From an examination of the work of Hardwick and Robertson,[17] we feel safe in assuming that, in all solutions we have used, the major species of cerium(IV) is the trissulfatocerate(IV) ion, $Ce(SO_4)_3^{=}$. Although, at present, equilibrium constants cannot be determined, a critical examination of the data of Denham and King[18] indicates that no higher tin(II) complexes than $SnSO_4$ are found in sulfuric acid solutions. Then we assume that the major (and reacting) species of tin(II) is the ion-pair (or complex), $SnSO_4$, thus the rate of the reaction may be moderately slow, compared to a reaction involving Sn^{++} and $Ce(So_4)_3^{=}$. If these are indeed the reacting species, it is not unreasonable to expect the rate to be independent of ionic strength,[16] although predictions at these high ionic strengths are not strictly justified.

The following mechanism is consistent with the "normal" second-order reaction which occurs at moderate sulfate ion concentrations

$$SnSO_4 + Ce(SO_4)_3^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{tin intermediate} \quad (1)$$

$$\text{tin intermediate} + Ce(SO_4)_3^{=} \xrightarrow{k_2} SnSO_4^{++} + 2Ce(SO_4)_2^{-} \quad (2)$$

If the first of these reactions is the rate-determining step and the steady-state approximation is made for the tin intermediate, and if k_{-1} is small, then the rate expression is obtained

$$\frac{-d[Ce(SO_4)_3^{=}]}{dt} = 2k_1[SnSO_4][Ce(CO_4)_3^{=}] \quad (3)$$

which is in agreement with the experimentally observed rate law.

The products shown for equation 2 are based on information available in the literature,[19,20] but there are no data which clearly establish the nature of the products of reaction 1. Equally probable are products such as $SnSO_4^{+} + Ce(SO_4)_2^{-} + SO_4^{=}$ or a tin–cerium complex [*e.g.*, $SnCe(SO_4)_x^{6-2x}$]. As we have indicated in the introduction, we are not without precedent in postulating tin(III) as an intermediate.

We have obtained no experimental evidence concerning the nature or properties of the intermediate, aside from its reactivity. Visible and ultraviolet spectrophotometry give no evidence of an intermediate interaction complex [$SnCe(SO_4)_x^{6-2x}$] or a tin(III) species. That adding excess cerium(III) produces a negligible effect on the rate may mean that no sulfatocerate(III) is formed in reaction 1 or simply that k_{-1} is very small.

We cannot postulate a mechanism for the "accelerated" second-order reactions from the information found in the experimental data and can only point out that the observed second-order rate is suggestive of stepwise oxidation of tin(II).

Likewise the only statement that can be made concerning the first-order reactions is that the experimental evidence seems to indicate that the rate-determining step must be the adsorption of the tin(II) on some internally formed, colloidal, tin(IV) species.

Conclusions

It then appears that, in the absence of tin(IV) colloids, the oxidation of tin(II) by cerium(IV) in 1–3*M* sulfuric acid solutions proceeds along a two step path. The experimental evidence is compatible with the possibility that tin(III) exists as an intermediate; however, the data do not exclude alternatives such as tin–cerium sulfate complexes (*e.g.*, the $SnCe(SO_4)_x^{6-2x}$, which we have discussed). Of course, such a tin–cerium intermediate may contain either tin(III) and cerium(III) or tin(II) and cerium(IV).

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EAST LANSING, MICHIGAN

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[17] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818, 828 (1951).

[18] H. G. Denham and W. E. King, *J. Chem. Soc.*, 1251 (1935).

[19] F. H. Spedding and S. Jaffe, THIS JOURNAL, **76**, 884 (1954).

[20] C. H. Brubaker, Jr., *ibid.*, **77**, 2671 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Measurement of Diffusion Currents at Cylindrical Electrodes Using a Current Integrator

BY GLENN L. BOOMAN, EVAN MORGAN AND A. L. CRITTENDEN

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The measurement of charge transferred during an increment of time shortly after the beginning of electrolysis has been found to provide an accurate method for studying diffusion currents at solid microelectrodes. By the use of short times of electrolysis, convection processes are avoided. Results obtained are in agreement with theory.

The use of solid electrodes for voltammetry at constant potential is often complicated by the contribution of convection processes to the mass transfer process. Mathematical treatments of diffusion currents at several shapes of stationary electrodes have been developed.[1] With plane or cylindrical electrodes, diffusion currents decrease with increasing time and no steady state should be observed. Limiting currents at cylindrical electrodes were observed by Laitinen and Kolthoff,[2] but convection apparently was involved. If convective processes are to be avoided, currents must be measured as functions of time at short times after the start of electrolysis. Such measurements

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[1] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chap. 3.

[2] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).

usually require the use of an oscillograph, the accuracy of which is often not very satisfactory. In the work reported here, it has been found convenient to measure the total charge transferred during small increments of time after the beginning of electrolysis. The use of analog integrator circuits permits the charge measurement to be made with good accuracy and allows the value of the integral to be recorded by a relatively slow recording potentiometer after electrolysis is stopped. Repeated experiments at different applied potentials can be performed quickly by the use of a simple mechanical means for destroying the concentration gradient remaining from the preceding electrolysis. In this respect the method is similar to the behavior of dropping mercury electrodes. Curves obtained plotting charge *versus* applied potential appear similar to polarograms obtained with dropping electrodes.

A cylindrical wire electrode appears to be the most convenient form of solid microelectrode for voltammetry. Expressions for the diffusion current at cylindrical electrodes have been given by Rius and co-workers.[3] Using the notation of

$$i = nFAD_0C^\circ \frac{1}{r_0}\left[(\pi\phi)^{-1/2} + {}^1/_2 - {}^1/_4\left(\frac{\phi}{\pi}\right)^{1/2} + {}^1/_8\,\phi\ldots\right] \quad (1)$$

Delahay where i is the current at time t, D_0 is the diffusion coefficient, F is the faraday, C° is the concentration of the reducible or oxidizable species in the bulk of the solution, A is the area of the electrode of radius r_0, n is the number of electrons involved in the reaction, and ϕ is the dimensionless quantity $D_0t/r^2{}_0$. Equation 1 may be integrated to give the total charge transferred q

$$q\Big]_{t_1}^{t_2} = nFAC^\circ r_0\left[2\,\frac{\phi_2{}^{1/2} - \phi_1{}^{1/2}}{\sqrt{\pi}} + {}^1/_2(\phi_2 - \phi_1) - {}^1/_6\,\frac{\phi_2{}^{3/2} - \phi_1{}^{3/2}}{\sqrt{\pi}} + \frac{1}{16}\,(\phi_2{}^2 - \phi^2{}_1]\ldots\right] \quad (2)$$

where the subscripts 1 and 2 refer to the times after beginning of electrolysis when integration is begun and stopped.

Experimental

The current integrator circuit was of conventional design, stabilized by a chopper amplifier.[4] The platinum microelectrode was connected to the input of the d.c. amplifier in the integrator circuit and was kept at ground potential by the action of this amplifier and the integrating capacitor connected between the amplifier input and output. Since the input impedance of the integrator amplifier was high, essentially all cell current must appear as a change in potential across the integrating capacitor. This potential was applied to a Brown "Elektronik" recording potentiometer have a 4 sec. full-scale response, using suitable shunts to adjust the sensitivity. Calibration of the integrator circuit, recorder and shunts was accomplished by replacing the electrolysis cell with precision resistors and measuring the potential drop across the resistors. The ability of the integrator to follow large initial currents was checked by charging precision capacitors (0.1 to 10 mfd.) to known potentials. These were allowed to discharge into the integrator circuit. Results obtained were in agreement with those obtained using resistors. The accuracy of the integrator and potentiometer was better than ±0.5%.

The potential applied to the electrolysis cell was obtained with a potentiostat circuit. A potential source was adjusted to provide the desired potential at one input of a differential amplifier, to the other input of which a small calomel reference electrode was connected. Any potential difference between the reference electrode and the potential source was amplified and applied to a large working calomel electrode in such a way as to bring the potential of the reference electrode into agreement with the potential source.

Time information was obtained by counting preset numbers of 60 cycle line pulses using an array of binary scaler units and suitable gating circuits. At the beginning of electrolysis a relay is closed connecting the platinum microelectrode to the integrator and allowing current to flow. A second relay was connected across the terminals of the integrating capacitor. If integration was to be started at the beginning of electrolysis, this second relay was opened before electrolysis. Otherwise, it was opened after a fixed time to start integration. At the end of integration the first relay was opened. A few seconds were allowed for the recorder to record the potential across the integrating capacitor. During this time a second capacitor was discharged through a small solenoid mechanically linked to the microelectrode. This resulted in a single excursion of the microelectrode in the cell. The integrating capacitor was then shorted and the recorder returned to zero by closing the relay connected across the capacitor. A few seconds were allowed to permit the recorder to return to zero and to allow the solution in the cell to come to rest. A new integration could then be begun. A stepping relay was provided to change the potential of the potential source during the time provided for returning the recorder to zero. In this way curves of charge *versus* potential could be recorded in times comparable to those used for conventional recording polarographs. From occasional checks of line frequency, it was estimated that times were accurate to better than ±0.5%.

An "H" type electrolysis cell[5] was used. One compartment contained a saturated calomel working electrode. The other compartment contained the platinum microelectrode together with a salt bridge leading to a small saturated calomel reference electrode. The platinum electrode was made by sealing a length of wire into the end of a 6 mm. diameter glass tube about 25 cm. long. The wire was concentric with the tube and was used in a vertical position. The tube was inserted into the cell through a large serum stopple so that 5 cm. of its length extended above the stopple. The stopple provided a flexible, air-tight seal. The upper end of the glass tube was attached by a pivoted linkage to the armature of the solenoid. Energizing the solenoid pivoted the tube about the serum stopple so that a sharp translation of the platinum wire normal to its axis occurred. The distance travelled was 1.5 cm. The electrode used was 0.80 mm. in diameter and 5.5 mm. in length. The glass tube was immersed about 3 mm. in the electrolyte. The electrode wire was buffed to remove burrs and was cleaned periodically using chromic acid. The entire cell was immersed in a water-bath held at 25 ± 0.1°.

Solutions were prepared from Reagent Grade chemicals dissolved in water redistilled in a borosilicate still. When necessary, solutions were deaerated with nitrogen and nitrogen passed over the solutions during electrolysis. The reduction of ferricyanide ion and the oxidation of ferrocyanide ion were studied using solutions of the potassium salts in 0.25 M KCl. The reduction of hydrogen ion was studied using solutions of HCl in 0.25 M KCl. For the oxidation of iodide ion, solutions of KI in 0.25 M KNO_3 were used. The concentrations of the oxidizable or reducible ions were varied from 2.00 to 0.200 millimolar.

Results

Conditions at the Beginning of Electrolysis. In the treatment of the data below, it is assumed that no concentration gradient exists in the solution at the beginning of electrolysis, and that no stirring or convection effects are present. The validity of these assumptions is indicated by the observa-

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[3] A. Rius, S. Polo and J. Llopis, *Anales fis. y quim.* (*Madrid*), **45**, 1029 (1949). The solution to the analogous heat transfer problem is given by H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, pp. 280–282. The results are summarized by P. Delahay, ref. 1.

[4] G. A. Korn and T. M. Korn, "Electronic Analog Computers," McGraw-Hill Book Co., Inc., New York, N. Y., 1952.

[5] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

tion that repeated electrolyses in the same solution gave values of q which agreed within the accuracy of the recorder, provided that the time of electrolysis did not exceed about ten seconds. This was observed for several reactions at a variety of concentrations. If longer times were used, less agreement was found, presumably because of convection, although fairly satisfactory results were obtained at times somewhat longer than ten seconds. The cell was mounted on a rubber pad but no special precautions against vibration were found to be necessary. If, during an electrolysis, the electrode was disturbed, a change in q was observed, but the next electrolysis a few seconds later was always found to be in agreement with preceding data. Attempts to destroy the concentration gradient by the use of rotary stirrers, rotary motion of the electrode, or with slow motions of the electrode either failed to remove the gradient quickly or left the solution in motion so that stirring did not subside quickly. Using the relay arrangement described, satisfactory results were easily obtained and no critical adjustments were necessary. The same charge was measured whether only one, or several excursions of the electrode were used. The time necessary for stirring effects to disappear after the excursion was found to be less than three seconds. Also, the time required for the recorder to record the value of the integral and return to zero would prevent use of much shorter times.

Diffusion Currents.—Well-defined diffusion current regions where charge transferred was essentially independent of potential were found for the oxidation of ferrocyanide ion to ferricyanide, the oxidation of iodide ion to iodine, the reduction of hydrogen ion, and the reduction of ferricyanide ion to ferrocyanide. Diffusion charges were measured at potentials of +0.40, +0.70, −0.70 v. and 0.0 v., *versus* S.C.E., respectively. Diffusion charges were measured for each of the above reactions for a variety of concentrations and integrating from zero time to times from 0.100 to 6.40 sec. In all cases, q was found to be a linear function of concentration at constant integration time. Results obtained in the reduction of ferricyanide are given in Fig. 1. Residual charge was found to be generally less than 3 μcoulombs and varied somewhat with potential. Residual charge is believed to be largely attributable to the initial charging of the electrical double layer. All values of charge were corrected for this residual charge except for Fig. 1. Figure 2 shows the variation of diffusion charge with the parameter ϕ_2 for integrations starting from zero time for millimolar solutions. The dashed line represents the curve calculated from equation 2. Usually the first three terms were large enough to be included.[6] At small values of ϕ_2 the first term only, represented by the solid line, is adequate. Diffusion to the end of the electrode

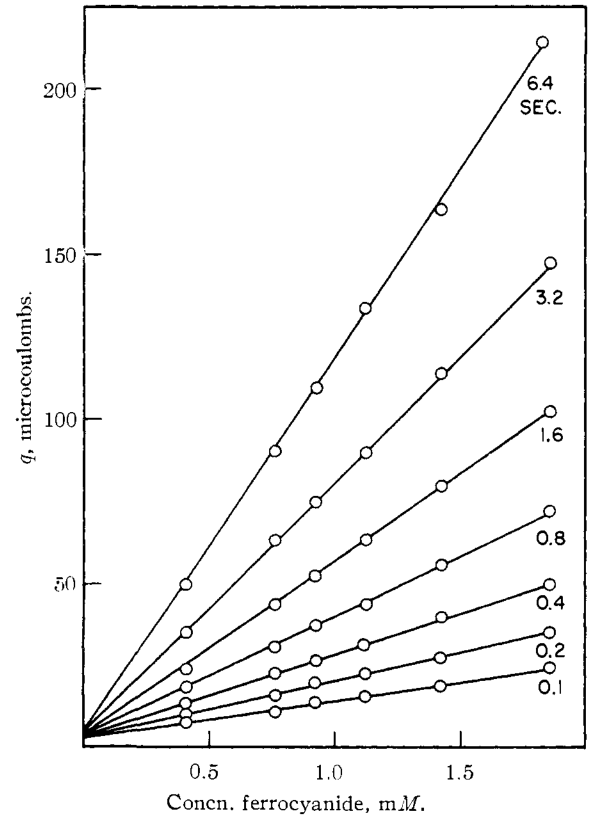

Fig. 1 —Diffusion charge *versus* concentration for integrations beginning at zero time.

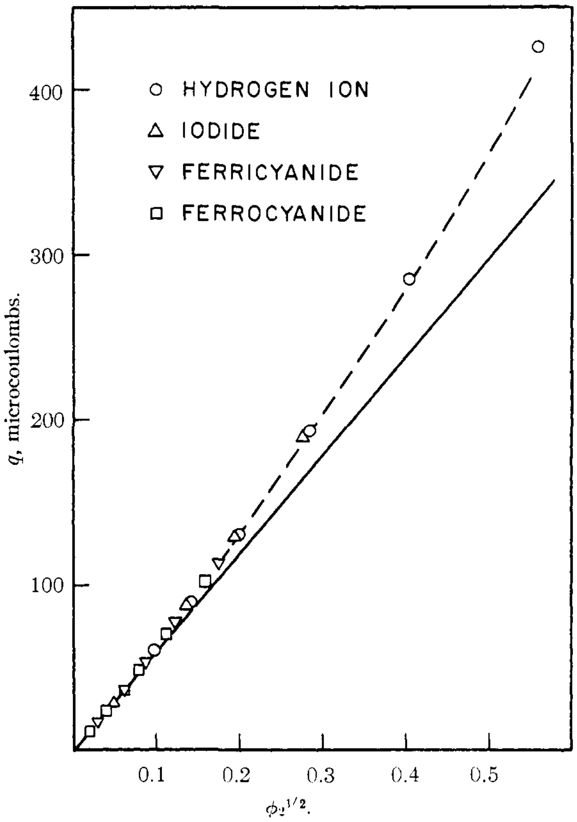

Fig. 2.—Relation between the diffusion charge and the parameter ϕ_2.

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[6] The values of the diffusion coefficients used were: ferrocyanide 6.4×10^{-6}, ferricyanide 7.6×10^{-6}, iodide 1.9×10^{-5} and hydrogen 8.1×10^{-5} cm.^{2} sec.$^{-1}$. The first two were taken from M. v. Stackelberg, M. Pilgram and V. Toome, *Z. Elektrochem.*, **57**, 342 (1953). The latter were estimated from ionic conductance at infinite dilution using data from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 2nd ed., 1950, p. 172.

was ignored except that the area of the end was included in the electrode area.

A number of electrolyses were performed beginning the integration some time after the beginning of electrolysis. Residual charges were noticeably lower in such cases. A series of observed diffusion charges are given in Table I, together with calculated values from equation 2.

The discrepancies between calculated and observed diffusion charges are believed to be principally due to uncertainties in the dimensions of the electrode and in the values of diffusion coefficients. For these reasons, agreements closer than a few per cent. are probably fortuitous, particularly for the larger values of ϕ, where higher terms in the equation must be included. The linear relation between concentration and diffusion charge for any one reaction is not dependent on the accuracy with which ϕ is known, and proportionality to concentration was followed more closely, within 1% for concentrations large enough so that residual charge was not a large part of the total charge. The results indicate that no significant convection effects were present and that the experimental circumstances correspond closely to equation 1.

TABLE I

DIFFUSION CHARGES

Ion	$t_1 - t_2$, sec.	q, μ coulomb Calcd.	Obsd.
I^-	0.091– 0.191	9.25	9.56
	0.691– 0.791	4.13	4.25
	2.991– 3.191	4.35	4.53
	11.99 –12.79	9.85	10.44
$Fe(CN)_6^{-3}$	0.091– 0.191	5.78	5.76
	0.691– 0.791	2.54	2.57
	2.991– 3.191	2.62	2.67
	11.99 –12.79	5.69	5.99
$Fe(CN)_6^{-4}$	0.091– 0.191	5.28	5.33
	0.691– 0.791	2.32	2.35
	2.991– 3.191	2.38	2.44
	11.99 –12.79	5.15	5.50

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SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Applications of Coulometric Methods to Kinetic Studies[1]

BY PAUL S. FARRINGTON AND DONALD T. SAWYER

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The principles of coulometric analysis have been applied to the study of kinetic systems. Through coulometric generation of reactants, rate constants can be determined rapidly and precisely. A new technique for the determination of rates of hydrolysis for aliphatic esters has been developed. Rate constants have been redetermined for ethyl acetate and ethyl lactate. A procedure has also been worked out for determining the relative rates of hydrogenation of olefins in solution at a platinum–black catalyst. The relative rate constants for the hydrogenation of cyclohexene, octene-1 and decene-1 have been determined. Both methods permit the determination of reaction rates at constant concentrations of the reactants.

The coulometric generation of chemical titrants has been a subject of wide interest, especially when applied to micro-analytical methods.[2] Since the amount of titrant may be computed by Faraday's law from the number of coulombs passed through the solution, small quantities of material can be determined more accurately and conveniently than by the usual volumetric techniques.

The many advantages which coulometric methods offer for analysis prompted the investigation of adapting coulometric techniques to the study of kinetics. The two kinetic systems selected for study were chosen because they satisfied certain specific requirements. The first, the basic hydrolysis of water-soluble aliphatic esters, had the desirable features of occurring in an aqueous solution, having widely studied mechanisms and rate constants, and having a simple rate law. The second study, the hydrogenation of aliphatic olefins in solution, provided a non-aqueous system which helped to indicate the broad applicability of the coulometric method. This study was brought about by an attempt to develop a semi-micro method for the analysis of olefins. It was proposed to hydrogenate the double bonds by coulometric generation of hydrogen on platinum black catalyst. However, the slowness of the rate of reaction prevented progress in the development of an analytical procedure, and prompted a study of the kinetic factors involved.

These two systems provided ample opportunity to investigate the general applicability of coulometry to kinetics. The rate constants are of interest themselves, since there are discrepancies in the previously published ester hydrolysis data,[3-5] and since there are very few data of any nature for the rates of hydrogenation of olefins in solution.[6,7]

It should be emphasized that the purpose of the work presented herein was not to determine, or redetermine, a large body of fundamental physical

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(1) Abstracted from a thesis submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy at the University of California, Los Angeles by Donald T. Sawyer.

(2) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953.

(3) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, Clarendon Press, 1933, p. 86.

(4) H. Olsson, *Z. physik. Chem.*, **133**, 242 (1928).

(5) E. Tommila and S. Hietala, *Acta Chem. Scand.*, **8**, 257 (1954).

(6) National Bureau of Standards, "Tables of Chemical Kinetics," Circular of the National Bureau of Standards 510, U. S. Printing Office, Washington, D. C., 1951, p. 99.

(7) H. A. Smith and H. T. Meriwether, THIS JOURNAL, **71**, 413 (1949).