JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 79 MARCH 12, 1957 NUMBER 5

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Anodic Chronopotentiometry with Platinum and Gold Electrodes. The Iodide–Iodine–Iodate System

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RECEIVED SEPTEMBER 20, 1956

Chronopotentiograms of iodide ion oxidation at platinum and gold anodes in dilute sulfuric or perchloric acid show two inflections (transition times). The first corresponds to $I^- \rightarrow I_2$ and the second to $I_2 \rightarrow IO_3^-$. The oxidation of iodine to iodate ion is accompanied by oxidation of the platinum or gold anode, and with small concentrations of iodide ion this causes the ratio of transition times to be larger than the value expected for successive 1- and 5-electron oxidations. A method of correcting for this electrode oxidation is presented. This correction will generally be necessary in chronopotentiometry with platinum and gold anodes whenever the potential is more oxidizing than *ca.* 1 v. *vs.* N.H.E.

In a previous study[1] of the coulometric titration of iodide ion persuasive evidence appeared that the elemental iodine, to which iodide ion in acid medium is initially oxidized at a platinum anode, is further oxidized to iodate ion at a potential slightly below that at which water is oxidized. However, Kolthoff and Jordan,[2] on the basis of polarographic measurements with a platinum micro anode, had previously concluded that iodine was oxidized only to hypoiodous acid in dilute sulfuric or perchloric acid media.

These discrepant conclusions prompted the present investigation, which conclusively proves that iodate ion, rather than hypoiodous acid, is the oxidation product of iodine in dilute sulfuric or perchloric acid solutions at both platinum and gold anodes. The anomalous polarographic behavior of iodine with platinum or gold anodes stems from oxidation of the electrode itself. This oxidation apparently is associated with the formation of oxide films on the anode. During the recording of a polarogram such films are formed and correction for their effects is very difficult. This same oxidation of the anode also occurs, of course, when the chronopotentiometric technique is used, but correction for it can be made.

Experimental

Chronopotentiometry consists of polarizing a working electrode with constant current and observing the potential of the working electrode with respect to a reference electrode as a function of time. With current density properly matched to concentration of the electroactive substance, the potential–time curve displays an inflection at a "transition time" which is a function of the concentration of the electroactive substance, the number of electrons involved in the electrode reaction, and, in some cases, depends on kinetic characteristics of the reaction. The principles of the technique have been excellently reviewed by Gierst and co-workers[3] and by Delahay.[4]

Measurements were made with both bright platinum and gold working anodes, which were each flat sheets 1 cm.^{2} in area (one side) mounted vertically in the solution. The auxiliary cathode was a large platinum electrode (area 35 cm.^{2}) immersed directly in the solution. With the working and auxiliary electrodes both in the test solution the solution composition was not altered by electrolysis—because the reaction at the cathode was just the reverse of that at the anode—so that several successive measurements could be made reproducibly with the same solution.

It was essential to keep the test solutions free of chloride ion and other substances which are oxidizable at potentials below that at which iodine is oxidized. Therefore the potential of the working anode was observed against a saturated mercurous sulfate–potassium sulfate reference electrode (potassium nitrate salt bridge), but the data have been transformed to the more familiar saturated calomel electrode scale for presentation. Care was taken to so position the electrodes that the iR drop between the tip of the salt bridge and the working anode was kept negligibly small.

Precise temperature control was not necessary for the purpose of the measurements, but the solution temperature was within ±2° of 25°. To avoid oxidation of iodide ion by

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[1] J. J. Lingane, C. H. Langford and F. C. Anson, *Anal. Chim. Acta*, in press (1956).

[2] I. M. Kolthoff and J. Jordan, THIS JOURNAL, **75**, 1571 (1953).

[3] L. Gierst and A. Juliard, Proc. Int. Comm. Electrochem. Thermodyn. and Kinetics, 2nd Meeting, Tamburine, Milan, 1950, pp. 117, 279; *J. Phys. Chem.*, **57**, 701 (1953); L. Gierst and Ph. Mechelynck, *Anal. Chim. Acta*, **12**, 79 (1955).

[4] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chap. 8.

oxygen dissolved air was removed from the test solution with nitrogen.

Between successive trials with the same solution the solution was stirred briefly with a magnetic stirrer, but was allowed to become quiescent before a measurement.

The electrolysis current (constant at each value to ±0.01%) was supplied by an instrument previously described.[5] The potential–time curves (chronopotentiograms) were recorded with a Varian G-10 potentiometer recorder, which had a 2 sec. full scale deflection time and 100 mv. intrinsic range, and was provided with a 1 megohm potential divider in the input to extend the range. Manual measurements of transition times were also made by observing the time required for the working anode to reach the previously ascertained potential at the midpoint of the inflection in the potential–time curve. Time was measured with a Standard Electric Time Co. model S-10 clock. The current density was matched to the iodide ion concentration to yield transition times shorter than about 100 sec. (usually 10 to 30 sec.), to ensure that diffusion would be the controlling transfer process at the working anode.

Data and Discussion

As shown by the typical recordings in Fig. 1, the anodic chronopotentiogram of iodide ion shows two inflections, the first corresponding to the oxidation of iodide ion to iodine, and the second to further oxidation above the elemental state. The ratio of the two transition times τ_1 and τ_2 is governed by the relative numbers of electrons involved in the two stages. Since the first stage is known to be $I^- \rightarrow I_2$ the second step can be identified by measuring τ_2/τ_1.

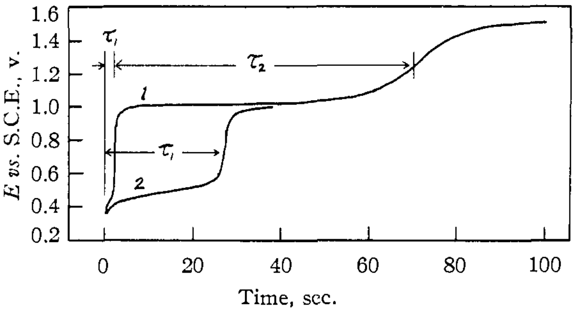

Fig. 1.—Typical chronopotentiograms for oxidation of 2 mmolar iodide ion in 1 *F* perchloric acid at a platinum anode. Current densities were (1) 1.18 and (2) 0.325 milliamp./cm.^{2}. The first inflection at time τ_1 corresponds to $I^- \rightarrow I_2$ and the second at time τ_2 to $I_2 \rightarrow IO_3^-$.

In the present instance the two transition times are so disproportionate that the first becomes too small for accurate measurement when the current density is selected large enough to produce the second transition in less than about 100 sec. (compare curve 1 in Fig. 1.) Hence in each case a second trial was performed at a sufficiently smaller current density so that the first transition time was large enough to measure accurately (see curve 2 in Fig. 1). By relations described below the first transition time observed at the smaller current density was converted to the value it would have had at the larger current density.

The characteristics of the chronopotentiograms with a gold anode are essentially the same as with a platinum anode. The only difference is that the potential change at the second inflection is somewhat larger because the oxidation of water occurs at a slightly greater potential on gold than on platinum.

For the reaction of a single substance at the electrode, or for the first of several successive reaction stages, and providing that linear diffusion is the controlling transfer process, the fundamental

$$i\tau_1^{1/2} = \frac{\pi^{1/2} nFAD^{1/2}C}{2} \qquad (1)$$

relation is the Sand equation[6] where i is the constant current (amp.), τ_1 the only or first transition time (sec.), n the number of electrons transferred, F the faraday (96,493 coulombs), A the electrode area (cm.^{2}), D the diffusion coefficient (cm.^{2}/sec.) of the electroactive substance, and C its concentration (moles/cc.) in the body of the solution. For a given solution, with linear diffusion controlling the electrode reaction, the quantity $i\tau^{1/2}$ is constant independent of current density.

For the sum of the transition times in a two stage process, like the present one, it follows from relations that have been derived and discussed by Berzins and Delahay[7] that

$$i(\tau_1 + \tau_2)^{1/2} = \frac{\pi^{1/2} FAD^{1/2}C}{2}(n_1 + n_2) \qquad (2)$$

where the second transition time τ_2 is measured from the first (*i.e.*, $\tau_1 + \tau_2$ is the total time to the second inflection), and n_1 and n_2 are the individual electron requirements for the two stages.

From equations 1 and 2 we have

$$\frac{i_2(\tau_1 + \tau_2)^{1/2}}{i_1\tau_1^{1/2}} = \frac{n_1 + n_2}{n_1} \qquad (3)$$

where i_1 and i_2 may either be identical or different, because for a given solution $i_2(\tau_1 + \tau_2)^{1/2}$ and $i_1\tau_1^{1/2}$ are both constants. Since $n_1 = 1$ for the first transition, n_2 can be evaluated from the observed values of $i_2(\tau_1 + \tau_2)^{1/2}$ and $i_1\tau_1^{1/2}$.

The results of such measurements with both gold and platinum anodes, and with sulfuric and perchloric acid solutions, with various concentrations of iodide ion are summarized in Table I. The iodide ion concentration was (except in one case) restricted to values small enough so that the solubility of iodine (1.33 mmolar) was not exceeded, because the foregoing relations would be invalid if solid iodine precipitated at the electrode surface.

For successive oxidations of iodide ion to iodine and iodate ion the value of $(n_1 + n_2)/n_1$ should be 6. With the larger concentrations of iodide ion this is the value observed, but with the smallest iodide ion concentrations the *apparent* value of $(n_1 + n_2)/n_1$ becomes as large as 9. If iodine were oxidized to periodate ion n_2 would be 7 and $(n_1 + n_2)/n_1$ would be 8. However, this interpretation is untenable *a priori* in view of the fact that the potentials of the iodine–periodate and iodate–periodate couples are both larger (more oxidizing) than that of the iodine–iodate couple, and so close to the potential at which water is oxidized that a second potential inflection as distinct as that observed is most unlikely. The truth is that the iodine is oxidized only to iodate ion, but the concomitant oxidation of the platinum and gold anodes

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(5) J. J. Lingane, *Anal. Chem.*, **26**, 1021 (1954).

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

(7) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 4205 (1953).

TABLE I

Current, mamp.	$i\tau_1^{1/2}$, mamp. sec.$^{1/2}$	Current, mamp.	$i(\tau_1 + \tau_2)^{1/2}$, milliamp. sec.$^{1/2}$	$(n_1 + n_2)/n_1$, observed	T corr. from eq. 8, sec.	$(n_1 + n_2)/n_1$, corr.
1. 1 F H_2SO_4; 2.11 mformal KI; gold electrode						
0.260	1.83	1.603	10.4	5.7	4.3	5.4
.361	1.78	2.180	10.4	5.7	2.9	5.4
.500	1.79	2.995	10.7	5.9	2.0	5.4
1.000	1.82					
Av.	1.81					
2. 1 F H_2SO_4; 1.88 mformal KI; gold electrode						
0.192	1.45	1.396	8.15	5.8	4.6	5.4
.239	1.42	2.000	8.23	5.8	3.0	5.3
.337	1.39	2.770	8.50	6.0	2.0	5.3
.449	1.39					
Av.	1.41					
3. 1 F H_2SO_4; 1.88 mformal KI; platinum electrode						
0.235	1.47	1.065	8.55	5.9	3.4	5.8
.325	1.42	1.407	8.40	5.8	2.4	5.6
.499	1.42	1.995	8.45	5.9	1.5_5	5.6
	———	2.694	8.64	6.0	1.0_8	5.7
Av.	1.44					
4. 1 F H_2SO_4; 0.94 mformal KI; gold electrode						
0.146	0.778	0.667	5.06	6.5	8.8	6.0
.186	.776	0.913	5.12	6.6	6.1	5.9
.250	.770	1.300	5.38	6.9	4.1	6.1
	———	1.800	5.59	7.2	2.4_2	5.9
Av.	0.775					
5. 1 F $HClO_4$; 0.94 mformal KI; gold electrode						
0.140	0.805	0.729	5.24	6.6	8.0	6.0
.189	.798	0.932	5.32	6.7	6.0	6.0
.250	.795	1.297	5.52	6.9	4.1	6.1
	———	1.882	5.80	7.3	2.7	6.1
Av.	0.799					
6. 1 F H_2SO_4; 0.94 mformal KI; platinum electrode						
0.132	0.770	0.729	5.34	6.9	4.0	6.7
.190	.770	0.932	5.32	6.9	3.0	6.6
.249	.772	1.297	5.50	7.1	2.0	6.7
	———	1.804	5.87	7.6	1.38	7.0
Av.	0.771					
7. 1 F H_2SO_4; 0.54 mformal KI; platinum electrode						
0.0623	0.396	0.474	3.04	7.7	5.2	7.2
.0865	.392	.657	3.16	8.0	3.5	7.4
.120	.390	.937	3.39	8.6	2.4	7.7
	———	1.296	3.68	9.4	1.6	8.4
Av.	0.393					
8. 1 F H_2SO_4; 0.54 mformal KI; gold electrode						
0.0716	0.405	0.511	3.10	7.6	9.9	6.5
.105	.407	0.712	3.28	8.0	6.8	6.6
.152	.414	1.012	3.56	8.7	4.6	6.9
Av.	0.409					
9. 1 F H_2SO_4; 0.54 mformal KI; gold electrode						
0.0680	0.398	0.504	3.05	7.6	10.0	6.5
.0958	.398	0.717	3.22	8.0	6.8	6.5
.126	.406	1.012	3.50	8.7	4.7	6.8
	———	1.298	3.63	9.1	3.5	6.7
Av.	0.401					

causes τ_2 to be abnormally large, and consequently produces an *apparent* value of $(n_1 + n_2)/n_1$ larger than 6 when the iodide ion concentration is relatively small.

From equations 1 and 2 the quantities $i\tau_1^{1/2}$ and $i(\tau_1 + \tau_2)^{1/2}$ in Table I should both be constant, independent of current density, for a given iodide ion concentration. This is true with the largest iodide ion concentration for both quantities, and for $i\tau_1^{1/2}$ at all iodide ion concentrations. However, as the iodide ion concentration is decreased $i(\tau_1 + \tau_2)^{1/2}$ displays a marked increase with increasing current density. This behavior clearly indicates that the oxidation of iodine to iodate ion is accompanied by another electrode reaction. This co-reaction is oxidation of the electrode itself.

There is good evidence in the literature, particularly in the papers of Hickling[8] and Kolthoff and Tanaka,[9] that oxide films are formed on platinum and gold electrodes by anodic polarization in noncomplexing media like dilute sulfuric or perchloric acids.

This interpretation is substantiated by the chronopotentiograms in Figs. 2 and 3 of platinum and gold electrodes in 1 F sulfuric acid solutions containing no iodide. With both electrodes a distinct potential halt occurs before the electrode potential reaches the value at which water is oxidized (curve 1). If, after the first trial, the chronopotentiogram is repeated without subjecting the electrodes to a reducing treatment the potential halt no longer appears, and the potential immediately assumes the value at which water is oxidized (curves 2). However, if the electrodes are subjected to a reducing treatment between each trial (immersion for several minutes in an acidic iodide solution, or cathodic polarization, followed by thorough washing), curves 1 in Figs. 2 and 3 become reproducible.

Data for the transition times of curves 1 in Figs. 2 and 3 observed with various currents are presented in Table II. For each electrode the product

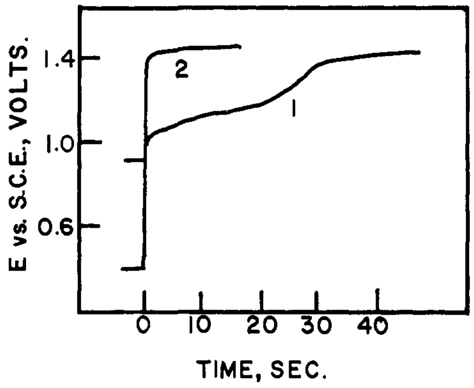

Fig. 2.—Chronopotentiogram for the platinum anode in 1 F sulfuric acid with no iodide present, at a current density of 0.15 milliamp./cm.^{2}. Curve 1 is for a previously reduced electrode, and curve 2 resulted when the trial was repeated.

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[8] A. Hickling, *Trans. Faraday Soc.*, **41**, 333 (1945); **42**, 518 (1946); A. Hickling and W. Wilson, *J. Electrochem. Soc.*, **98**, 425 (1951).

[9] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 632 (1954).

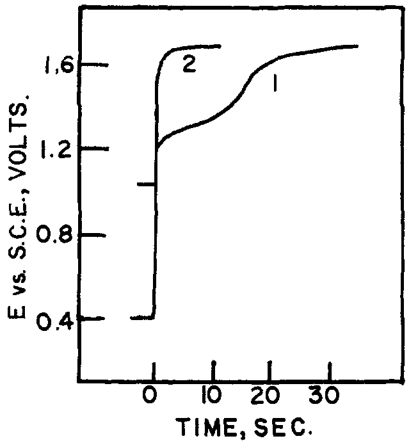

Fig. 3.—Chronopotentiogram for the gold anode in 1 F sulfuric acid with no iodide present, at a current density of 0.20 milliamp./cm.^{2}. Curve 1 is for a previously reduced electrode, and curve 2 resulted when the trial was repeated.

$i\tau$ is individually a constant; *i.e.*, the quantity of electricity passed up to the transition time is constant independent of the current density. Evidently the transition time corresponds for each electrode to the formation of an oxide film of a definite, limited thickness. The most likely oxides (hydrated) are PtO and Au_2O_3.

It seems reasonable to suppose (as do Hickling and Wilson for the oxidation of hydrogen peroxide) that the oxide films formed on the electrodes are involved in the kinetics of the oxidation of iodine to iodate. Accordingly one would expect essentially all of the electrode oxidation to take place just after the transition time for the oxidation of iodide and before any oxidation of iodine begins. On this basis it is possible to calculate appropriate corrections for the observed values of $(\tau_1 + \tau_2)$ by determining how much of the constant current is used only in oxidizing the electrode.

TABLE II

1. Pt electrode in 1 F H_2SO_4, no iodide			2. Au electrode in 1 F H_2SO_4, no iodide		
Current, mamp.	τ, sec.	$i\tau$, mcoulombs	Current, mamp.	τ, sec.	$i\tau$, mcoulombs
0.0747	21.7	1.6	0.101	39.0	3.9
.150	10.2	1.5	.197	18.7	3.6
.300	5.45	1.6	.278	13.1	3.7

Berzins and Delahay[7] have calculated the variation in the flux of a species at the electrode surface subsequent to the transition time for the species. These authors write (after their original equation is corrected for minor errors)

$$\left(\frac{\partial C_1}{\partial x}\right)_{x\,=\,0} = \frac{\mathrm{i}}{nAFD_1}\left[\frac{1}{2} + \frac{1}{\pi}\sin^{-1}\frac{\tau_1 - t'}{\tau_1 - t'}\right] \quad (4)$$

where C_1 is the concentration of the reacting species, x is the distance from the electrode surface, τ_1 is the transition time for the first step in the chronopotentiogram, t' is the time measured from τ_1, and the other terms are as defined for equation 1.

In the present case equation 4 can be used to calculate the flux of iodide ion at the electrode following the first transition time. The current due just to iodide oxidation is

$$i_I = An_1FD_{I^-}\left(\frac{\partial C_{I^-}}{\partial x}\right)_{x\,=\,0} = i\left[\frac{1}{2} + \frac{1}{\pi}\sin^{-1}\frac{\tau_1 - t'}{\tau_1 + t'}\right] \quad (5)$$

whence the current due to film formation (under the stated assumptions) is

$$i - i_1 = i\left[1 - \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau_1 - t'}{\tau_1 + t'}\right] \quad (6)$$

Now we need only to integrate the right hand side of equation 6 with respect to t' and equate the result to the amount of electricity needed to form the electrode films. Thus

$$\int_0^T i\left[\frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau_1 - t'}{\tau_1 + t'}\right]\mathrm{d}t = Q \quad (7)$$

where Q is the quantity of electricity and T the time needed to film the electrode (Table II). Integration of equation 7 gives

$$Q = i\left[\frac{T}{2} - \frac{1}{\pi}\left(T\sin^{-1}\frac{\tau_1 - T}{\tau_1 + T} + 2\,(\tau_1 T)^{1/2} - 2\tau_1\tan^{-1}\left(\frac{T}{\tau_1}\right)^{1/2}\right)\right] \quad (8)$$

The solution of equation (8) for T yields the time which must be subtracted from the observed values of $(\tau_1 + \tau_2)$ to correct for electrode oxidation. The effect of applying the correction to the data in Table I is shown in the last column of Table I. The data in this column show greatly improved constancy for the corrected values of $(n_1 + n_2)/n_1$ for the data obtained with the gold electrode, and somewhat improved constancy for the data obtained with the platinum electrode. The poorer constancy and larger deviation from the expected value of 6 observed with the platinum electrode is most probably due to oxidation of water as explained below.

Because of the rather awkward form of equation 8 the correction of measured values of $\tau_1 + \tau_2$ for electrode oxidation is tedious. A rapid and simpler method of obtaining an approximate correction is to extrapolate a plot of $(n_1 + n_2)/n_1$ *vs.* current to zero current. The zero current intercept gives a value for $(n_1 + n_2)/n_1$ which is a good approximation to the value which would be observed in the absence of any electrode oxidation. Figure 4 shows three such plots and the intercepts to which they are linearly extrapolated.

From eq. 8 and other considerations $(n_1 + n_2)/n_1$ would not be expected to be a strictly linear function of current. However, divergence from linearity is small enough so that this empirical technique yields results in essential agreement with those derived with the aid of eq. 8.

The corrected values for $(n_1 + n_2)/n_1$ obtained by both methods of correction correspond to oxidation of iodine to iodate for the second step of the chronopotentiogram. The theoretical value for $(n_1 + n_2)/n_1$ for iodate formation is 6, and the observed agreement is considered satisfactory in view of the fact that there is a possibility of several factors contributing to the deviation of the corrected values for $(n_1 + n_2)/n_1$ from 6.0. First, the electrode may not reach its final state of oxidation be

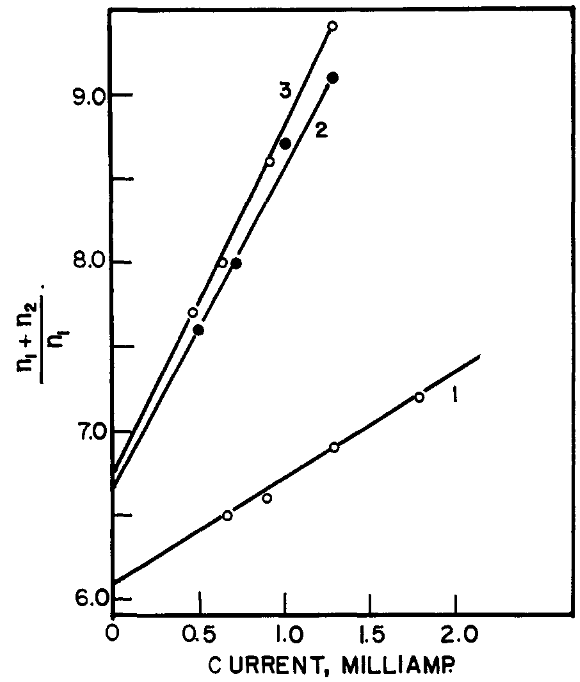

Fig. 4.—Current dependence of observed values of $(n_1 + n_2)/n_1$. (1) 0.94 milliformal potassium iodide with a gold anode; (2) 0.54 milliformal potassium iodide with a gold anode; (3) 0.54 milliformal potassium iodide with a platinum anode; all solutions 1 F in sulfuric acid.

fore oxidation of iodine commences. If this is the case the correction calculated from equation 8 will be too small and the corrected values for $(n_1 + n_2)/n_1$ will be high. This effect contributing to high values for $(n_1 + n_2)/n_1$ would be most prominent in the less concentrated iodide solutions where correction for electrode oxidation is relatively most significant. Secondly, it is likely that with the platinum electrode after the first inflection some oxidation of water is occurring along with the oxidation of iodine. The effect will be to increase the second transition time and will become increasingly important as the iodide concentration is decreased and the contribution from water oxidation increases. This concomitant oxidation of water is probably the chief cause of the much higher values obtained for $(n_1 + n_2)/n_1$ when a platinum electrode was used with the more dilute solutions. Correction for this type of side reaction is not so straightforward in chronopotentiometry as it is in current potential measurements where a residual current curve is easily determined.

Finally, it is quite probable that the iodate which is formed at the electrode following the first transition time, and is diffusing back into the solution, will react with the iodide which is diffusing toward the electrode to form iodine.

The conclusions to which this study has led are not in agreement with those of Kolthoff and Jordan.[2] These authors obtained current–potential curves for iodide solutions at rotated platinum electrodes which showed a first, well developed wave corresponding to oxidation of iodide to iodine and a second, much more poorly defined wave containing a pronounced maximum. Since this second wave was approximately twice the height of the first wave Kolthoff and Jordan concluded that iodide ion was oxidized to hypoiodous acid at the potentials where the second wave occurred. In view of the results of Hickling,[8] Kolthoff and Tanaka,[9] and of the present study, and, since the second wave observed by Kolthoff and Jordan disappeared completely when the electrode was polarized from oxidizing to reducing potentials, it seems clear that Kolthoff and Jordan were observing an increase in current due to oxidation of the platinum electrode and not to the formation of +1 iodine.

One would expect from the present chronopotentiometric measurements that Kolthoff and Jordan should have observed an increase in current due to oxidation to iodate ion. To check this expectation the current potential curves in Figs. 5 and 6 were obtained with stationary platinum and gold microelectrodes in unstirred, acidic iodide solutions. The curve in Fig. 5 shows the second wave observed by Kolthoff and Jordan occurring at just the potential at which oxidation of the platinum electrode has been observed to commence in the present study. No limiting current for oxidation to iodate is shown in Fig. 5 but there is an indication of another oxidation wave which is masked by the commencement of water oxidation. It should be noted that it is not necessary that the current–potential curve for oxidation of iodine on platinum show a limiting iodate current containing no contribution from oxidation of water in order to observe a potential inflection for iodate formation chronopotentiometrically. It is only necessary

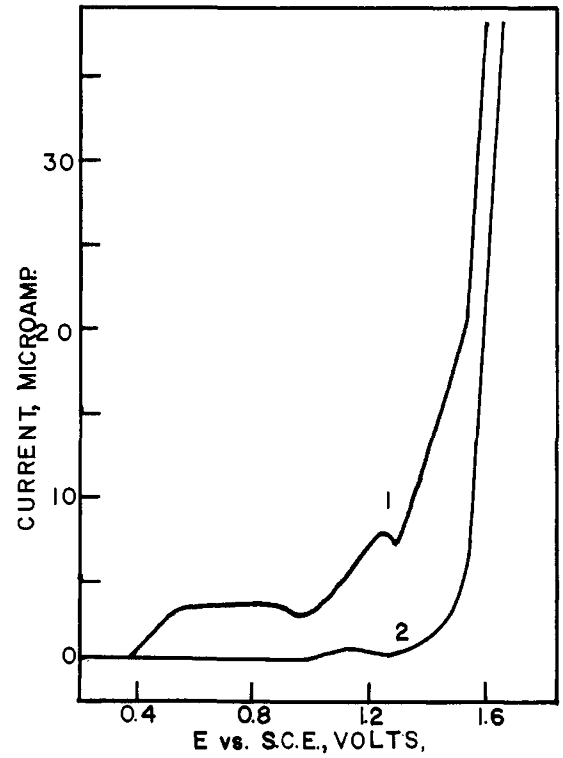

Fig. 5.—(1) Current-potential curve for 0.94 milliformal iodide ion in 1 F sulfuric acid with a platinum microelectrode; (2) residual current.

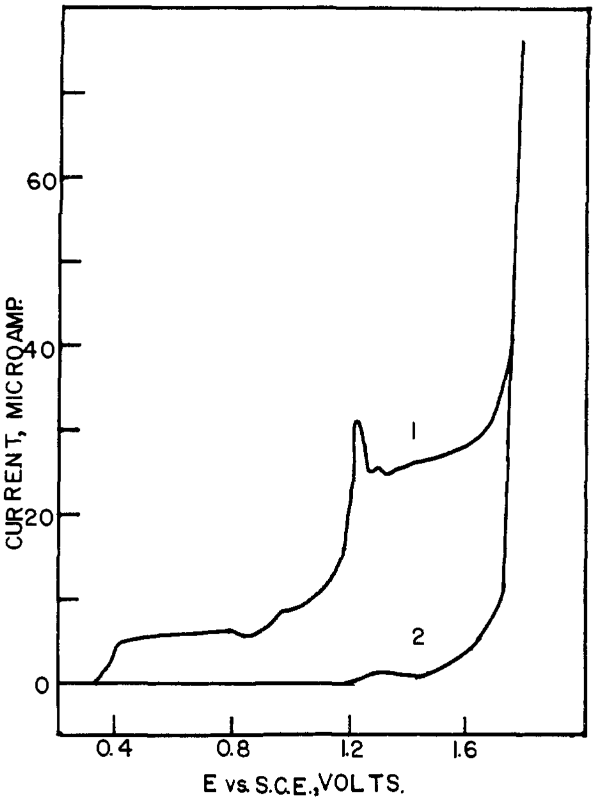

Fig. 6.—(1) Current–potential curve for 0.94 milliformal iodide ion in 1 *F* sulfuric acid with a gold microelectrode; (2) residual current.

that the current–potential curve show some current limited section corresponding to zero iodine concentration at the electrode surface. The current-density and rate of electrode potential change are quite different in chronopotentiometric and current–potential experiments, but it was not possible to explain the apparent discrepancy between the two experimental results by controlling these variables. It is probable that this difference between chronopotentiometric and polarization curve techniques is associated with the nature and rate of formation of the oxidized film on the electrode and with the film's reactivity. It is hoped that the continued study of this phenomenon will lead to a better understanding.

The current–potential curve in Fig. 6 for the gold microelectrode shows a sharp maximum at the potential where gold is oxidized, followed by a fairly well defined limiting current section prior to oxygen evolution. This much more definite indication of iodine oxidation at a gold electrode results from the significantly more oxidizing potentials at which water is oxidized on gold.

The second limiting current observed with the gold microelectrode is not six times as large as the first iodide limiting current, and it should not be if oxidation to iodate is occurring. Reaction between the iodate diffusing away from the electrode and the iodide diffusing toward the electrode will result in iodine being formed. This iodine will now diffuse both toward and away from the electrode since its concentration will be negligible both at the electrode surface and in the body of the solution. The effect of this reaction will be to decrease the current because of both the smaller diffusion coefficient of iodine and the diffusion of some of the iodine away from the electrode. Conversely, since iodine will have been accumulating at the electrode all during the time the iodide limiting current was observed, when oxidation of iodide above iodine commences there already will be some iodine at the electrode and in the solution near the electrode which will also be oxidized. This will tend to increase the limiting current observed for oxidation to iodate. The resultant of these opposing effects is not readily calculable but in view of their qualitative significance and direction of operation the observed ratio of 4.4 for the two limiting currents with the gold anode is compatible with oxidation to iodate.

Acknowledgment.—We are grateful to Dr. William Klemperer and Dr. C. N. Reilley for helpful discussions. Appreciation is expressed to the Mallinckrodt Chemical Works for partial financial support and to the National Heart Institute for a fellowship held by one of us (F.C.A.).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Kinetics of the Manganate–Permanganate Exchange Reaction[1]

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RECEIVED OCTOBER 15, 1956

In 0.16 *f* NaOH the isotopic exchange reaction between MnO_4^{--} and MnO_4^- obeys over a wide range of reactant concentrations the law rate = $k(MnO_4^{--})(MnO_4^-)$. At 0° the value of k is 710 ± 30 M^{-1} sec.$^{-1}$. The experimental activation energy is 10.5 ± 1.0 kcal. The rate increases with increasing electrolyte concentration. The rate depends on the nature of the cations present but is affected very little by the nature of the anions. At constant electrolyte concentration $k_{CsOH} > k_{KOH} > k_{NaOH} = k_{LiOH}$.

In a previous communication[2] we reported the successful rate measurement of the rapid isotopic exchange reaction between manganate and permanganate ions. In this paper we report the results of additional kinetic studies.

Experimental

Chemicals.—Mallinckrodt "analytical reagent" grade chemicals were used without further purification, except for the following. NaOH, Baker and Adamson "reagent special" was used. KOH, Mallinckrodt "analytical re-

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[1] This work was supported by the National Science Foundation. The paper was abstracted from the Ph.D. thesis of John C. Sheppard, Washington University, 1955.

[2] J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **75**, 5133 (1953).