Willman.[8]

Of the solvents employed in the present study, acetic acid was purified as: 99–100% glacial acetic acid (E. Merck) was refluxed with a little solid $K_2Cr_2O_7$ for about 5 hours on a sand-bath and then distilled in an all-glass Pyrex apparatus provided with $CaCl_2$ guard tube directly into a clean, dry Jena bottle. The distillate so obtained was then frozen out, the liquid portion was discarded and the crystals (m.p. 16.6°) were collected and stored in Jena bottles which were kept in a closed chamber containing some dehydrated silica gel. The sample so obtained was finally characterized by ultraviolet spectrophotometry.

One hundred per cent. A.R. quality formic acid (E. Merck) was used as such without any initial treatment; the acid and the prepared solutions as well were preserved in a closed chamber kept in a refrigerator.

Solutions of HCl were obtained by absorbing in the respective solvents, in almost complete absence of air, HCl gas prepared from concd. H_2SO_4 and NaCl (E. Merck, G.R., oven-dried at 105–110°) and dried by passing through concd. H_2SO_4. Due to very low solubility of HCl in acetic acid, solutions of concentrations higher than 0.00533 N could not be studied in this solvent. Aliquots of the HCl solutions so prepared were taken in water and then estimated either by weighing as AgCl or by back titration of $AgNO_3$ added in

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(1) Chemistry Department, The Florida State University, Tallahassee, Florida.

(2) N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3047 (1927).

(3) (a) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, **23**, 337 (1951); (b) R. T. Moore, *et al.*, *ibid.*, **23**, 1639 (1951); (c) C. N. Pifer and E. G. Wollish, *ibid.*, **24**, 300 (1952); (d) W. Seaman and E. Allen, *ibid.*, **23**, 592 (1951).

(4) J. S. Fritz, *ibid.*, **22**, 1028 (1950).

(5) R. A. Glenn, *ibid.*, **25**, 1916 (1953).

(6) H. S. Harned, THIS JOURNAL, **60**, 336 (1938).

(7) H. I. Schlesinger and A. W. Martin, *ibid.*, **36**, 1589 (1914).

(8) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934).