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Effect of Electrode Configuration and Transition Time in Solid Electrode Chronopotentiometry

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▶ To determine the optimum electrode and transition time range for chronopotentiometric analysis, the transition time constant, $i_o \tau^{1/2}/C^\circ$, was measured for the reduction of silver(I) and lead(II), and the oxidation of iodide and hydroquinone, over a transition time range of 0.001 to 300 seconds. The transition time constant increased at long transition times, due to spherical contributions to diffusion and natural convection. Increase at short transition times was ascribed to charging of the double layer, electrode oxidation, and roughness of the electrode. By employing a horizontal electrode, with a glass mantle, oriented so that density gradients were not produced, $i_o \tau^{1/2}/C^\circ$ was maintained constant to ±0.2% with transition times of 7 to 145 seconds.

ALTHOUGH the theoretical basis of chronopotentiometry is well established, and several preliminary experimental studies indicate its general analytical applicability, relatively few applications to actual analytical problems have been made. Unlike polarography, in which current is a dependent variable, chronopotentiometry requires the choice of a current density, which may vary over a wide range, depending upon the transition time desired. Several papers recommend choosing the current density to obtain short transition times (0.3 to 1 second) (*10*, *19*), while other authors prefer transition times in the range of 10 to 60 seconds (*3*, *14*, *18*). Chronopotentiometry with solid electrodes also allows the choice of an electrode

from a number of different types that have been used, which include: disk electrodes (platinum disk embedded in glass) (*3*, *9*, *10*, *20*), foil electrodes (*9*, *10*, *14*, *18*, *20*), cylindrical wire electrodes (*9*, *10*, *19*, *20*), and wire loop electrodes (*20*). This paper discusses factors which affect choice of electrode and transition time range.

The fundamental equation of chronopotentiometry is

$$\frac{i_o \tau^{1/2}}{C^\circ} = \frac{\pi^{1/2} F n D^{1/2}}{2} = 8.55 \times 10^4 n D^{1/2} \tag{1}$$

where i_o is the current density (microamperes per square centimeter), τ is the transition time (seconds), C° is the concentration of the electroactive species (millimoles per liter), n is the number of faradays per mole of reaction, D is the diffusion coefficient of the electroactive species (square centimeters per second), and F is the faraday. This equation is derived under the assumption that semi-infinite linear diffusion is the only means of mass transfer of the electroactive species to the electrode surface. This equation predicts that $i_o \tau^{1/2}/C^\circ$ [the transition time constant (*16*)] should be constant over any range of current densities or transition times for a given reaction at the same electrode. Although no previous evaluation of the transition time constant over a very wide range of transition times has been made, practically every chronopotentiometric study has noted a decrease in $i_o \tau^{1/2}/C^\circ$ with decreasing transition time (increasing current density). Delahay (*4*) ascribed

this decrease to heating of resistors in the current source during a trial, leading to a decrease in current density, but other authors found this variation, even when the current was held constant. Lingane (*14*) suggested that failure to take into account the blank transition time for the supporting electrolyte alone may contribute to this variation. However, even at a constant concentration of the electroactive species, C°, $i_o \tau^{1/2}$ is found to vary with current density. Davis and Ganchoff (*3*) recently studied this variation in the reduction of MnO_4^-, $Cr_2O_7^{-2}$, Ce(IV), Fe(III), and V(V) at a platinum electrode. The variation was apparent in all of these reductions (transition times of about 5 to 80 seconds) and could not be eliminated by any choice of graphical method for evaluating τ. The authors resorted to the expedient of making all measurements at a given transition time (30 ± 2 seconds); yielding an average deviation of 0.6% over a fivefold concentration range.

To ascertain the cause of this variation and to define the conditions under which the transition time constant is truly constant, $i_o \tau^{1/2}/C^\circ$ was measured with plane electrodes of different construction and orientation in the solution over a very wide range of current densities and transition times.

EXPERIMENTAL

Cell. The cell used in these studies comprised a 400-ml. electrolysis beaker with a platinum foil auxiliary electrode (3 × 3 cm.) enclosed in a chamber separated from the main cell

by a medium porosity sintered-glass disk. A low resistance saturated calomel electrode or saturated mercurous sulfate electrode (13) was used as a reference electrode. Oxygen was removed by passing nitrogen into both chambers. The cell was placed in a thermostat at $25.00° \pm 0.05°$ C.

Electrodes. The unshielded platinum electrode was a Beckman metallic electrode, inlay style, No. 1273, with a projected area of 0.212 sq. cm. The shielded electrode was a platinum disk, sealed in 14-mm. soft glass, attached to a short length of 7-mm. glass tubing (Figure 1). This piece was attached to 7-mm. glass tubing of various shapes by a short length of Tygon tubing. Contact was made to the platinum by pushing a copper wire, coiled in the shape of a spring, against the disk.

Apparatus. The electrolysis current (constant to $\pm 0.2\%$) was supplied by the instrument described by Lingane (12), powered by either batteries or a Model 1204 B power supply (General Radio Co., Cambridge, Mass.). The potential-time curves for transition times longer than 5 seconds were recorded on the instrument previously described (2), which consisted of a pH meter Model 7664 (Leeds & Northrup Co., Philadelphia, Pa.) input to the Y-axis of a Moseley 3S X-Y recorder (F. L. Moseley Co., Pasadena, Calif.) yielding an input impedance of 2000 megohms. The X-axis of the recorder was set on the time base, allowing full-scale (11-inch) sweeps of 10, 50, 100, and 500 seconds. The recorder required 0.5 second for full-scale pen travel on the Y-axis. The time base was calibrated at every trial by simultaneously timing with a Model S-10 (Standard Electric Time Co., Springfield, Mass.) timer.

Short transition times were measured by applying the potential to the Y-input of a Model 401-A oscilloscope (Allen B. DuMont Laboratories, Inc., Clifton, N. J.) (input impedance about 2 megohms) and photographing the resulting trace with a DuMont oscilloscope camera Type 353, equipped with Polaroid Land Model 95 camera back, and designed to give a 1:1 object to image ratio. The time base of the oscilloscope was calibrated using a Model 200 CD wide range oscillator (Hewlitt-Packard Co., Palo Alto, Calif.) which in turn had been calibrated against a time mark generator Type 180 A (Tetronix, Portland, Ore.). Two chronopotentiograms and a time calibration were recorded on each print (Polapan Type 44 film). It is necessary to record a time base on each print to avoid errors due to variations in film size and nonlinearity of the oscilloscope time base (which changed by about 10% during a sweep).

Chemicals. The iodide solution was prepared from dried reagent grade potassium iodide. Test solutions, which were $1.0M$ in H_2SO_4, were deaerated with nitrogen before adding the iodide solution, to avoid air oxidation of iodide.
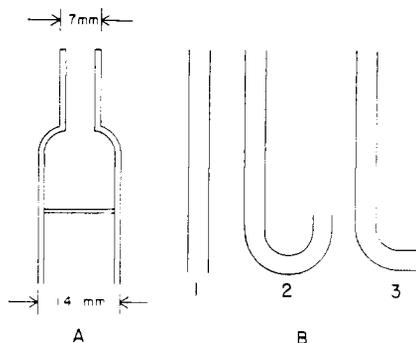

Figure 1. Electrode

A. Shielded electrode
B. Tubes to which shielded electrode is attached, providing
  1. Horizontal electrode, diffusion upwards
  2. Horizontal electrode, diffusion downwards
  3. Vertical electrode

Hydroquinone was purified by recrystallizing twice from water, and drying in a vacuum desiccator.

The lead solution was prepared from test lead dissolved in nitric or perchloric acid.

The silver solution was prepared from dried reagent grade silver nitrate.

Procedure. The working electrode was generally pretreated before each day's use by immersing briefly in nitric acid, water, hydrochloric acid, and finally washing well with water. The first two trials of the day were generally discarded.

The solution was deaerated in the thermostat for about 15 minutes. The nitrogen, thermostat, and stirrer were turned off about 2 minutes before each trial to allow the test solution to come to rest. The recorder time base was started and the current was switched from the dummy resistor to the cell and its value determined, several times, if possible, by measuring the voltage drop over a General Radio Co. Type 500 resistor with a potentiometer. After the transition, the current was switched off, time noted, and the thermostat and stirrer were turned on.

During trials in which lead or silver was plated on the electrode, the deposit was stripped off after each trial by reversing the direction of the current until the electrode potential rose to about 0.2 volt above its stripping potential. The solution inside the mantle of the shielded electrodes was flushed several times before a trial by a medicine dropper arranged for this purpose.

When the oscilloscope was used to record the potential-time curves, the current was measured immediately preceding the trial. The controls were set to driven sweep and internal synchronization, with synchronization level set so that a sweep was triggered when the current was passed to the cell. The transition time was determined by measuring the distance from the initial rise to the transition with an x-ray film reader, and comparing this to the distance occupied by a certain number of

cycles on the signal generator trace, photographed on the same piece of film.

RESULTS

Unshielded Disk Electrode. The variation of $i_o\tau^{1/2}/C°$ for the reduction of silver and lead, and the oxidation of iodide and hydroquinone, at several concentrations, with τ, is shown in Figures 2, 3, and 4. Each point in these figures represents the mean of at least two, and usually three or more, trials. The chronopotentiometric reduction of iron(III) also shows this behavior. For all of these electrode processes, $i_o\tau^{1/2}/C°$ increases at both short and long transition times, and has its minimum value and smallest variation in the range of 10 to 40 seconds. The usual decrease of the transition time constant with increasing current density is present only for transition times longer than about 5 seconds. The experimental variation of $i_o\tau^{1/2}/C°$ must be due to differences between the assumptions made in the theoretical treatment and the actual experimental conditions.

The increase at long transition times is the result of both nonlinearity of diffusion and convection. The increase at short transition times is due to the charging of the electrode double layer, roughness of the electrode surface, and oxidation of the electrode itself.

Nonlinearity of Diffusion. The concentration of a substance, C, during a chronopotentiometric determination, as a function of distance from the electrode, x, and time t, follows the expression:

$$C(x,t) = C° - \frac{i_o}{nFD}\left\{\frac{2t^{1/2}D^{1/2}}{\pi^{1/2}}\exp\left(-x^2/4Dt\right) - x\,\mathrm{erfc}\,(x/2D^{1/2}t^{1/2})\right\} \quad (2)$$

Calculation of concentration profiles for $n = 1$, $D = 1.00 \times 10^{-5}$ sq. cm. per second, $C° = 5.00$ mmole per liter, $i_o = 169$ μa. per sq. cm. (equivalent to τ of 64 seconds) yields "diffusion layer thicknesses" [taken arbitrarily where $C(x,t)$ is 95% of $C°$ (10)] of 0.017, 0.049, and 0.060 cm. at t of 10, 25, 49, and 64 seconds, respectively. Since a disk electrode with a radius of 0.26 cm. was employed, the thickness of the diffusion layer is not negligible compared to the dimensions of the electrode, and the diffusion is not strictly linear, but has a somewhat spherical nature.

Mamantov and Delahay (15) calculated the transition time for chronopotentiometry with diffusion to a spherical electrode of radius r_o as following the expression:

$$\frac{nFDC°}{i_o r_o} = 1 - \exp\,(D\tau/r_o{}^2)\,\mathrm{erfc}\,(D^{1/2}\tau^{1/2}/r_o) \quad (3)$$

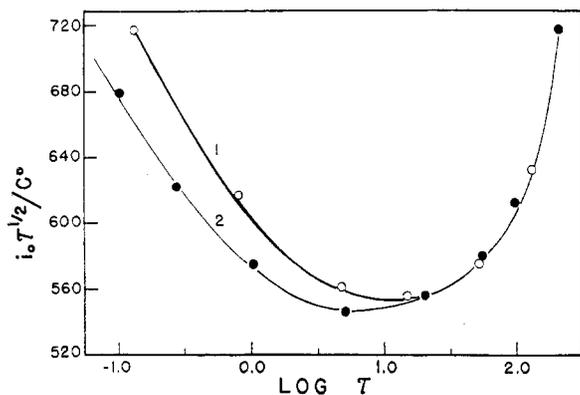**Figure 2.** Variation of $i_o\tau^{1/2}/C°$ (μa. — sec.$^{1/2}$/ sq. cm. — millimole per liter) with log τ (seconds) for oxidation of hydroquinone at unshielded disk electrode (0.21$_2$ sq. cm.)

τ measured at ca. +0.46 v. vs. S.C.E.
1. 5.00mM hydroquinone in NBS buffer pH 7
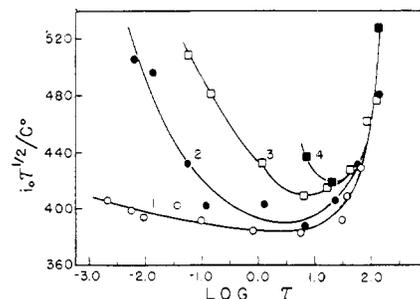2. 10.00mM hydroquinone in NBS buffer pH 7

Figure 3. Variation of $i_o\tau^{1/2}/C°$ with log τ for oxidation of iodide at unshielded disk electrode

τ measured at ca. 0.70 v. vs. S.C.E.
1. Iodide concentration, 10mM in 1.0M H_2SO_4
2. 5.00mM
3. 1.00mM
4. 0.10mM

Calculations of $i_o\tau^{1/2}/C°$ as a function of τ for the reduction of silver(I), assuming "effective radii" of 0.13 and 0.26 cm. are shown in Figure 4. Equation 3 becomes essentially the same as that for linear diffusion, Equation 1, when $D^{1/2}\tau^{1/2}/r_o$ <0.07 (so that 1 — $\exp(D\tau/r_o^2)$ erfc $(D^{1/2}\tau^{1/2}/r_o)$ is the same, within 0.5%, as $(2D^{1/2}\tau^{1/2}/\pi^{1/2}r_o)$. For transition times of about 64 seconds, the effective radius must be larger than about 0.3 cm.

Convection. Lingane (14) [referring to the work of Laitinen and Kolthoff (11)] suggested that an electrode provided with a glass mantle which restricts diffusion to lines normal to the electrode surface might be useful in chronopotentiometry. When these were constructed by sealing platinum disks into glass mantles with various types of cements, spurious waves, perhaps caused by adsorption of impurities from the cement on the electrode, often appeared in the potential-time curves. By sealing the disk directly into soft glass, this difficulty was avoided. Electrical contact to the disk was made directly with a copper wire, rather than by the familiar mercury contact, to avoid the possibility of mercury diffusion into the platinum, with consequent change in its surface and behavior.

Natural convection, which arises spontaneously because of density differences, is very effective in causing stirring at an electrode surface. Ibl (8) has shown that the limiting current for the reduction of copper(II) at a vertical cathode (3 × 2 cm.) in unstirred solution was only about a third as large as that with the electrode rotating with a peripheral velocity of 31 mm. per second. Natural convection must, therefore, be avoided in chronopotentiometry by orienting

Table I. Variation of $i_o\tau^{1/2}/C°$ with Transition Time for the Reduction of Silver(I) at Unshielded and Shielded Electrodes of Several Orientations

Silver(I) concentration was 5.00mM, in 0.20M KNO_3 and 0.01M HNO_3, and temperature was 25.00° ± 0.05° C.

	i_o, μa./ Sq. Cm.)	τ, Sec.	$i_o\tau^{1/2}/C°$, μa.- Sec.$^{1/2}$ Sq. Cm. Mmole/l.
Unshielded electrode[a]	192.0	192.5	532
	232.0	114.1	495
	265.8	64.1	426
	381.1	28.1	403
	772.0	6.23	392
	1,742	1.362	407
	3,300	0.536	482
	6,180	0.171	511
	9,340	0.120	646
	14,010	0.0813	798
Shielded electrodes[b]			
(1) Horizontal, diffusion upwards	114.6	303.0	399.6
	165.6	145.2	397.6
	248.6	63.5	396.8
	429.2	21.6	398.0
	719.0	7.57	396.2
	1,905	1.198	415
	6,480	0.114	440
	14,510	0.0263	472
(2) Horizontal, diffusion downwards	No transition for i_o < 215 μa./sq. cm.		
	215.5	109	451
	223.3	91.9	428
	242.1	71.7	411
	270.2	55.4	402
	291.1	47.6	402
	410.8	24.0	405
	468.8	18.39	401
	721.0	7.87	403
	2,151	1.048	440
(3) Vertical	No transition for i_o < 210 μa./sq. cm.		
	220.4	183	597
	230.0	110	482
	245.5	80.6	441
	358.8	31.38	402
	470.7	18.20	402
	730.4	7.66	405
	2,285	0.886	430
	4,586	0.236	440

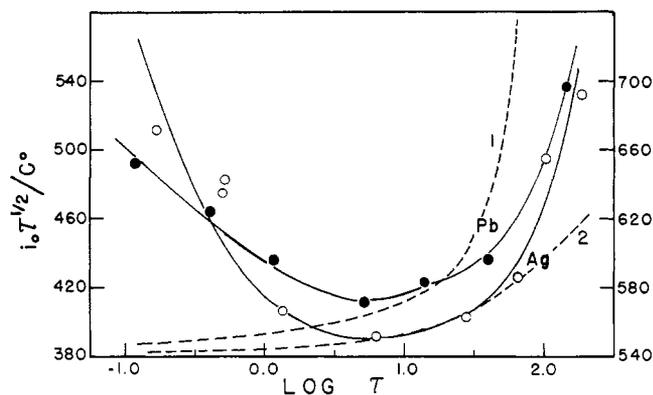[a] Projected area = 0.212 sq. cm.
[b] Projected area = 1.00 sq. cm.

Figure 4. Variation of $i_0\tau^{1/2}/C^\circ$ with log τ for reduction of silver(I) and lead(II) at unshielded disk electrode

Left axis, Silver(I), 5.00mM in 0.2M NaNO$_3$ solution
τ measured at ca. -0.24 v. vs. saturated mercurous sulfate electrode
Right axis, Lead(II), 5.00mM in 0.2M NaNO$_3$ solution
τ measured at ca. -0.72 v. vs. S.C.E.
- - - Calculated for spherical diffusion for $n = 1$, $D = 1.95 \times 10^{-5}$; sq. cm. per sec., $C^\circ = 5.00$mM, for an "effective radius" of (1) 0.13 and (2) 0.26 cm.
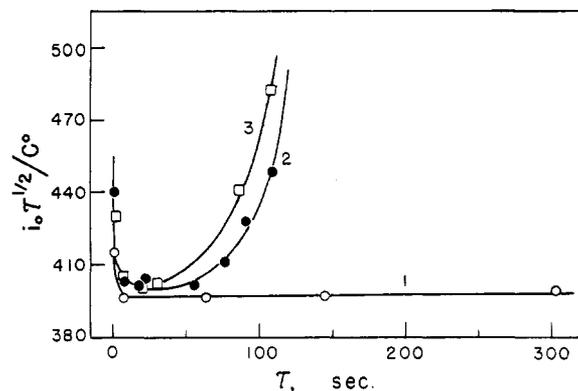

Figure 5. Variation of $i_0\tau^{1/2}/C^\circ$ with τ for reduction of silver(I) at shielded electrode

Silver(I), 5.00mM in 0.20M KNO$_3$ and 0.01M HNO$_3$ reduced at an electrode (1.0$_0$ sq. cm.) provided with glass mantle oriented
1. Horizontally, diffusion upward
2. Horizontally, diffusion downward
3. Vertically
τ measured at ca. -0.28 v. vs. saturated mercurous sulfate electrode

the electrode so that density gradients, produced as a result of the electrode reaction, are in such a direction that natural convection does not occur.

The cathodic chronopotentiometry of silver(I) at a shielded platinum electrode in various orientations was performed in a manner analogous to that of Laitinen and Kolthoff (11). The variation of $i_0\tau^{1/2}/C^\circ$ with τ for the reduction of a 5.00mM silver nitrate solution at an electrode oriented (see Figure 1) (1) horizontally, diffusion upwards, (2) horizontally, diffusion downwards, and (3) vertically, are shown in Figure 5. The results for this series, compared to reduction at an unshielded electrode, are given in Table I.

When the electrode is oriented so that natural convection may occur, as in (2) and (3), $i_0\tau^{1/2}/C^\circ$ increases with decreasing current density, and for transition times longer than 60 seconds, convection contributes appreciably to mass transfer to the electrode. Even at shorter transition times (5 to 60 seconds), the transition time constant is about 1.5% higher than for orientation (1). On the other hand, when the electrode is oriented so that the density gradient is in the same direction as the concentration gradient, (1), $i_0\tau^{1/2}/C^\circ$ is constant to ±2 parts per thousand (standard deviation) over transition times of 7 to 145 seconds. Even with a transition time of 303 seconds, $i_0\tau^{1/2}/C^\circ$ is only 0.6% higher than the average of the results at shorter transition times.

The effects of natural convection and nonlinearity of diffusion appear to be primarily responsible for variation of $i_0\tau^{1/2}/C^\circ$ at long transition times. The role of variable forced convection (vibrations, etc.) when these factors are controlled is small. Trials during which the thermostat stirrer was operat-

ing gave transition times that differed but slightly from those in which the cell was maintained as vibration free as possible.

Short Transition Times. The effect of charging of the electrical double layer (4, 7) and of oxidation of the electrode itself (1) on chronopotentiometry has been described. A possible (albeit approximate) method of treating the effect of double layer charging and electrode oxidation is to consider that the total current density, i_o, is composed of three constant currents, i_e, the current due to the electrochemical reaction, i_c, the current which contributes to the charging of the double layer, and i_{ox}, the current contributing to the oxidation of the electrode. Since $Q_c = (C_1)_{av}$. $\Delta E = i_c\tau$ [where $(C_1)_{av}$. is the average double layer capacity in the voltage interval ΔE] and $Q_{ox} = i_{ox}\tau$, then:

$$i_o = \frac{nFD^{1/2}\pi^{1/2}C^\circ}{2\tau^{1/2}} + \frac{(C_1)_{av.}}{\tau}\Delta E + \frac{Q_{ox}}{\tau}$$

(4)

$$\frac{i_o\tau^{1/2}}{C^\circ} = \frac{nFD^{1/2}\pi^{1/2}}{2} + \frac{(C_1)_{av.}}{C^\circ\tau^{1/2}}\Delta E + \frac{Q_{ox}}{C^\circ\tau^{1/2}}$$

(5)

Equation 5 indicates that as the transition time decreases, $i_o\tau^{1/2}/C^\circ$ increases, due to charging of the double layer and oxidation of the electrode. The transition time constant also increases with decreasing concentration, C°, as seen in Figures 2 and 3. Equation 5 is very approximate, since it assumes that the charging of the double layer takes place constantly during the electrolysis, whereas it actually occurs to its largest extent near the transition time, where the rate of change of potential is greatest. That this equation tends to overcorrect for electrode capacity effects can be seen by deriving a similar

equation assuming that the total current contributes to the charging of the double layer for a time τ_c, at the transition. This derivation yields a correction term of the same form as that in Equation 5, but only about one half as large.

Calculation of $(C_1)_{av.}$ for the various reactions, by plotting $i_o\tau^{1/2}/C^\circ$ vs. $1/\tau^{1/2}$, assuming Equation 5 to hold, yielded apparent double layer capacities which were 2 to 5 times greater than those usually given for platinum electrodes [in the order of 20 to 30 μf. per sq. cm. (17)]. Since Equation 5 should yield values of $(C_1)_{av.}$ which are too small, it appears that another effect (other than electrode oxidation, which was important only for the oxidation of hydroquinone) tends to cause an increase of $i_o\tau^{1/2}/C^\circ$ at short transition times.

Gerischer and Delahay pointed out (5) that the roughness of a solid electrode might play a role in chronopotentiometric measurements. The roughness will not be significant when the electrolysis duration is so long that the diffusion layer thickness is much larger than the depth of electrode crevices. At short transition times (less than about 1 second), the amount of reaction occurring in the crevices, and diffusion in the crevices, becomes significant, and the "effective area" of the electrode appears larger, causing an increase in $i_o\tau^{1/2}/C^\circ$.

CONCLUSIONS

The solid electrode which is most applicable to chronopotentiometry is a disk sealed in glass tubing, and mounted horizontally, with diffusion taking place either upwards or downwards depending upon the relative densities of the products and reactants. If the rate of elec-

trolysis is being governed by the rate of mass transfer to the electrode, which takes place solely by linear diffusion at this electrode, $i_o\tau^{1/2}/C^\circ$ should be constant over a fairly wide transition time range—e.g., 10 to 60 seconds. This is especially important in the analysis of multicomponent mixtures, where components giving rise to later transitions will be more affected by nonlinearity of diffusion and convection. Furthermore, meaningful diffusion coefficients and transition time constants can only be calculated under these conditions.

The optimum range of transition times for analytical application is 10 to 60 (or more) seconds. The interference of electrode double layer capacitance, oxidation, and roughness takes place at short transition times, and measurements in this region are, in general, less accurate and more difficult to make. The use of long transition times also enables measurement of smaller concentrations of electroactive substances. The ratio of Q_c to Q_e, the electricity consumed in the electrochemical reaction, is (4):

$$\frac{Q_c}{Q_e} = \frac{(C_1)_{\text{av.}} \cdot \Delta E}{i_e\tau} = \frac{2(C_1)_{\text{av.}} \cdot \Delta E}{\pi^{1/2}nFD^{1/2}C^\circ\tau^{1/2}}$$

Assuming $(C_1)_{\text{av.}}$ is 20 μf. per sq. cm. and ΔE is 0.1 volt, for Q_c to be smaller than 1% of Q_e, $C^\circ > 2.34 \times 10^{-6}/nD^{1/2}\tau^{1/2}$ moles per liter, so that, for a given electrode reaction, the longer the transition time employed (the smaller the current density), the

lower the concentration that can be determined. For a one-electron reaction, with D of 1.0×10^{-5} sq. cm. per second and a transition time of 100 seconds, the minimum concentration that can be measured is $7.4 \times 10^{-5}M$. Using present techniques, it is unlikely that concentrations much below $10^{-5}M$ can be determined chronopotentiometrically (6).

Although this study was primarily concerned with solid electrodes, some of the results should be applicable to mercury electrodes as well. In general, mercury pool electrodes will be useful at shorter transition times, since $(C_1)_{\text{av.}}$ is generally smaller, and oxide film formation and roughness factors are absent. A mercury pool is usually shielded by the walls extending above it, so that diffusion is usually linear. However since diffusion always takes place in a downward direction to a mercury pool, interference from natural convection will occur for many electrode reactions. Under these conditions short transition times would be most desirable.

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Coulometric Generation and Back-Titration of Intermediate Reagents at Controlled Potential

Application to the Determination of Plutonium

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▶ Coulometric reagents for secondary processes may be electrolytically generated and back-titrated at controlled electrode potential rather than controlled electrolysis current. Some of the advantages of this technique and the factors to be considered are mentioned, and the technique is illustrated by application to the indirect determination of plutonium(VI) with iron(II).

THE development in recent years of completely electronic instruments (1, 5) has aroused interest in controlled-potential coulometric titrimetry as a practical and routine method of analysis.

These instruments are simple to operate, require minimum operator attention, eliminate the need for chemical or mechanical coulometers, and yet exhibit a very high degree of precision and accuracy. With instruments such as these, intermediate reagents for secondary coulometric titrations can be conveniently generated at controlled electrode potential rather than at controlled electrolysis current.

A number of advantages are to be gained by this technique in addition to those already known for controlled-potential and controlled-current coulometric titrimetry. Some degree of selectivity is available when this technique is used and, in fact, the successive generation of different intermediates becomes practical. Perhaps more important is the fact that an intermediate reagent can be prepared in excess and, if its couple is reversible, the excess back-titrated electrolytically; this technique is particularly useful for slow reactions or for reactions that must be driven to completion. No indicator electrode system is required, because the magnitude of the electrolysis current itself indicates the degree of completion of the electrolysis. The effect of interfering substances can sometimes be eliminated by this technique. The application of the controlled-potential