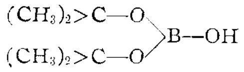
from 120° to one approaching the 108° of a regular pentagon. This provides a driving force for the addition of hydroperoxide ion leading to an intermediate analogous to I with tetrahedral boron.[16]



VI

Thus the concentration of this type of intermediate would be increased, resulting in a greater rate of reaction if the rate of the subsequent slow step is comparable to that involving I.

A systematic investigation of the effects of various chelating agents on the rate of the reaction is now in progress.

Acknowledgment.—It is a pleasure to acknowledge substantial support of this work by the Office of Naval Research under contract Nonr 806(01).

DURHAM, NEW HAMPSHIRE

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(16) *Cf.* N. Vermaas, *Rec. trav. chim.*, **51**, 67 (1932). A limitation in this postulate is implicit in the data and discussion of Vermaas in the fact that some mono-1,2-diol borates (*e.g.*, that from pinacol, VI) are not strong acids, *i.e.*, the boron in these esters does not show a great tendency to assume the tetrahedral configuration.

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

Theory of Electrolysis at Constant Current in Unstirred Solution. III. Experimental Study of Potential–Time Curves

BY PAUL DELAHAY AND CALVIN C. MATTAX

RECEIVED JUNE 29, 1953

Experimental methods for the precise recording of potential–time curves are described and applied to various electrode processes. The theoretical treatment of reversible electrode processes is verified in the cases of the reduction of ferricyanide, thallous and cadmium ions. The properties of potential–time curves obtained by reversing the current at the transition time are also in good agreement with theory. The features of experimental potential–time curves for the irreversible reduction of oxygen, nickel(II) and cobalt(II) in various electrolytes also agree well with theory. The analysis of potential–time curves for the reduction of chromate ion in 1 molar sodium hydroxide indicates the occurrence of a stepwise process. Potentialities of the constant current method in the study of electrode processes are discussed, and the possible application to analytical determinations is mentioned. Experimental data determined by the present method are used in the verification of the theory of irreversible polarographic waves previously developed.

Theoretical treatments of potential–time curves were developed in two previous publications.[1,2] It is the purpose of the present paper[3] to determine experimentally the validity of some of the conclusions previously reported. A detailed description of a convenient apparatus for the precise recording of potential–time curves also will be given.

Experimental

Electrolytic Cell.—Electrolytic cells were designed to reproduce as well as possible the conditions of semi-infinite linear diffusion at the polarizable electrode. Solid electrodes (platinum) and mercury pool electrodes were used. The cells designed for the latter type of electrode will be first described. A mercury pool electrode was used previously,[1,2] but various modifications in design were introduced, and the two types of cell represented in Fig. 1 finally were adopted.

The cells were composed of three electrodes: the mercury pool, the auxiliary platinum electrode and the reference electrode. The first two electrodes were connected to the constant current power supply, and the voltage between the mercury pool and the reference electrode was recorded. The mercury pool was renewed before each recording. In the case of cell A, one arm of the three-way stopcock was connected to a mercury reservoir of 200 ml. A constant level was thus obtained. The stopcock was closed to avoid contamination of the mercury in the reservoir. A mercury pool of reproducible area was obtained in cell B by introducing a known volume of mercury in the cell. The diameter of the mercury pool in cell A was 1.4 cm., but even larger diameters are advisable in order to minimize the effect of the mercury meniscus. The area of the mercury pool varies with potential, because the interfacial tension mercury-solution—and consequently the curvature of the meniscus—depend on the potential of the mercury pool. The movement of the surface of the pool causes a slight stirring of the solution, and a departure from conditions of mass transfer under the sole influence of diffusion. In cell B the diameter of the mercury pool was approximately 2.5 cm.

A commercial saturated calomel electrode (Beckman industrial model) was used. To avoid errors resulting from the ohmic drop in the solution the reference electrode was immersed in a sleeve whose tip (outside diameter 1 mm.) was very close (0.5 mm. or less) to the surface of the mercury pool. Since the value of the potential of the auxiliary platinum electrode was unimportant, both compartments of the cell were filled with the solution being electrolyzed. Diffusion from one compartment to the other was practically prevented by a disk of fritted glass as in H cells used in polarography. No plug of agar agar as customarily used in polarography was needed.

Cell A is somewhat more convenient to use than cell B because of the ease of renewing the mercury pool and the simplicity of design. This cell thus can be recommended for exploratory work or for analytical determinations. It has, however, the disadvantage of not providing for a uniform distribution of current density (asymmetric position of the auxiliary electrode with respect to the mercury pool). This disadvantage is eliminated in cell B of Fig. 1. The results reported below were obtained with cell A, but it was verified that the operation of cell B is entirely satisfactory.

The platinum electrode used in the reduction of ferricyanide was constructed by sealing a platinum disk (approximately 0.8 cm.^{2}) in a glass sleeve in the form of a U-tube. The platinum disk was horizontal, and the lid of the sleeve extended approximately 0.5 cm. above the disk.[4]

The temperature of the electrolyzed solution was 30 ± 2°.

Recorder and Related Equipment.—The electrolytic cell in series with resistance R_1 (Fig. 2) was connected to a commercial power supply with electronic regulation of the output voltage (200–300 v.).[5] The current intensity was determined from the ohmic drop in a calibrated resistance R_2, the

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(1) P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

(2) T. Berzins and P. Delahay, *ibid.*, **75**, 4205 (1953).

(3) For a brief survey of literature see ref. 1 and 2.

(4) H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

(5) Even better regulation of the current could be obtained by using automatic regulation of the current as in coulometric titrations. See, for example, D. D. De Ford, C. J. Johns and J. N. Pitts, *Anal. Chem.*, **23**, 941 (1951); C. N. Reilley, R. H. Adams and N. H. Furman, *ibid.*, **24**, 1044 (1952).

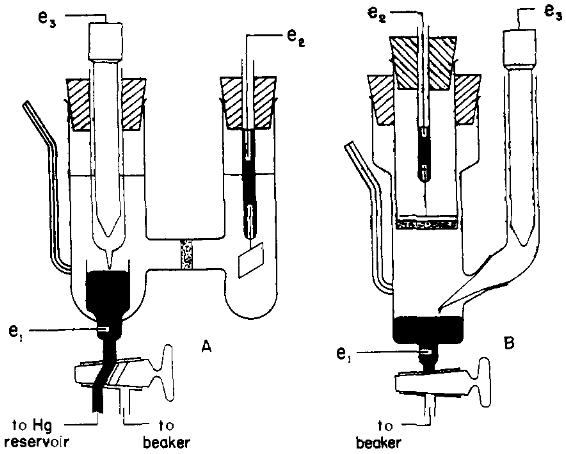

Fig. 1.—Cells for electrolysis at constant current.

cell being short-circuited by means of switch S_4 (to avoid progressive polarization and a drift in reading). The current intensity measured in this manner was slightly too high since there was no counter e.m.f. of the cell. The corresponding relative error is of the order of 0.3% (total applied voltage 300 v., counter e.m.f. of 1 v.). A manually operated quadruple pole double throw relay was inserted in the cell to reverse the current through the cell at some stage of the electrolysis (the time elapsed during the reversal of current is smaller for a relay than for a toggle switch). At the time of the current reversal, resistance R_5 was automatically introduced in the circuit by relay RL 1, and the current thus could be decreased during electrolysis with reversed current. This is advantageous because the transition time for the reversed process is only one-third of the transition time for the direct process when the current density is the same in both processes.[2] When the current density during the reversed process is decreased the transition time increases and more precise results are obtained.

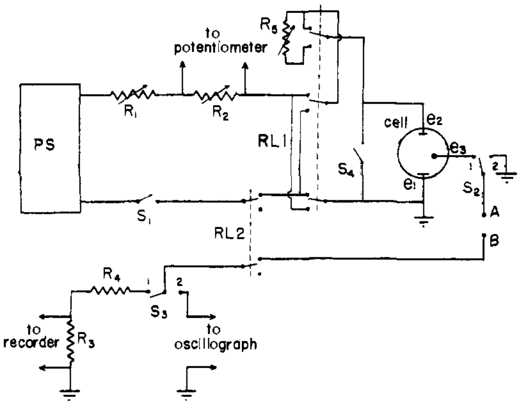

Fig. 2.—Schematic diagram of circuit for the recording of potential-time curves: R_1, R_5, resistance from 10.000 ohms to 10 megohms in decade steps; other data in text.

The voltage between the mercury pool (grounded) and the reference electrode was applied to a Brown recorder having a pen speed of 1 second for full scale deflection, a chart speed of 480 inches per hour, and a sensitivity corresponding to full scale deflection for a 2.5 millivolt input voltage. A compensating voltage was applied to the input of the recorder for the following reason. In the initial step of a potential-time curve there was generally a rapid and large (several tenths of a volt) variation of the potential of the mercury pool electrode. Only low sensitivities could thus be used and potentials were inaccurate. This was avoided by compensating almost completely the change of voltage corresponding to the initial segment of the potential-time curve. The compensating voltage, supplied by a student potentiometer (switch S_2 in position 1), was applied between points A and B. The input of the recorder was disconnected from point B (relay RL 2) before the electrolysis was started. In this manner the pen of the recorder was not swung violently against the zero point of its course before recording. The electrolysis was started by closing relay RL 2, the motor driving the chart of the recorder being always started a few seconds before the closing of relay RL 2 to avoid missing the initial segment of the potential-time curve.

The recorder scale was calibrated by turning switch S_2 in position 2, and applying a known voltage (potentiometer to AB) to the recorder. The sensitivity of the recorder was adjusted by means of resistance R_3. The resistance of the circuit connected to the cell e_1e_3 was approximately 1 megohm (R_4 = 1 megohm) and the current drawn from the cell e_1e_3 was approximately 0.2-1 microampere. This current was negligible in comparison with the current through e_1e_2 (100 microamperes or more). A preamplifier was not used, to avoid making the potential readings dependent on the gain of this instrument.[6] In analytical applications of the method one is interested primarily in measuring the transition time, and the use of a preamplifier (direct-reading *p*H meter for example) is recommended.[7]

Potential-time curves also could be observed on the screen of a du Mont 304 H cathode ray oscillograph (switch S_3 in position 2). The signal actuating the driven sweep of the oscillograph was taken from the positive terminal of the coil of relay RL 2, the negative terminal of the coil being grounded (not shown in Fig. 2).

Solutions were freed from dissolved oxygen before electrolysis by bubbling nitrogen according to conventional polarographic practice. No maximum suppressor as used in polarography was needed.

Description and Discussion of Results

Potential-Time Curves for Reversible Processes.—The tracing of a potential-time curve for the reduction of cadmium ion on mercury and for the corresponding reoxidation process is shown in Fig. 3. Reversible cathodic potential-time curves such as the one of Fig. 3 obey the following equation when the reaction product is soluble, either in the electrode (mercury) or the solution[1]

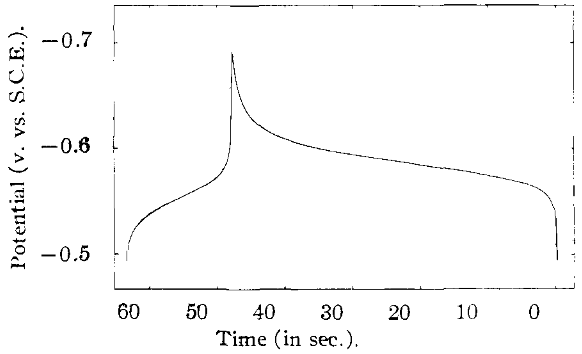

Fig. 3.—Potential-time curves for the reduction of 4 m*M* Cd^{++} and the subsequent anodic oxidation of cadmium amalgam; 1 *M* potassium nitrate.

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \qquad (1)$$

where E is the potential of the electrode, τ the transition time, t the time elapsed since the beginning of electrolysis, and $E_{1/2}$ is defined by

$$E_{1/2} = E^0 + \frac{RT}{nF} \ln \frac{f_O D_R^{1/2}}{f_R D_O^{1/2}} \qquad (2)$$

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[6] However, recorders with input current as low as 10^{-18} amp. and in which the feature of continuous balance is preserved are commercially available.

[7] Dr. C. N. Reilley of the University of North Carolina has used a preamplifier in analytical applications of this method (private communication).

where E^0 is the standard potential for the electrode process being considered, the f's are activity coefficients, and the D's diffusion coefficients. According to equation 1 a plot of log $[(\tau^{1/2} - t^{1/2})/t^{1/2}]$ against E should yield a straight line of reciprocal slope $2.3RT/nF$. Such plots for a few electrode reactions are shown in Fig. 4. The experimental reciprocal slopes of 0.061 for thallium and 0.032 for cadmium are in good agreement with the theoretical values of 0.060 and 0.030, respectively. The slope 0.068 for ferricyanide is somewhat higher than the expected value 0.060, possibly because of the use of an unbuffered supporting electrolyte. Experimental reciprocal slopes even for results obtained with the mercury pool are slightly higher than the theoretical values at least for three reasons: (1) distortion of the E–t curve by the recorder; (2) interference of convection with diffusion at the electrode; (3) uncertainty in the determination of the transition time from the E–t curve.

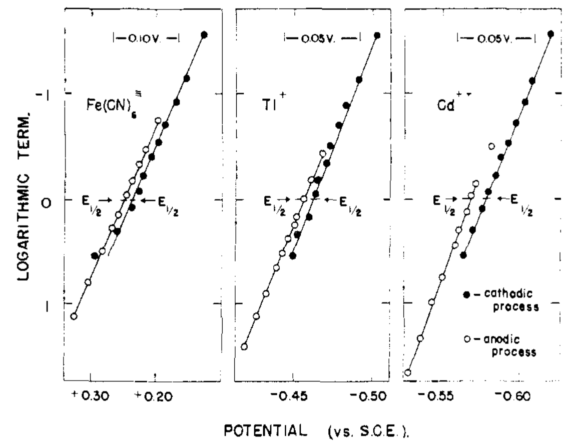

Fig. 4.—Logarithmic plot for reversible electrode processes: 4 mM reducible substance; 1 M potassium nitrate for Tl^+ and Cd^{++}, 1 M potassium chloride for ferricyanide.

The equation of the potential–time for the reoxidation process is[2]

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - [(\tau + t')^{1/2} - 2t'^{1/2}]}{(\tau + t')^{1/2} - 2t'^{1/2}} \quad (3)$$

where the notations are the same as in equations 1 and 2 and where t' is the time elapsed since the transition time τ. According to 3 the logarithmic term varies linearly with potential, and the reciprocal slope of the resulting line is $2.3RT/nF$ (decimal logarithm). This slope is the same as for the logarithmic plot for the cathodic process. The validity of this conclusion is apparent from the diagram of Fig. 4.

According to equations 1 and 3 the potentials $E_{1/2}$ are the same for the cathodic and anodic curves. The potential $E_{1/2}$ corresponds to $t = \tau/4$ for the cathodic curve[1] and to $t' = 0.222(\tau/3)$ for the anodic curve.[2] Finally $E_{1/2}$ from 2 is the same as the corresponding polarographic half-wave potential.[1] Experimentally it was found that there is a difference of the order of 10 millivolts between the cathodic and anodic values of $E_{1/2}$ (Table I). This could be caused by a slight degree of irreversibility of the electrode processes, but it is more likely that differences between the cathodic and anodic values of $E_{1/2}$ result from the ohmic drop in solution between the tip of the sleeve of the reference electrode (Fig. 1) and the polarized electrode. With current intensities of the order of 100 microamp. the ohmic drop between two points at a distance of 1 mm. or so in a 1 molar electrolyte (potassium nitrate or chloride) is a few millivolts, the cross section area of the cell being of the order of 1–2 cm.^{2}. Since the current was reversed during reoxidation, the difference between cathodic and anodic values of $E_{1/2}$ is the double of the ohmic drop. The average of the two values of $E_{1/2}$ would be correct experimental value of $E_{1/2}$ if it were not for the ohmic drop in the circuit e_1e_3 as resulting from the current consumption by the input element of the recorder. The corresponding correction and corrected values of $E_{1/2}$ are listed in Table I together with polarographic half-wave potentials.[8] The agreement is good if one takes into account: (1) the usual error of approximately ±0.005 v. for polarographic half-wave potentials; (2) possible minor errors on the values of $E_{1/2}$ as determined by the constant current method; (3) the difference between the temperatures at which our $E_{1/2}$ values (30 ± 2°) and the polarographic half-wave potentials were determined (25°).

TABLE I

POTENTIALS $E_{1/2}$ (IN VOLTS *vs.* S.C.E.)

	Cathodic	Anodic	Correction	Corrected	Polarographic (25°)
Cd^{++}	−0.578	−0.569	−0.006	−0.580	−0.586[a]
Tl^+	− .463	− .455	− .004	− .463	− .475[b]
$Fe(CN)_6^{---}$	.240	.252	.007	.253	.24[c]

[a] See ref. 8, 1st edition, p. 482. [b] See ref. 8, p. 520. [c] Approximate value of standard potential.

Potential–Time Curves for Irreversible Electrode Processes.—The tracing of a potential–time curve for the reduction of nickel(II) is shown in Fig. 5. As previously shown[1] the potential should vary abruptly at time $t = 0$ (neglecting the charging of the double layer) for a totally irreversible electrode process which involves only one rate-

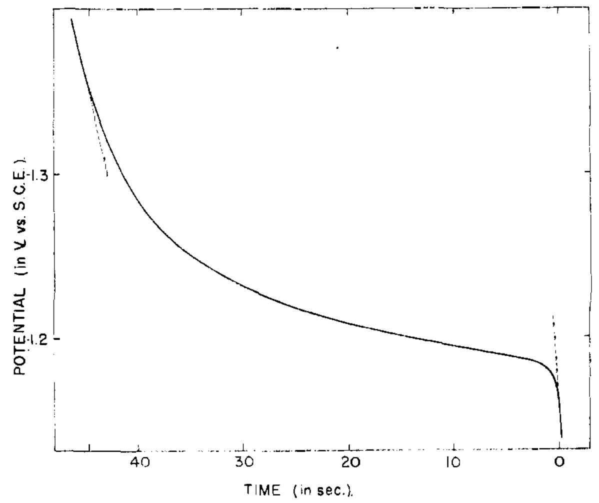

Fig. 5.—Potential–time curves for the irreversible reduction of Ni(II) in 1 M potassium chloride.

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(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

determining step. This is virtually the case in Fig. 5 and for the other electrode processes studied here (see below).[9]

A plot of log $\{1 - (t/\tau)^{1/2}\}$ against E should yield a straight line whose reciprocal slope is $(2.3\ RT)/\alpha n_a F$, α being the transfer coefficient for the cathodic process and n_a the number of electrons involved in the rate-determining step.[1] Such diagrams are shown in Fig. 6 for various irreversible processes. Values of αn_a deduced from Fig. 6 were: 0.49 for oxygen in acetate buffer, 0.59 for oxygen in sodium hydroxide, 1.33 for nickel in potassium thiocyanate, 0.70 for nickel in potassium chloride and 0.82 for cobalt. Values of E for $t = 0$ were determined from Fig. 6 and corrections were made as for the potentials $E_{1/2}$ above, taking 0.005 v. as the ohmic drop between mercury and the tip of the sleeve of the reference electrode. The formal rate constant $k_{f,h}$ at $E_{t=0}$ was calculated by applying the previously[1] derived equation

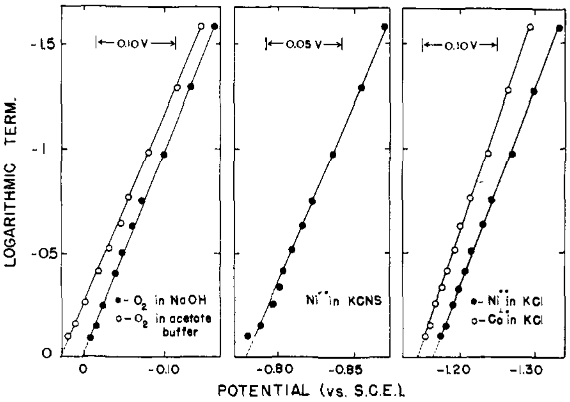

Fig. 6.—Plots of log $\{1 - (t/\tau)^{1/2}\}$ *vs.* potential for totally irreversible electrode processes; 4 mM reducible substance; 1 M potassium chloride for Ni(II) and Co(II); 0.5 M potassium thiocyanate for Ni(II); acetate buffer (1 M in acetate and acetic acid) and 1 M sodium hydroxide for oxygen.

$$E_{t=0} = \frac{RT}{\alpha n_a F} \ln \frac{nFk_{f,h}C^0}{i^0} \qquad (4)$$

where C^0 is the bulk concentration of reducible substance in moles cm.$^{-3}$, and i^0 is the current *density*. The rate constant $k^0_{f,h}$ at the potential $E = 0$ in the normal hydrogen electrode scale was finally computed from

$$k_{f,h} = k^0_{f,h} \exp(-\alpha n_a FE/RT) \qquad (5)$$

Values of log $k^0_{f,h}$ as deduced from the data of Fig. 6 were as follows: −13.41 for nickel in thiocyanate, −12.53 for nickel in potassium chloride, and −13.69 for cobalt. The value of $k^0_{f,h}$ for the reduction of oxygen was not calculated because the concentration C^0 of this substance was not determined. These data are used below.

Summarizing, one can determine by the present method the parameters αn_a and $k^0_{f,h}$ which characterize the kinetics of a totally irreversible electrode process involving one step.

Example of Process Involving Kinetic Complications.—Chromate ion in 1 molar sodium hydroxide is reduced in at least two steps.[10] Such kinetic complications may sometimes be detected by anomalous shape of the log $\{1 - (t/\tau)^{1/2}\}$ *vs.* E diagram as shown in Fig. 7: a marked departure from linearity is observed. Oscillographic recordings of potential–time curves confirmed the occurrence of a stepwise reduction (Fig. 8).[11]

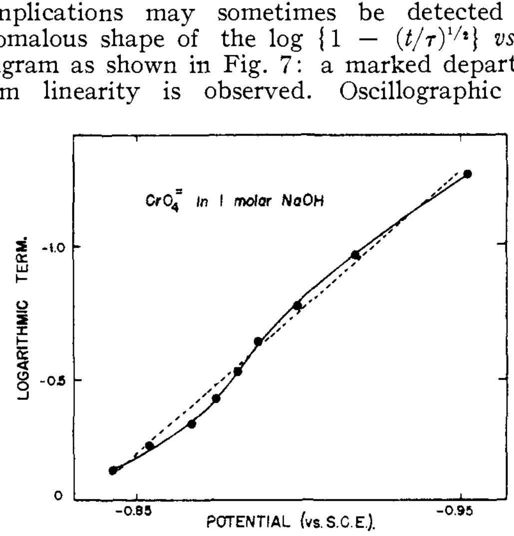

Fig. 7.—Plot of log $\{1 - (t/\tau)^{1/2}\}$ *vs.* potential for the reduction of chromate ion in 1 M sodium hydroxide.

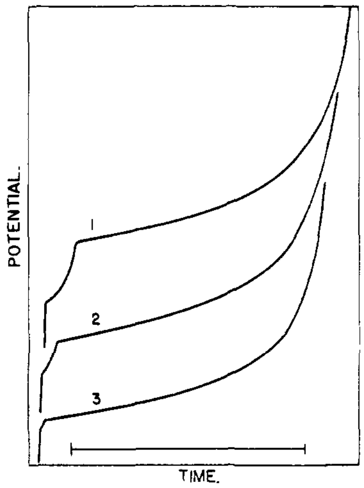

Fig. 8.—Potential–time curves for the reduction of chromate ion in 1 M sodium hydroxide, duration corresponding to the unit of time: 0.020 sec. (curve 1), 0.090 sec. (curve 2), 0.74 sec. (curve 3).

When the transition time was larger than 1 sec. an apparently normal potential–time curve was observed except for a very small distortion at the foot of the curve (curve 3). As the transition time was shortened two steps were observed (curves 1 and 2). No conclusion can be drawn from the relative values of the transition times because of kinetic complications, but it is probable that chromium(IV) is formed as intermediate. Chemi-

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[9] A perfectly sharp angle nevertheless was not observed even when potential–time curves were recorded by means of a cathode ray oscillograph. This discrepancy probably results from some kinetic complications which are not taken into account in the present treatment. The effect appears minor in the cases studied here.

[10] T. Berzins and P. Delahay, THIS JOURNAL, **75**, 5716 (1953).

[11] Experimental results obtained by Mr. G. Mamantov.

cal evidence for the formation of chromium(IV) has been advanced by Westheimer.[12]

Verification of the Theoretical Treatment of Irreversible Polarographic Waves

The experimentally determined values of αn_a and $k^0_{f,h}$ reported above can be used in a test of the theoretical treatment of irreversible polarographic waves developed by various authors.[13–14] The half-wave potential for irreversible waves, whose characteristics are determined by a single rate-determining step, is[13d]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k^0_{f,h}}{\lambda D_O{}^{1/2}} \qquad (6)$$

where $E_{1/2}$ is referred to the normal hydrogen electrode, λ is a quantity which varies with drop time, D_O is the diffusion coefficient of the substance being reduced, and the other notations are those of equation 5. For usual drop times from 2 to 4 sec., λ is such that $\log \lambda$ is comprised between -0.33 and -0.47. Values of $E_{1/2}$ obtained from equation 6 and for a drop time of 4 sec. were as follows (*vs.* S.C.E.): 0.75 v. for nickel(II) in 0.5 *M* potassium thiocyanate, -1.14 v. for nickel(II) in 1 *M* potassium chloride, and -1.09 v. for cobalt(II) in 1 *M* potassium chloride. The corresponding experimental values as reported in the literature are: -0.70,[15] -1.1 and -1.2 v.,[16] respectively. The agreement is good since there are two causes of discrepancy. (1) Polarographic half-wave potentials were measured in presence of some maximum suppressor such as gelatin, whereas the calculated $E_{1/2}$ values were determined from data obtained without maximum suppressor. This is important because the product αn_a varies when traces of substances such as gelatin are added to the solution.[13c] (2) The treatment of irreversible polarographic waves developed so far is only approximate because the equation of the wave was derived by *adapting* to the case of the dropping mercury electrode the solution of the corresponding boundary value problem for semi-infinite linear diffusion.

It should be added that data obtained from the constant current method were interpreted by assuming that the electrode process involves only one rate-determining step without kinetic complications. The same hypothesis was made in the derivation of equation 6. Hence the good agreement between calculated and experimental half-wave potentials does not imply that this hypothesis is correct. However, a relatively conclusive proof of the validity of this hypothesis is to be found in the fact that the logarithmic diagrams of Fig. 6 are linear as predicted by theory.

Application to Analytical Chemistry

This investigation dealt mainly with the experimental verification of theoretical results previously reported, but it is useful to attempt to assess the potentialities of the constant current method as an analytical tool. The square root of the transition time is proportional to the concentration of reducible—or oxidizable—substance as shown by the equation (semi-infinite linear diffusion)

$$\tau^{1/2} = \frac{\pi^{1/2} n F D_O{}^{1/2} C^0}{2 i^0} \qquad (7)$$

which was first derived by Sand.[17] Since D_O can be kept constant in a series of comparative runs, the precision on $\tau^{1/2}$ is primarily determined by three factors: (1) the degree to which convective transfer interferes with the diffusion process; (2) the precision with which τ can be determined experimentally; (3) the precision on the current *density*. No definitive information is available on these various factors, but a few comments can be made. Firstly, it is probable that there is no serious interference by convection as long as the transition time does not exceed 1–2 minutes. The experimental results reported in this paper support indirectly this view. If proper precautions were taken to avoid vibrations of the cell, much longer transition times could probably be measured accurately. Secondly, transition times can probably be measured with a relative error of the order of a few tenths of a per cent. although the precision might not always be as good because of distortion of potential–time curves. The current *density* need not be known exactly in comparative measurements, but it should be constant. Since currents can easily be measured with a relative error of ±0.1%, the main source of error is the variation of the area of the electrode from one measurement to another. Our limited experience with mercury pool electrodes is that transition times are reproducible within ±2% but undoubtedly this error could be decreased. In conclusion the constant current method might be a useful new tool in analytical chemistry.

Acknowledgment.—It is a pleasure to acknowledge the support of Research Corporation in the course of this investigation.

BATON ROUGE, LOUISIANA

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(12) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

(13) (a) P. Delahay, THIS JOURNAL, **73**, 4944 (1951); (b) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); (c) J. E. Strassner and P. Delahay, *ibid.*, **74**, 6232 (1952); (d) P. Delahay, *ibid.*, **75**, 1430 (1953).

(14) M. G. Evans and N. S. Hush, *J. chim. phys.*, **49**, C 159 (1952).

(15) For 1 molar potassium thiocyanate.

(16) For 0.1 molar potassium chloride.

(17) H. J. S. Sand, *Phil. Mag.*, 1, 45 (1901).