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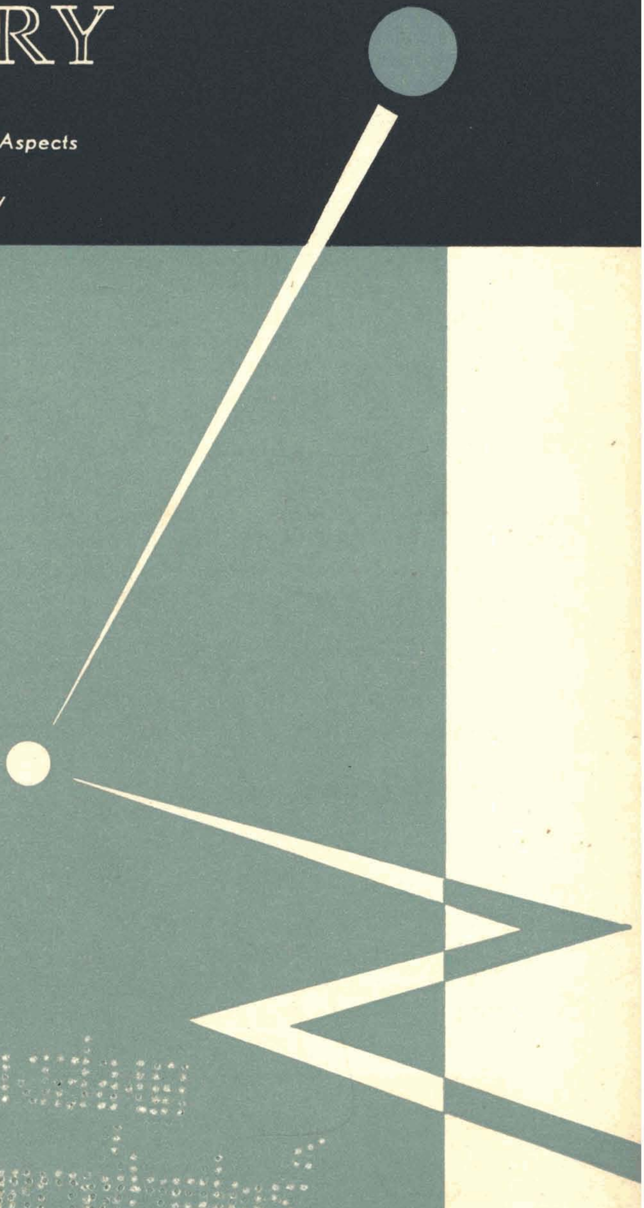
*International Journal Dealing with all Aspects*
*of Electroanalytical Chemistry,*
*Including Fundamental Electrochemistry*



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# SUMMARIES OF PAPERS PUBLISHED IN JOURNAL OF ELECTROANALYTICAL CHEMISTRY

## Vol. 8, No. 3, September 1964

### CHRONOPOTENTIOMETRIC INVESTIGATION OF THE REDUCTION OF THE CHLORIDE COMPLEXES OF GOLD

The electrolytic reductions of $AuCl_4^-$ and $AuCl_2^-$ in hydrochloric acid were studied at a gold electrode by chronopotentiometry. At concentrations of $10^{-3}$ and $10^{-2}$ *M*, $AuCl_4^-$ is reduced in a single three-electron wave. Two chronopotentiometric waves are observed with mixtures of $AuCl_4^-$ and $AuCl_2^-$ in which the concentration of the latter exceeds the equilibrium concentration. The first, more oxidizing wave is due to the reduction of $AuCl_2^-$ and the second wave is due to the reduction of $AuCl_4^-$.

D. H. EVANS AND J. J. LINGANE,

*J. Electroanal. Chem.*, 8 (1964) 173–180.

### THE POLAROGRAPHIC AND CHRONOPOTENTIOMETRIC CHARACTERISTICS OF REVERSIBLE STEP-WISE ELECTRODE REACTIONS

A theory is presented of diffusion-controlled electrode reactions involving one potential-determining intermediate species, from the point of view of polarographic and chronopotentiometric methods of study. A means of analysis is proposed which utilises directly the current* voltage or potential–time co-ordinates, and allows determination of the equilibrium constant for intermediate formation, and detection of intermediate dimerisation. The method is applied to the polarographic reduction of pyrazine.

J. M. HALE,

*J. Electroanal. Chem.*, 8 (1964) 181–199.

### CHRONOPOTENTIOMETRY OF PLUTONIUM IN MINERAL ACID MEDIA

The chronopotentiometric behavior of plutonium(III), plutonium(IV), and plutonium(VI) at a platinum electrode in various mineral acid media has been studied in order to determine the diffusion coefficients of the different plutonium species, the effects of surface oxidation of the platinum electrode, and the possible analytical usefulness of chronopotentiometry for the determination of plutonium.

The reduction of plutonium(IV) to plutonium(III) at a platinum wire cathode in perchloric, sulfuric, nitric, and hydrochloric acid solutions has been investigated. The relatively small diffusion coefficient of plutonium(IV) in each of these media plus the spontaneous chemical oxidation of the platinum electrode by plutonium(IV) result in a significant positive error in chronopotentiometry with concentrations of plutonium(IV) below 0.01 *M*.

Chronopotentiograms for the oxidation of plutonium(III) to plutonium(IV) in sulfuric acid show one wave due to oxidation of plutonium(III) followed by a second wave attributable to the formation of a platinum oxide film. Plutonium(III) in sulfuric acid medium chemically reduces the oxide film. The electro-oxidation of plutonium(III) in perchloric acid medium gives a well-defined chronopotentiogram at either pre-reduced or pre-oxidized electrodes.

The chronopotentiometric reduction of plutonium(VI) in a 1 *F* perchloric acid solution proceeds in a step-wise fashion first to plutonium(V) and then to plutonium(III). For the experimental conditions employed, there was no evidence to show that plutonium(V) undergoes significant disproportionation in the perchloric acid medium.

D. G. PETERS AND W. D. SHULTS,

*J. Electroanal. Chem.*, 8 (1964) 200–229.

# PRE-TREATMENT AND ADSORPTIVE PROPERTIES OF PLATINUM ELECTRODES

The nature of the major factors which are involved in the common methods of pre-treatment and their influence on the adsorptive properties were studied for smooth platinum electrodes by cathodic charging curves, cyclic voltammetry, and voltammetry with superimposed a.c. current. The differences of the current–potential curves and the capacitive component–potential curves during the first cycle and the subsequent cycles are discussed. It is shown to what extent these differences result from a contamination of the surface, introduced by the pre-treatment.

M. W. BREITER,

*J. Electroanal. Chem.*, 8 (1964) 230–236.

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# POLAROGRAPHY OF TITANIUM

## IV. SALICYLATE AND SULPHOSALICYLATE COMPLEXES OF TETRAVALENT TITANIUM

Polarographic studies of tetravalent titanium in salicylate and sulphosalicylate media revealed the successive appearance of different titanium–salicylate or titanium–sulphosalicylate complexes.

The complexes are derived from each other by a process of hydrolysis. Two salicylate complexes were detected and three sulphosalicylate complexes.

In the presence of excess complexing agent and in the pH range of 1–9 the equilibrium of the different species could be represented as follows:

$$[\mathrm{Ti(OH)R}_n]^{(3-n)+} \xrightleftharpoons{(\mathrm{OH})^-} [\mathrm{Ti(OH)_2R}_n]^{(2-n)+} \xrightleftharpoons{(\mathrm{OH})^-} [\mathrm{Ti(OH)_3R}_n]^{(1-n)+}$$

A mechanism is proposed which accounts for the different polarographic waves.

G. M. HABASHY,

*J. Electroanal. Chem.*, 8 (1964) 237–244.

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# A. C. POLAROGRAPHY OF COMPLEX METAL IONS

*(Short Communication)*

S. L. GUPTA AND M. K. CHATTERJEE,

*J. Electroanal. Chem.*, 8 (1964) 245–247.

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# THE ANALYSIS OF CATHODIC WAVES

*(Short Communication)*

J. M. HALE AND R. PARSONS,

*J. Electroanal. Chem.*, 8 (1964) 247–249.

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# POLAROGRAPHIC CELL WITH PERMANENT EXTERNAL REFERENCE ELECTRODE

*(Short Communication)*

V. KALOUS,

*J. Electroanal. Chem.*, 8 (1964) 250–252.

# CHRONOPOTENTIOMETRIC INVESTIGATION OF THE REDUCTION OF THE CHLORIDE COMPLEXES OF GOLD

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(Received June 11th 1964)

## INTRODUCTION

The two well-known chloride complexes of gold, $AuCl_2^-$ and $AuCl_4^-$, provide an interesting system for electrochemical investigation. It might be anticipated that $AuCl_4^-$ could be reduced in two steps, first to $AuCl_2^-$, then to metallic gold, by analogy with the reduction of cupric ion in chloride media[1]. The instability of $AuCl_2^-$ with respect to its disproportionation into $AuCl_4^-$ and metallic gold could invest the system with an interesting complication analogous to that found with the reduction of oxygen at gold electrodes in alkaline solutions,[2] *viz.*, the product of the first reduction step disproportionates causing a lengthening of the first transition time.

That these expectations are not fulfilled in the case of the reduction of $AuCl_4^-$ is the primary experimental contribution of this communication. $AuCl_4^-$ is reduced in a single three-electron chronopotentiometric wave at a gold electrode. The reason that $AuCl_2^-$ is not detectable as an intermediate is that its own reduction proceeds at a more oxidizing potential than the reduction of $AuCl_4^-$. This fact was experimentally verified by a chronopotentiometric study of mixtures of $AuCl_2^-$ and $AuCl_4^-$. It was found that the $AuCl_2^-$ wave precedes the $AuCl_4^-$ wave. Thus, if $AuCl_2^-$ is an intermediate in the reduction of $AuCl_4^-$, it is reduced as soon as it is formed and it is not detectable as an intermediate by the chronopotentiometric technique.

## EXPERIMENTAL

All chronopotentiometric measurements were carried out in the same cell and with the same electrical circuit described earlier[3].

The working electrode[2] was fabricated from 20 mil gold wire. All but a 1-cm portion of the wire was coated with a layer of Tygon paint (Type K-63, U.S. Stoneware Co., Akron, Ohio.). Test solutions were de-aerated with pre-purified nitrogen (99.98%, Air Reduction Co.). Transition time measurements were made by a manual technique in which the electrolysis current and a stop-clock were simultaneously actuated and the potential of the working electrode *vs.* the reference electrode was observed as a function of time on an oscilloscope (Dumont Model 304-H). The electrolysis current and stop-clock were stopped when the potential reached the pre-determined transition potential and the transition time was read directly from the clock (Model S-10, Standard Electric Time Co.). For illustrative purposes complete chronopotentiograms were recorded with a Sargent Model MR recording potentiometer.

Solutions of $HAuCl_4$ in hydrochloric acid were prepared determinately by dissolving pure metallic gold in *aqua regia* and evaporating to a few millilitres in a quartz vessel. This solution was treated with concentrated hydrochloric acid and the evaporation was repeated to remove oxides of nitrogen. The latter process was repeated twice and finally the last small volume was diluted to the desired volume with 1 *M* hydrochloric acid[4].

Mixtures of $AuCl_2^-$ and $AuCl_4^-$ in which the concentration of $AuCl_2^-$ was greater than the equilibrium concentration were prepared by anodizing a gold electrode in 1 *M* hydrochloric acid. This process has been described in detail elsewhere[5]. The concentration of $AuCl_4^-$ in these mixtures was determined by measuring the absorbance of a suitably diluted sample of the solution at 312 m$\mu$ in 1-cm fused silica cells with a Beckman Model DU spectrophotometer.

## REDUCTION OF $AuCl_4^-$

A typical chronopotentiogram for the reduction of $10^{-3}$ *M* $AuCl_4^-$ at a gold wire electrode is shown in Fig. 1, curve 1. The solution was stirred vigorously between trials, then allowed to become quiet for one minute before each chronopotentiogram was recorded. After about ten trials the surface of the electrode began to acquire a dull appearance due to the formation of finely divided gold. This process could be reversed by simply anodizing the electrode for about a minute, a process which causes the dissolution of metallic gold as $AuCl_2^-$. This was done at regular intervals to restore the electrode to its original luster and thus avoid increase in effective electrode area due to electrodeposited gold.

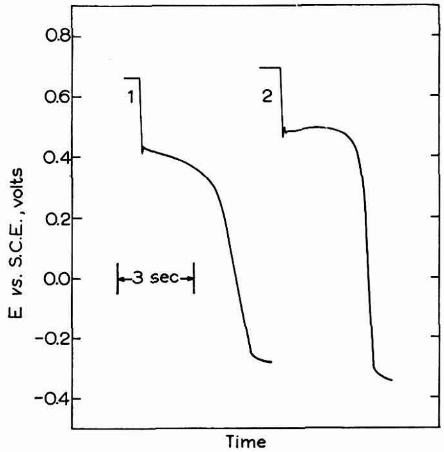

Fig. 1. Typical chronopotentiograms for the reduction of $AuCl_4^-$ in 1 *M* hydrochloric acid at a gold wire electrode. Curve 1, $1.006 \times 10^{-3}$ *M* $AuCl_4^-$, $i = 89.09$ $\mu$A; curve 2, $1.016 \times 10^{-2}$ *M* $AuCl_4^-$, $i = 860$ $\mu$A. Electrode area = 0.173 cm², radius = 0.0255 cm, temp. = 25.0 ±0.1°.

The open-circuit potential (with stirring) of the gold electrode was +0.64 V *vs.*

S.C.E. (+0.88 V *vs.* N.H.E.). This potential is 60 mV less oxidizing than the potential calculated from the standard potential of the $AuCl_4^-/Au$ couple (+1.002 V *vs.* N.H.E.[5]) and the bulk concentration of $AuCl_4^-$ ($1 \cdot 10^{-3}$ *M*). However, it has been demonstrated[5] that the potential of a gold electrode in chloride media is determined by the concentration of $AuCl_2^-$ through the $AuCl_2^-/Au$ couple ($E_0 = 1.154$ V *vs.* N.H.E.[5]). Thus, a potential of +0.88 V *vs.* N.H.E. (with stirring) corresponds to a steady-state concentration of $AuCl_2^-$ at the electrode surface of the order of $6 \cdot 10^{-5}$ *M*. However, the potential of the working electrode becomes more oxidizing during the quiescent period, eventually becoming +0.91 V *vs.* N.H.E. (+0.67 V *vs.* S.C.E.) just before the electrolysis begins (*cf.* Fig. 1, curve 1), because the $AuCl_2^-$ formed by the reduction of $AuCl_4^-$ by the gold surface accumulates at the electrode surface since it is not being stirred away.

$$AuCl_4^- + 2\ Au + 2\ Cl^- \rightarrow 3\ AuCl_2^- \qquad (1)$$

The potential after the quiescent period corresponds to a steady-state concentration of the order of $10^{-4}$ *M* $AuCl_2^-$, about one-tenth the $AuCl_4^-$ concentration. The actual constitution of the solution is altered in the region near the electrode surface. The possible effect of this chemical reaction on the chronopotentiometry of $AuCl_4^-$ will be discussed later. It should be pointed out that the occurrence of reaction (1) at the electrode surface (0.173 cm$^2$) does not appreciably diminish the bulk concentration of $AuCl_4^-$ in the more than 100 ml of test solution.

Transition times as a function of current density are summarized in Table 1.

TABLE 1

CATHODIC CHRONOPOTENTIOMETRY OF $10^{-3}$ *M* $AuCl_4^-$

Transition times measured at 3-min. intervals. Transition potential = 0.0 V *vs.* S.C.E. Times are averages of three trials. Average deviation given in parentheses. Concn. of $AuCl_4^- = 1.00_6 \times 10^{-3}$ *M*. Supporting electrolyte was 1 *M* hydrochloric acid. Gold wire electrode, area = 0.173 cm$^2$, radius = 0.0255 cm. Temp. = 25.0 ±0.1°.

$i_{corr.} = i_{obs.} - 12.8/\tau$ (see text)

| $\tau$ *(sec)* | $i_{obs.}$ *(μA)* | $i_{corr.}$ *(μA)* | $i\tau^{1/2}/AC°$ *(A sec$^{1/2}$ cm/mole)* *Observed* | *Corrected* |
|---|---|---|---|---|
| 0.99 (±0.01) | 166.7 | 153.8 | 954 | 880 |
| 1.56 (±0.00) | 135.2 | 127.0 | 971 | 912 |
| 2.32 (±0.02) | 111.6 | 106.1 | 978 | 929 |
| 3.63 (±0.05) | 89.09 | 85.56 | 976 | 937 |
| 4.96 (±0.06) | 77.51 | 74.93 | 993 | 960 |
| 6.49 (±0.05) | 67.52 | 65.55 | 990 | 961 |
| 7.71 (±0.03) | 63.03 | 61.37 | 1007 | 980 |
| 10.19 (±0.02) | 55.56 | 54.31 | 1020 | 997 |
| 12.46 (±0.05) | 51.72 | 50.69 | 1050 | 1029 |
| 16.20 (±0.13) | 45.70 | 44.91 | 1058 | 1039 |
| 20.07 (±0.36) | 42.22 | 41.58 | 1088 | 1071 |

Since some of the current in each trial was consumed in charging the electrode double layer, the actual current corresponding to the reduction of $AuCl_4^-$ was less than the observed current. An adequate correction for this effect is afforded by the relationship[3,6]

$$i_{\text{corr.}} = i_{\text{obs.}} - Q/\tau \qquad (2)$$

where $Q$ is the quantity of electricity required to polarize the electrode to the transition potential in the absence of reducible material. In this case, $Q$ was experimentally determined by measuring the quantity of electricity required to polarize the working electrode from 0.7 to 0.0 V *vs.* S.C.E. in de-aerated 1 *M* hydrochloric acid containing no gold. A series of ten trials at two different current densities yielded an average value of 12.8 ±0.6 μC. The values of $i_{\text{corr.}}$ and $[i\tau^{\frac{1}{2}}/AC^{\circ}]_{\text{corr.}}$ are included in Table 1.

The morphology of the chronopotentiograms is somewhat changed when the concentration of $AuCl_4^-$ is increased to 0.01 *M*. A typical chronopotentiogram for reduction of $AuCl_4^-$ at this concentration is presented in Fig. 1, curve 2. In this case the open circuit potential (+0.69 V *vs.* S.C.E.) does not change significantly when a stirred solution is allowed to become quiet. This is because the initial concentration of $AuCl_4^-$ is very near to the concentration, $9.8 \times 10^{-3}$ *M*, which would be obtained if the reaction reached equilibrium[5]. Because of the form of reaction (1) the relative stability of $AuCl_4^-$ with respect to its reduction by metallic gold increases with increasing total gold concentration.

In addition, the chronopotentiogram now has a potential minimum near the beginning of the electrolysis followed by an increase in potential, a maximum, and then the usual inflection to cathodic potentials as the transition time is approached. The unique shape of this chronopotentiogram is difficult to explain with certainty. It should first be noted that there is a rather large potential jump at the beginning of the electrolysis and the main part of the chronopotentiogram occurs at potentials about 0.2 V less oxidizing than the least oxidizing of the gold couples, $E^{\circ}_{AuCl_4^-, AuCl_2^-} =$ 0.684 V *vs.* S.C.E.[5] This indicates that the electrolytic reactions are occurring quite irreversibly and that the exact interpretation of the maximum in curve 2, Fig. 1, will be a complex function of the various kinetic parameters of the possible electrode reactions.

A tentative explanation which fits most of the facts is that at high $AuCl_4^-$ concentrations the real surface area of the electrode increases during the electrolysis due to the formation of a rough electrode-deposit of gold. Thus the current density decreases and, therefore, the over-potential for the reduction process decreases, causing an increase in the potential of the electrode. Finally the diffusion of $AuCl_4^-$ is unable to keep up with the demand of the constant current and the potential inflects in the cathodic direction causing the maximum in the chronopotentiogram.

This behavior is not observed with $10^{-3}$ *M* $AuCl_4^-$ since the quantity of gold deposited during chronopotentiometric electrolysis is much less than it is for $10^{-2}$ *M* $AuCl_4^-$, and thus the real surface area does not increase as much. This is evidenced by the fact that a single chronopotentiometric trial with $10^{-2}$ *M* $AuCl_4^-$ causes a visible darkening of the electrode surface due to electro-deposited gold but about ten trials are required to obtain a visible surface change with $10^{-3}$ *M* $AuCl_4^-$ (see above).

However, the particles of metallic gold formed on the electrode must extend into the solution a distance which is small compared to the thickness of the diffusion layer since the observed values of $i\tau^{\frac{1}{2}}/AC^{\circ}$ for $10^{-2}$ *M* are not different from those for $i\tau^{\frac{1}{2}}/AC^{\circ}$ at $10^{-3}$ *M*. If the particles extended a significant distance into the diffusion layer, the effective area of the electrode for the diffusion process would be increased and $i\tau^{1/2}/AC^\circ$ for $10^{-2}$ *M* would be expected to be larger than for $10^{-3}$ *M* $AuCl_4^-$. With $10^{-2}$ *M* $AuCl_4^-$ it was necessary to remove anodically electro-deposited gold between each trial since a single chronopotentiometric electrolysis was sufficient to cause a visible darkening of the electrode surface. The electro-deposited gold was removed by anodizing at the same current for a time equal to the preceding cathodic electrolysis time. By this technique the electrode surface retained a lustrous appearance and the effective area of the electrode did not change as evidenced by the reproducibility of transition times.

Transition times as a function of current density are presented in Table 2. As would be expected, the correction for charging the electrical double layer is much less important for $10^{-2}$ *M* $AuCl_4^-$ than it was for $10^{-3}$ *M* $AuCl_4^-$ (*cf.* Table 1).

The data of Tables 1 and 2 are plotted in Fig. 2 in the form of $i\tau^{1/2}/AC^\circ$ *vs.* $\tau$. The solid curve represents the theoretical curve for the three-electron reduction at a cylindrical electrode[7]. The theoretical curve was calculated with the aid of a table of correction factors for cylindrical electrode chronopotentiometry[8]. The diffusion coefficient used in these calculations was $1.06 \times 10^{-5}$ cm²/sec, a value which best fits the experimental data. This compares closely to the polarographically determined value[9] of $1.04 \times 10^{-5}$ cm²/sec in pH = 5 acetate buffer of ionic strength equal to 0.1.

TABLE 2

CATHODIC CHRONOPOTENTIOMETRY OF $10^{-2}$ *M* $AuCl_4^-$

Transition times measured at 3-min. intervals. Transition potential = 0.0 V *vs.* S.C.E. Times are averages of three trials. Average deviation given in parentheses. Concn. of $AuCl_4^- = 1.01_6 \times 10^{-2}$ *M*. Supporting electrolyte was 1 *M* hydrochloric acid. Gold wire electrode, area = 0.173 cm², radius = 0.0255 cm. Temp. = 25.0 ±0.1°.

$i_{corr.} = i_{obs.} - 12.8/\tau$ (see text)

| $\tau$ *(sec)* | $i_{obs.}$ *(μA)* | $i_{corr.}$ *(μA)* | $i\tau^{1/2}/AC^\circ$ *(A sec$^{1/2}$ cm/mole)* *Observed* | *Corrected* |
|---|---|---|---|---|
| 0.68 (±0.00) | 1860 | 1841 | 873 | 864 |
| 0.92 (±0.01) | 1590 | 1576 | 868 | 861 |
| 1.29 (±0.00) | 1383 | 1373 | 894 | 888 |
| 2.45 (±0.02) | 1020 | 1015 | 909 | 904 |
| 3.50 (±0.00) | 860.0 | 856.3 | 916 | 912 |
| 4.28 (±0.00) | 790.0 | 787.0 | 930 | 927 |
| 5.98 (±0.01) | 671.2 | 669.1 | 934 | 931 |
| 7.68 (±0.02) | 610.0 | 608.3 | 962 | 960 |
| 9.30 (±0.04) | 557.8 | 556.4 | 969 | 966 |
| 14.45 (±0.08) | 471.7 | 470.8 | 1021 | 1019 |
| 20.39 (±0.99) | 427.7 | 427.1 | 1099 | 1098 |

The close agreement between the experimental points and the theoretical curve demonstrates that the reduction of $AuCl_4^-$ is a three-electron diffusion-controlled process at both concentration levels in the range of transition times between one and twenty seconds. Figure 2 also demonstrates that the reduction of $AuCl_4^-$ by the metallic gold of the electrode during the quiescent time does not significantly affect the magnitude of the transition time. The data for $10^{-2}$ *M* $AuCl_4^-$ with which there is little pre-reduction, agree closely with the data for $10^{-3}$ $M$ where a considerable amount of $AuCl_2^-$ is formed at the electrode. This is due to the fact that the number of equivalents of reducible gold is not changed by the reaction so that, although the $AuCl_4^-$ concentration near the electrode is decreased, an equivalent amount of reducible $AuCl_2^-$ is formed and the number of equivalents of gold available for reduction is unchanged.

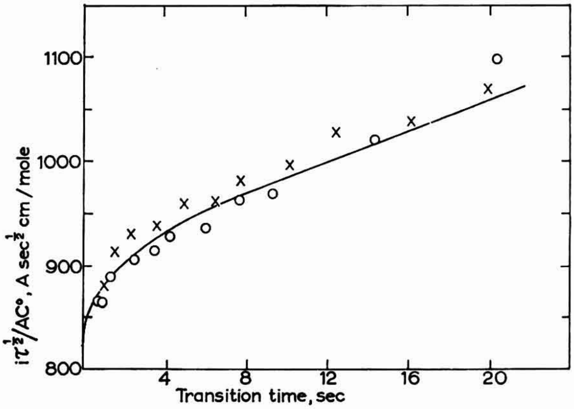

Fig. 2. $i\tau^{\frac{1}{2}}/AC°$ (corrected) as a function of transition time for the reduction of $AuCl_4^-$ at a gold cathode. Crosses, data for $1.00_6 \times 10^{-3}$ $M$ $AuCl_4^-$ from Table 1; circles, data for $1.01_6 \times 10^{-2}$ $M$ $AuCl_4^-$ from Table 2. Solid curve is theoretical curve for 3-electron process calculated with $D = 1.06 \times 10^{-5}$ cm²/sec and radius = 0.0255 cm.

### REDUCTION OF MIXTURES OF $AuCl_4^-$ AND $AuCl_2^-$

Although $AuCl_4^-$ itself does not produce a double chronopotentiometric wave, two waves are obtained with mixtures of $AuCl_4^-$ and $AuCl_2^-$ if the concentration of the latter is greater than the equilibrium concentration. In such solutions, the homogeneous disproportionation of $AuCl_2^-$ is very slow, so that, in the absence of catalytic surfaces, the solutions are fairly stable.

Solutions containing a mixture of $AuCl_4^-$ and $AuCl_2^-$ can be obtained by anodizing a gold electrode in 1 $M$ hydrochloric acid. In one experiment, a gold gauze electrode (projected area = 160 cm²) was anodized in 125 ml of 1 $M$ hydrochloric acid for 2000 sec at 26.90 mA. Since the dissolution proceeds with 100% current efficiency under these conditions[5], the total normality of gold in the solution can be calculated from the current, time of electrolysis and volume of solution *via* Faraday's law. The normality was $4.46_1 \times 10^{-3}$ $N$. The concentration of $AuCl_4^-$ can be determined at any moment by withdrawing a sample of solution and determining the absorbance in the ultraviolet. The molar absorptivity[5] of $AuCl_4^-$ at 312 mμ in 1 $M$ hydrochloric acid is 5560 l/mole cm. The concentration of $AuCl_2^-$ can then be calculated by difference from the total normality and the concentration of $AuCl_4^-$ by the equation

$$[AuCl_2^-] = N_T - 3\,[AuCl_4^-] \tag{3}$$

where $N_T$ is the total normality of gold in solution.

The solution described above was prepared in the chronopotentiometric cell.

After generating the gold species, the gold gauze electrode was removed and a cylindrical gold wire electrode (area = 0.173 cm²) was inserted and curve 1, Fig. 3, was recorded using a current of 102.3 μA. Within a few minutes a sample of the solution was withdrawn and the concentrations of $AuCl_4^-$ and $AuCl_2^-$ were determined. The large gold gauze electrode was then returned to the cell and the solution was stirred with nitrogen for 2 h. During this time $AuCl_2^-$ disproportionated at the large gold gauze electrode and the $AuCl_4^-$ concentration increased. Then the gauze electrode was removed, the cylindrical gold electrode was placed in the cell and curve 2, Fig. 3, was recorded at the same current. Again a sample of solution was removed for analysis. The process was repeated and curve 3 was recorded 2 h after curve 2. Finally, 18 h after curve 3, curve 4 was recorded.

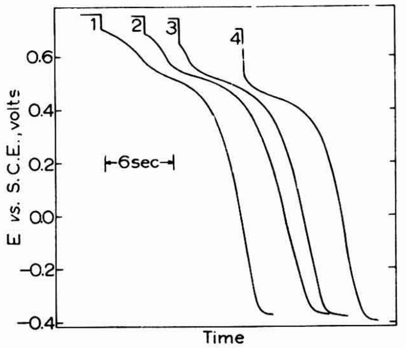

Fig. 3. Chronopotentiograms for the reduction of mixtures of $AuCl_2^-$ and $AuCl_4^-$. Curve 1, solution freshly prepared; curve 2, solution equilibrated with large gold gauze electrode for 2 h; curve 3, equilibration for a total of 4 h; curve 4, equilibration for a total of 22 h. Total normality of gold = $4.46_1 \times 10^{-3}$ *N*. $i$ = 102.3 μA. Electrode area = 0.173 cm², radius = 0.0255 cm, temp. = 25.0 ±0.1°.

Table 3 summarizes the relevant data from Fig. 3. The concentration data were obtained from spectrophotometric measurements as described above. The magnitude of $\tau_1$ decreases as the concentration of $AuCl_2^-$ decreases. Assuming for the moment that the first wave is due to the reduction of $AuCl_2^-$ to metallic gold, $i\tau_1^{\frac{1}{2}}/AC^\circ_{AuCl_2^-}$ should be constant. That this is more or less true is demonstrated in column 5, Table 3. (The quantities are expected to be only approximately constant because of variations due to cylindricity).

TABLE 3

REDUCTION OF MIXTURES OF $AuCl_2^-$ AND $AuCl_4^-$

Data pertain to chronopotentiograms of Fig. 3. Total normality of gold = $4.46 \times 10^{-3}$ *N*. $i$ = 102.3 μA. Electrode area = 0.173 cm², radius = 0.0255 cm. Temp. = 25.0 ±0.1°.

| *Time (h)* | $[AuCl_2^-]$ *(M)* | $[AuCl_4^-]$ *(M)* | $\tau_1$ *(sec)* | $i\tau_1^{\frac{1}{2}}/AC^\circ$ $(C^\circ = [AuCl_2^-])$ | $\tau_1 + \tau_2$ *(sec)* |
|---|---|---|---|---|---|
| 0 | $3.27 \times 10^{-3}$ | $3.97 \times 10^{-4}$ | 3.30 | 328 | 12.03 |
| 2 | $2.40 \times 10^{-3}$ | $6.85 \times 10^{-4}$ | 1.83 | 333 | 12.24 |
| 4 | $1.76 \times 10^{-3}$ | $9.01 \times 10^{-4}$ | 0.90 | 319 | 10.80 |
| 22 | $3.81 \times 10^{-4}$ | $1.36 \times 10^{-3}$ | —* | — | 8.49 |

* Transition time too short to be detected in Fig. 3.

In general, it was found to be rather difficult to obtain reproducible results for $\tau_1$ mainly because the first wave is poorly separated from the second and the separation decreases as the $AuCl_2^-$ concentration decreases. However, the dependence of $\tau_1$ on $AuCl_2^-$ concentration leaves little doubt that the first wave is due to the reduction of $AuCl_2^-$. The $AuCl_2^-$ concentration is so small in curve 4, Fig. 3, that $\tau_1$ is too short to be visible at this current density. From the observed values of $i\tau_1/^{\frac{1}{2}}AC^\circ$, it was calculated that $\tau_1$ in curve 4 should be only about 0.04 sec. A wave for the reduction of $AuCl_2^-$ was observed with the solution used to obtain curve 4 when the current density was appropriately decreased.

Since $AuCl_2^-$ disproportionates at the electrode surface during the quiescent period causing a decrease in $AuCl_2^-$ concentration and an increase in $AuCl_4^-$ concentration near the electrode surface, quantitative interpretation of the relative magnitudes of the first and second transition times would be very complex.

These experiments graphically illustrate the reason that $AuCl_4^-$ cannot be reduced in a step-wise fashion. The reduction wave for $AuCl_2^-$ occurs at a more oxidizing potential than the reduction wave for $AuCl_4^-$ so, if $AuCl_2^-$ were an intermediate in the reduction of $AuCl_4^-$, it would be reduced as soon as it were formed. This is to be expected from the standard potentials of the gold couples. However, if the overpotential for $AuCl_2^-$ reduction were great enough, its reduction wave could occur at a less oxidizing potential than the wave for $AuCl_4^-$ and the reduction of $AuCl_4^-$ might proceed in a step-wise fashion producing two chronopotentiometric waves. But, as Fig. 3 demonstrates, the overpotential for the reduction of $AuCl_2^-$ is not great enough to push the $AuCl_2^-$ wave below the $AuCl_4^-$ wave. This is not to say that $AuCl_2^-$ cannot be an intermediate in the reduction of $AuCl_4^-$ but rather that it could not be detected by chronopotentiometry if it were.

## ACKNOWLEDGEMENT

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## SUMMARY

The electrolytic reductions of $AuCl_4^-$ and $AuCl_2^-$ in hydrochloric acid were studied at a gold electrode by chronopotentiometry. At concentrations of $10^{-3}$ and $10^{-2}$ $M$, $AuCl_4^-$ is reduced in a single three-electron wave. Two chronopotentiometric waves are observed with mixtures of $AuCl_4^-$ and $AuCl_2^-$ in which the concentration of the latter exceeds the equilibrium concentration. The first, more oxidizing wave is due to the reduction of $AuCl_2^-$ and the second wave is due to the reduction of $AuCl_4^-$.

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# THE POLAROGRAPHIC AND CHRONOPOTENTIOMETRIC CHARACTERISTICS OF REVERSIBLE STEP-WISE ELECTRODE REACTIONS

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## INTRODUCTION

Many electrode reactions exist which, from casual inspection of the consequent current–voltage curves, evidently involve an intermediate electro-active in a potential range separated from that of the reactant. Generally such reactions can be described by the equations

$$O + n_2 e \rightarrow S \tag{1a}$$

$$S + n_1 e \rightarrow R \tag{1b}$$

in which $S$ represents the intermediate, $O$ the oxidised and $R$ the reduced species. Reactions (1a) and (1b) have standard potentials $E_2$ and $E_1$, respectively, whose separation may be expressed in terms of the classical equilibrium constant, $K_1$, of the intermediate formation reaction (1c):

$$n_1 O + n_2 R \rightleftharpoons (n_1 + n_2) S \tag{1c}$$

Thus:

$$E_2 - E_1 = \frac{RT}{n_1 n_2 F} \ln K_1$$

The appearance of two 'steps' in the polarographic wave, separately due to the reactions (1a) and (1b), requires that the intermediate $S$ has appreciable stability so that $K_1$ is large enough to make $E_2 - E_1$ of the order of 100 mV or greater. In the case of $n_1 = n_2 = 1$ for example, steps are not apparent for $K_1 < 50$, and reversible polarographic waves due to systems having values for $K_1$ in the region of $0 < K_1 < 50$ might easily be confused with irreversible waves having $K_1 = 0$.

Another possibility is that highly reactive intermediates are stabilised by dimerisation:

$$2\,S \underset{K_3}{\rightleftharpoons} D \tag{1d}$$

The dimer $D$ is electroactive, but its presence has an effect upon the shape of polarographic characteristics.

Similar comments apply to the potential–time curve resulting from galvanostatic polarisation of an electrode, at which reaction systems of type 1 supply the current.

Evidently, it is important to have criteria which identify the reaction mechanism responsible for the form of each experimental result, and which determine the equilibrium constants of reactions (1c) and 1(d). This problem has received some attention from previous workers, but their published treatments incorporate some unsatisfactory features. MÜLLER[1] and BRDIČKA[2] discussed reversible polarographic waves due to this system, following theories of potentiometric titration curves developed by MICHAELIS[3] and ELEMA[4]. Apart from restriction in these papers to the case $n_1 = n_2 = 1$, and to "cathodic wave conditions" an approximation was introduced into a surface boundary condition which is now recognised as an assumption of a common diffusion coefficient for all of the species involved in the reaction. Furthermore the means of analysis of the current–voltage curve suggested by these authors was indirect, requiring prior determination of the above-mentioned equilibrium constants through the use of index potentials. The restrictions and the approximation are here removed, and a direct means of analysis is proposed which employs the whole of the current–voltage curve. The calculation is treated in a manner valid for dropping mercury, rotating disc, and plane electrodes.

The chronopotentiometric behaviour of these systems was treated by BERZINS AND DELAHAY[5], again for the case in which only substance $O$ is present in solution, and with the restriction that the potentials $E_1$ and $E_2$ are so well separated that reduction of $O$ is diffusion-controlled in the region of $E_1$. The determination of reversible potential–time curves in the situation of arbitrary separation of $E_1$ and $E_2$ was referred to by TESTA AND REINMUTH[6], but they did not proceed to discussion of means of analysis of experimental transients. The general case is treated here, and methods of determination of the equilibrium constants, quite analogous to those established for polarographic waves, are detailed.

The restriction to *reversible* polarographic and chronopotentiometric waves is retained, because the essential features of experimental results are thereby determined, and unambiguous means of analysis into the important parameters is found to be feasible. The modifications to wave shape introduced by irreversibility will be considered in a later paper.

In the first sections of the paper the solution in the special case $n_1 = n_2 = 1$, $K_3 = 0$ is outlined as an illustration of the mathematical method, then in later sections polarographic and galvanostatic conditions are separately specified in the general case of reaction (1). Finally polarographic waves due to pyrazine reduction are analysed in the recommended manner.

## THE SPECIAL CASE $n_1 = n_2 = 1$, NO DIMERISATION ($K_3 = 0$)

When equilibrium exists between all of the reactants in a consecutive reactions system, two Nernst equations may be written relating the surface concentrations. These are conveniently expressed in the form

$$1 - u_O = e^{f\eta}(1 - u_S) \tag{2}$$

$$1 - u_O = e^{2f\eta}(1 - u_R) \tag{3}$$

The values for $u$ are defined by:

$$u_i = \frac{C_i^b - C_i}{C_i^b} \tag{4}$$

with $i = O, S$, or $R$, and in which $C_i$ is the surface concentration and $C_i^b$ is the bulk concentration of species $i$; $f = F/RT$ where $F$ is the Faraday, $R$ is the gas constant and $T$ is the absolute temperature; $\eta = E - E_0$, where $E_0$ is the observed equilibrium potential of the system and $\eta$ is the overpotential of the working electrode. A third equation is required for the calculation of the surface concentration functions, and this may be derived by stipulation that the concentrations simultaneously satisfy diffusion equations appropriate to the electrode employed, and the boundary condition at the electrode surface:

$$\sum_i D_i \frac{\partial C_i}{\partial n} = 0 \tag{5}$$

$n$ represents the direction normal to the electrode surface, $D_i$ is the diffusion coefficient of species $i$, and the boundary condition (5) asserts that there is no accumulation of material at the electrode surface. Field-dependent terms have been omitted because it is assumed that the experimental conditions are those of standard polarographic practice, having an excess of indifferent electrolyte.

Koutecký and Koryta[7] have shown that functions $\psi_i$ which simultaneously obey diffusion equations of the type

$$\frac{\partial \psi_i}{\partial t} = D_i \frac{\partial^2 \psi_i}{\partial x^2} \quad 0 \leqslant x < \infty \tag{6}$$

and boundary conditions of the form of (5), also obey the relation

$$\sum_i \sqrt{D_i}\,\psi_i(x = 0) = \sum_i \sqrt{D_i}\,\psi_i(x \to \infty) \tag{7}$$

Hence the functions $u_i$, for example, are inter-related in the manner:

$$\sum_i \sqrt{D_i}\,C_i^b\, u_i(x = 0) = 0 \tag{8}$$

Equation (8) becomes identical with the surface boundary condition employed by Müller and Brdička, upon assumption that the $D_i$ have a common value. That eqn. (8) also applies to the dropping mercury electrode in the Ilkovič approximation, may be seen by transformation of the diffusion equation[8]

$$\frac{\partial \psi_i}{\partial l} = D_i \frac{\partial^2 \psi_i}{\partial x^2} + \frac{2x}{3t}\frac{\partial \psi_i}{\partial x} \tag{9}$$

into the form (6). This may be achieved for instance, by substituting

$$z = x\,t^{\frac{2}{3}} \quad \text{and} \quad \tau = \tfrac{3}{7}\,t^{7/8} \tag{10}$$

Then:

$$\frac{\partial \psi_i}{\partial \tau} = D_i \frac{\partial^2 \psi_i}{\partial z^2} \tag{11}$$

and

$$\sum_i D_i \frac{\partial \psi_i}{\partial z} = 0$$

The argument put forward by Koutecký and Koryta is directly applicable to these equations, so that the functions $\psi_i$ satisfy eqn. (7) and the functions $u_i$ satisfy eqn. (8), at a dropping mercury electrode in this approximation.

In the steady state the convective diffusion equation in one dimension applicable to a rotating disc electrode[9], may be written:

$$D_i \frac{d^2\psi_i}{dx^2} = v \frac{d\psi_i}{dx} \tag{12}$$

which is transformed into Laplace's equation by the substitution[10]:

$$z_i = \frac{\int_0^x e^{\int^x (v/D_i)dx} dx}{\delta_i}$$

where

$$\delta_i = \int_0^\infty e^{\int^x (v/D_i)dx} dx \tag{13}$$

Thus

$$\frac{d^2\psi_i}{dz_i^2} = 0 \quad (0 \leqslant z_i \leqslant 1)$$

and boundary condition (5) becomes

$$\sum_i \frac{D_i C_i^b}{\delta_i} \cdot \frac{du_i}{dz_i} = 0.$$

Following the method of KOUTECKÝ AND KORYTA, we define a function

$$\Psi = \sum_i \frac{D_i C_i^b}{\delta_i} u_i(z_i = z)$$

in which all the $u_i$ are calculated at the same value of $z$, *i.e.*, at appropriate values of $z_i$. $\Psi$ obeys Laplace's equation, and the condition

$$\frac{d\Psi}{dz} = 0 \quad \text{at} \quad z = 0.$$

It is therefore constant for all $z$, and in particular

$$\sum_i \frac{D_i C_i^b}{\delta_i} u_i(z_i = 0) = \sum_i \frac{D_i C_i^b}{\delta_i} u_i(z_i = 1) = 0 \tag{14}$$

Equations (8) and (14) may be combined in a more general form, by noting previously established formulae[8] for diffusion-limited currents at each of the electrodes of interest here:

Thus

$$i_{i,d} = \frac{FAC_i^b D_i}{\delta_i}$$

At a plane electrode

$$\delta_i = \sqrt{\pi D_i t}$$

at a dropping mercury electrode

$$\delta_i = \sqrt{\frac{3}{7}\pi D_i t}$$

at a rotating disc electrode

$$\delta_i = 1.63\, D_i^{\frac{1}{3}}\, \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}.$$

$\nu$ is the kinematic viscosity of the solution in which the disc is immersed, and $\omega$ is the rotation velocity of the electrode.

It follows that a boundary condition upon surface concentration functions $u_i = (C_i^b - C_i)/C_i^b$ is

$$\sum_i i_{i,d}\, u_i(x = 0) = 0 \tag{15}$$

Alternatively this relation may be written in terms of the dimensionless quantities:

$$r_1 = \frac{i_{S,d}}{i_{R,d}} \qquad r_2 = \frac{i_{O,d}}{i_{S,d}} \tag{16, 17}$$

with the result

$$u_R + r_1 u_S + r_1 r_2 u_O = 0 \tag{18}$$

Equations (2), (3) and (18) above, are sufficient for the determination of the surface concentration functions $u_i(x = 0)$. It is found that

$$u_O(0) = \frac{1 + r_1 e^{f\eta} - r_1 e^{2f\eta} - e^{2f\eta}}{1 + r_1 e^{f\eta} + r_1 r_2 e^{2f\eta}} \tag{19a}$$

$$u_R(0) = \frac{-r_1(1 + r_2 - e^{f\eta} - r_2 e^{2f\eta})}{1 + r_1 e^{f\eta} + r_1 r_2 e^{2f\eta}} \tag{19b}$$

$$u_S(0) = \frac{1 + r_1 r_2 e^{2f\eta} - r_1 r_2 e^{f\eta} - e^{f\eta}}{1 + r_1 e^{f\eta} + r_1 r_2 e^{2f\eta}} \tag{19c}$$

### *Derivation of the current at constant potential*

Although the expressions (19) are independent of time, time-dependence of the concentrations is observed at all points other than those at the surface and in the bulk of the solution. Thus the surface concentration gradient and hence the current is time-dependent. The latter is most easily calculated by construction of a boundary value problem in the functions

$$y_i = \frac{u_i(0) - u_i}{u_i(0)} \qquad i = O, S, \text{ and } R \tag{20}$$

$u_i$ (0) is the magnitude of the function $u_i$ at the electrode surface, as given by eqn. (19). Evidently

$$\left.\begin{aligned} y_i &= 0 \quad \text{at} \quad x = 0 \\ &= 1 \quad \text{at} \quad x \to \infty \\ &= 1 \quad \text{at} \quad t = 0 \end{aligned}\right\} \tag{21}$$

$x$ and $t$ represent the independent distance and time variables. Consider now the problem the solution of which is required for determination of the limiting current at the electrode in question. In terms of $v_i = C_i/C_i^b$ the boundary conditions are:

$$\left.\begin{aligned} v_i &= 0 \quad \text{at} \quad x = 0 \\ &= 1 \quad \text{at} \quad x \to \infty \\ &= 1 \quad \text{at} \quad t = 0 \end{aligned}\right\} \tag{21a}$$

which are identical with the conditions of eqns. (21). Furthermore, $y_i$ and $v_i$ satisfy the same differential equation, so that they are identical functions of distance and time.

But[8]

$$FAD_iC_i^b \left(\frac{\partial v_i}{\partial x}\right)_{x=0} = i_{i,d}$$

so that

$$\left(\frac{\partial v_i}{\partial x}\right)_{x=0} = \left(\frac{\partial y_i}{\partial x}\right)_{x=0} = \frac{i_{i,d}}{FAD_iC_i^b}$$

and in terms of $u_i$ once more we find:

$$\left(\frac{\partial u_i}{\partial x}\right)_{x=0} = -u_i(0)\frac{i_{i,d}}{FAD_iC_i^b} \tag{22}$$

The observed current has contributions from each of the electron transfer reactions (1a) and (1b)

$$i = i_{1a} + i_{1b}$$

Equality of the rates of electron transfer and reactant supply requires that:

$$i_{1a} = FAD_O\left(\frac{\partial C_O}{\partial x}\right)_{x=0} \quad \text{and} \quad i_{1b} = -FAD_R\left(\frac{\partial C_R}{\partial x}\right)_{x=0}$$

whence

$$\begin{aligned} i &= -FAD_OC_O^b\left(\frac{\partial u_O}{\partial x}\right)_{x=0} + FAD_RC_R^b\left(\frac{\partial u_R}{\partial x}\right)_{x=0} \\ &= i_{O,d}u_O(0) - i_{R,d}u_R(0) \end{aligned} \tag{23}$$

by eqn. (22). Substitution of $u_O(0)$ and $u_R(0)$ from eqns. (19a) and (19b) yields:

$$i_\infty = i_{O,d}\frac{2(1 - e^{2f\eta}) + \left(\frac{1}{r_2} + r_1 e^{f\eta}\right)(1 - e^{f\eta})}{1 + r_1e^{f\eta} + r_1r_2e^{2f\eta}} \tag{24}$$

The subscript $\infty$ connotes infinite reaction rate.

At constant potential the dependence of $i_\infty$ upon extraneous parameters such as time at the dropping or plane electrodes, and rotation speed at the rotating disc electrode, is of the same functional form as the dependence of $i_d$ upon these parameters—essentially because of the condition of diffusion control. Indeed this requirement is a principal diagnostic criterion for identification of a reversible system. At very high cathodic overpotentials $\eta \to -\infty$, a limiting current is observed, the magnitude of which is correctly predicted by eqn. (24) to be:

$$i_\infty = i_1 = 2\, i_{O,d} + i_{S,d} \tag{25}$$

Similarly at very high anodic overpotentials $\eta \to +\infty$

$$-i_\infty = i_2 = 2\, i_{R,d} + i_{S,d} \tag{26}$$

Anodic current is taken conventionally to be negative, and introduction of the minus sign here is necessary in order that $i_2$ is defined as a positive quantity. The ratio of cathodic to anodic limiting currents reduces to:

$$r = \frac{i_1}{i_2} = \frac{2\, r_1 r_2 + r_1}{2 + r_1} \tag{27}$$

Hence

$$i_\infty = \frac{i_1\,(1 - e^{f\eta})\left(1 + \dfrac{r_1 r_2}{r} e^{f\eta}\right)}{1 + r_1 e^{f\eta} + r_1 r_2 e^{2f\eta}} \tag{24a}$$

Prior calculation of $r_1$ and $r_2$ requires knowledge of the bulk concentrations of each of the species $O$, $S$, and $R$, yet it will often be the case that only the sum of the concentrations of these species is known. Information about these constants is contained in the shape of the current–voltage curve however, and can be extracted—for example by noting the significance of the 'half-wave potential', $E_{\frac{1}{2}}$. At this point the current is one half of the sum of the anodic and cathodic limiting currents, when in magnitude,

$$i_{\frac{1}{2}} = \tfrac{1}{2}(i_1 - i_2) = i_{O,d} - i_{R,d} \tag{28}$$

Substitution of eqn. (28) into eqn. (24) and some cancellation produces the result:

$$r_1 r_2 = e^{-2f\eta_{\frac{1}{2}}}$$

where

$$\eta_{\frac{1}{2}} = E_{\frac{1}{2}} - E_0$$

Hence the product $r_1 r_2$ is determined by the overvoltage of the half-wave potential from the equilibrium potential, so that together with the formula given for $r$, there is sufficient information for the calculation of $r_1$ and $r_2$.

A more satisfactory procedure depends upon a transformation of the whole current–voltage curve to the origin, $i_{\frac{1}{2}}$, $E_{\frac{1}{2}}$. At the same time it is expedient to introduce a reduced current and to determine the equation for the current–voltage characteristic in terms of the quantities[11]:

$$i_\infty{}' = \frac{i_\infty - i_{\frac{1}{2}}}{\frac{1}{2}(i_1 + i_2)} \quad \text{and} \quad \eta' = \eta - \eta_{\frac{1}{2}} \tag{29}$$

It is found that:

$$i_\infty{}' = \frac{1 - e^{2f\eta'}}{1 + p e^{f\eta'} + e^{2f\eta'}} \tag{30}$$

and the shape of the current–voltage curve depends only upon a parameter

$$p = \sqrt{\frac{r_1}{r_2}} = \frac{C_S{}^b}{\sqrt{C_O{}^b C_R{}^b}} \frac{D_S}{\delta_S} \sqrt{\frac{\delta_O \delta_R}{D_O D_R}} = \sqrt{K} \frac{D_S}{\delta_S f_S} \sqrt{\frac{\delta_O f_O}{D_O} \cdot \frac{\delta_R f_R}{D_R}} \tag{31}$$

$K$ is the thermodynamic equilibrium constant of the intermediate-formation reaction:

$$O + R \overset{K}{\rightleftharpoons} 2\,S$$

and the $f$'s are activity coefficients. In practice, the quantities $D, f$ and $\delta$ applicable to the species $S$, will be intermediate between those for species $O$ and $R$, and it is expected that $p$ will be very nearly equal to $\sqrt{K}$. Fig. 1 illustrates the variations of wave shape attributable to selected values of $p$; the cathodic branch only is shown, of the dependence of $i'$ on $f\eta'$ as predicted by eqn. (30). The curve is symmetrical with respect to inversion through the origin, as may be seen readily, for example, by multiplication of numerator and denominator on the right-hand side of eqn. (30) by $e^{-2f\eta'}$ when

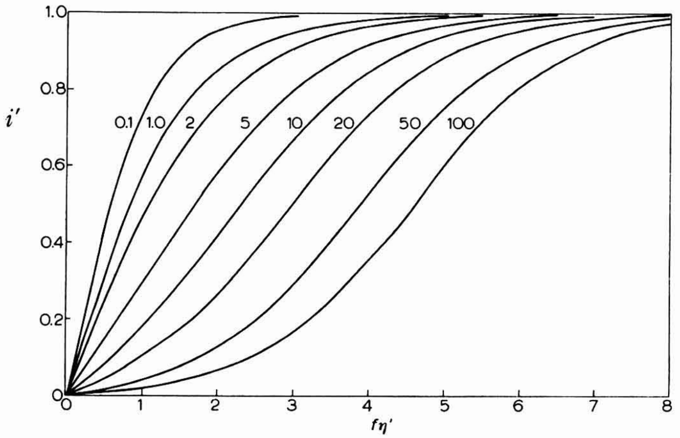


Fig. 1. Cathodic branch of dependence of $i'$ on $f\eta'$. The number attached to each curve is the appropriate value of $p$.

$$\eta' \to -\eta', \quad i_\infty' \to -i_\infty'$$

A basis for analysis of experimental polarographic waves due to consecutive reactions, is easily derived by rearrangement of eqn. (30); $pe^{f\eta'}$ is isolated from the remainder and the resultant expression is converted into its logarithmic form:

$$\ln \left\{ \frac{1}{i'} - 1 - e^{2f\eta'} \left( \frac{1}{i'} + 1 \right) \right\} = \ln p + f\eta' \tag{32}$$

The dimensionless quantities $i'$ and $f\eta'$ are calculated from the experimental current–voltage co-ordinates, and the left-hand side of eqn. (32) is computed and plotted against $f\eta'$.

A check on the reversible character of the wave, and of the applicability of this model, is provided by the requirement that the slope of the resultant straight line is unity. The intercept identifies the magnitude of the parameter $p$.

In the case of a 'cathodic' wave, having $C_S{}^b = C_R{}^b = 0$; $i_1 = 2\, i_{O,d}$, $i_2 = 0$ and

$$\eta' = E - E_{\frac{1}{2}}$$

where

$$E_{\frac{1}{2}} = E_m + \frac{RT}{2F} \ln \frac{D_R}{\delta_R f_R} \frac{\delta_O f_O}{D_O}$$

$E_m$ is the 'mean' potential, given by $E_m = \frac{1}{2}(E_1 + E_2)$.

It might be suspected that eqn. (30) was inapplicable in this case, because the functions $u_R$ and $u_S$ can have no meaning here, yet a re-derivation using quantities $V_i = C_i{}^b - C_i$ confirms its validity. An alternative representation which facilitates comparison with the work of BRDIČKA[2], is found by retracing one step to an expression in terms of $i$ rather than $i'$:

$$\frac{i}{2\, i_{O,d}} = \frac{1 + \frac{1}{2} p\mathrm{e}^{f\eta'}}{1 + p\mathrm{e}^{f\eta'} + \mathrm{e}^{2f\eta'}} \tag{33}$$

which equation becomes identical with eqn. (15a) of BRDIČKA's paper after making the approximation $p = \sqrt{K}$. Thus all discussion of the current–voltage curve in terms of gradients and index potentials presented by previous authors, is applicable here, though strictly $p$ is determined rather than $\sqrt{K}$. As an illustration of the observed shape of cathodic waves in these systems, the right-hand side of eqn. (33) is plotted against potential ($f\eta'$) for various values of $p$, in Fig. 2.

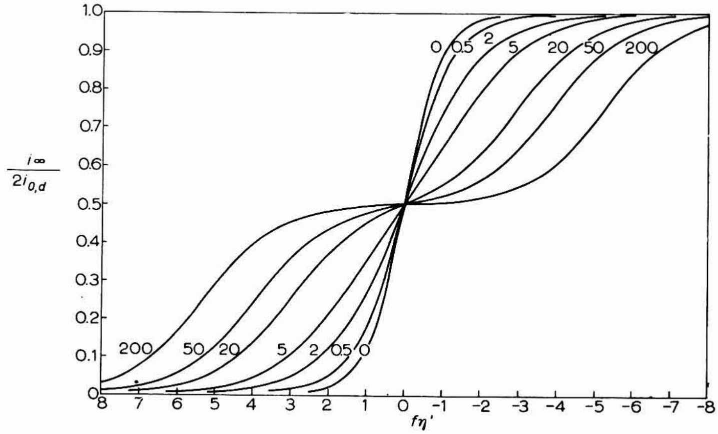


Fig. 2. Cathodic wave-shape. The number attached to each curve is the appropriate value of $p$.

Analysis of the reversible cathodic wave might be based upon eqn. (32), or upon eqn. (34) which results from rearrangement of eqn. (33).

$$\ln \left\{ \frac{2\, i_{O,d} - i\,(1 + \mathrm{e}^{2f\eta'})}{i - i_{O,d}} \right\} = \ln p + f\eta' \tag{34}$$

## GENERALIZATION TO THE CASE OF TWO MULTI-ELECTRON-TRANSFER STEPS, WITH DIMERISATION OF THE INTERMEDIATE SPECIES

We consider in this section the more general problem of a two-step polarographic wave, in which the individual steps might be of different heights, and in which there might be dimerisation of the intermediate species. The reaction system in equilibium is described by the equations:

$$O + n_2 e \rightleftharpoons S \tag{35a}$$

$$S + n_1 e \rightleftharpoons R \tag{35b}$$

$$n_1 O + n_2 R \rightleftharpoons (n_1 + n_2) S \tag{35c}$$

$$2\, S \rightleftharpoons D \tag{35d}$$

The stoichiometric numbers appearing in these reactions are consistent with conservation of charge.

Equilibrium conditions specify three relations among the four surface concentrations, namely:

$$\frac{C_O}{C_R} = \frac{C_O{}^b}{C_R{}^b}\, e^{(n_1+n_2)f\eta} = P \tag{36}$$

$$\frac{C_S{}^{(n_1+n_2)}}{C_O{}^{n_1} C_R{}^{n_2}} = K_1 \tag{37}$$

$$\frac{C_D{}^{(n_1+n_2)}}{C_O{}^{2n_1} C_R{}^{2n_2}} = K_2 \tag{38}$$

$\eta$ is the overpotential from the equilibrium potential of the electrode and $P$ is the equilibrium constant of the overall electrode reaction. $K_1$ and $K_2$ are the classical equilibrium constants for formation of the intermediate ($K_1$) and of the dimer ($K_2$) from $O$ and $R$.

As in the previous case, conservation of flux is required at the electrode surface, and provides the fourth relation necessary for determination of the individual concentrations. It is found that:

$$D_O \frac{\partial C_O}{\partial x} + D_S \frac{\partial C_S}{\partial x} + D_R \frac{\partial C_R}{\partial x} + 2\, D_D \frac{\partial C_D}{\partial x} = 0 \qquad \text{at } x = 0$$

whence previously employed arguments show that:

$$\frac{D_O}{\delta_O}(C_O{}^b - C_O) + \frac{D_S}{\delta_S}(C_S{}^b - C_S) + \frac{D_R}{\delta_R}(C_R{}^b - C_R) + \frac{2\, D_D}{\delta_D}(C_D{}^b - C_D) = 0 \tag{39}$$

The expression for $C_R$ derived from eqns. (36)–(39) is most conveniently written:

$$C_R = a \frac{\sqrt{b^2 + 4q\, e^{2n_1 f\eta'}} - b}{2q\, e^{2n_1 f\eta'}} \tag{40}$$

where the parameters $a$, $b$, $q$ and $\eta'$ are defined as follows:

$$a = C_R{}^b + \frac{D_S\delta_R}{\delta_S D_R} C_S + \frac{D_O\delta_R}{\delta_O D_R} C_O + \frac{2\, D_D\delta_R}{\delta_D D_R} C_D \tag{41}$$

$$b = 1 + p\, e^{n_1 f\eta'} + \frac{n_1}{n_2} e^{(n_1+n_2)f\eta'} \tag{42}$$

$$p = \left[\frac{n_1}{n_2}\right]^{n_1/(n_1+n_2)} \frac{i_{S,d}}{(i_{O,d}{}^{n_1} \cdot i_{R,d}{}^{n_2})^{1/(n_1+n_2)}} \tag{43}$$

$$q = 2\left[\frac{n_1}{n_2}\right]^{2n_1/(n_1+n_2)} \frac{i_1 + i_2}{n_1 + n_2} \frac{i_{D,d}}{(i_{O,d}{}^{n_1}\, i_{R,d}{}^{n_2})^{2/(n_1+n_2)}} \tag{44}$$

$$\eta' = \eta - \frac{1}{(n_1 + n_2)f} \ln \frac{n_1 i_{R,d}}{n_2 i_{O,d}} \tag{45}$$

In these equations, ratios of the previously defined limiting currents $i_{i,d}$ are written in abbreviation of the equivalent ratios in the quantities $D_iC_i{}^b/\delta_i = i_{i,d}/FA$, $p$ and $q$ are dimensionless parameters, and are related to the $1/(n_1 + n_2)$th powers of $K_1$ and $K_2$ respectively. Thus the magnitude of $p$ reflects the degree of intermediate formation, and in the case $n_1 = n_2 = 1$, becomes identical with the corresponding quantity defined by eqn. (31). Similarly $q$ is a measure of the extent of dimerisation, but is also related to the sum of the bulk concentrations of all of the species, represented by the factor:

$$\frac{i_i + i_2}{n_1 + n_2} = \frac{FAD_R a}{\delta_R}$$

$i_1$ and $i_2$ are the limiting cathodic and anodic currents observed in this system:

$$i_1 = (n_1 + n_2)i_{O,d} + n_1 i_{S,d} + 2\, n_1 i_{D,d} \tag{46}$$

$$i_2 = (n_1 + n_2)\, i_{R,d} + n_2 i_{S,d} + 2\, n_2 i_{D,d} \tag{47}$$

At intermediate potentials the current is derivable from the expression

$$\frac{i}{FA} = n_2 D_O \frac{\partial C_O}{\partial x} - n_1 D_R \frac{\partial C_R}{\partial x}$$

As in the paragraphs preceding eqn. (23), we note that the time independence of $C_i(0)$ (at constant potential) allows a relationship to be established between the surface concentration gradient $(\partial C_i/\partial x)_{x=0}$ of this problem, and that of the limiting current problem. Thus in analogy with eqn. (23) we find here:

$$i = n_2 i_{O,d} \frac{C_O{}^b - C_O(0)}{C_O{}^b} - n_1 i_{R,d} \frac{C_R{}^b - C_R(0)}{C_R{}^b}$$

Using eqns. (36) and (45) for the further reduction of this expression we find:

$$i' = \frac{i - \dfrac{n_2 i_1 - n_1 i_2}{n_1 + n_2}}{\dfrac{i_1 + i_2}{n_1 + n_2}} = n_1(1 - e^{(n_1+n_2)f\eta'}) \frac{C_R(0)}{a} \tag{48}$$

Hence the origin of the $i' - \eta'$ characteristic may be determined by the condition that

$$i = \frac{n_2 i_1 - n_1 i_2}{n_1 + n_2} \quad \text{when} \quad i' = 0.$$

Substituting foı $C_R(0)/a$ from eqn. (40) we have:

$$i' = \frac{n_1(1 - e^{(n_1+n_2)f\eta'})}{2q\, e^{2n_1 f\eta'}} \left\{\sqrt{b^2 + 4q\, e^{2n_1 f\eta'}} - b\right\} \tag{49}$$

which is the required expression for the current–voltage curve. Its shape depends upon $n_1$ and $n_2$, $p$ and $q$. By expansion of the square-root under appropriate conditions, the cathodic limit of $i'$ is found to be $n_1$, whilst on the anodic side the limiting value is $-n_2$. The same expansion serves to establish the identity of $i'$ as given by eqns. (49) and (30) in the particular case of $n_1 = n_2 = 1$, $q = 0$. If $n_1$ and $n_2$ differ from unity, the current–voltage curve is to be calculated from:

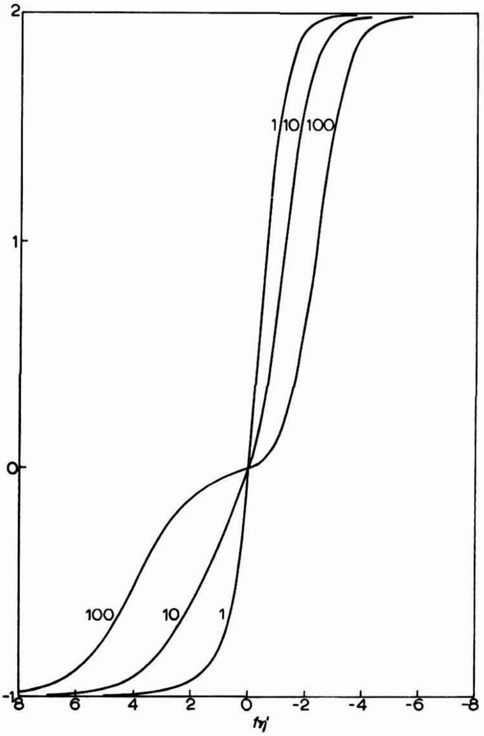


Fig. 3. Case of multi-electron transfer steps, $n_1 = 2$, $n_2 = 1$. The number on each curve indicates the appropriate magnitude of $p$: the dimerisation constant, $q$ , is zero for each curve.

$$i' = n_1 \frac{(1 - e^{(n_1+n_2)f\eta'})}{b} .$$

Curves illustrative of the case $n_1 = 2$, $n_2 = 1$, $q = 0$, and for three different magnitudes of $p$ are given in Fig. 3. In Fig. 4 is plotted the wave shape caused by complete dimerisation of the intermediate, in the special case $n_1 = n_2 = 1$, $p = 0$, $q = 100$; the relatively small influence of a ten-fold variation in $q$ upon the wave having $p = 20$ is exposed in Fig. 5.

A means of analysis of an arbitrary wave which might have complications due to partial dimerisation of the intermediate, may be derived from eqn. (49). By squaring

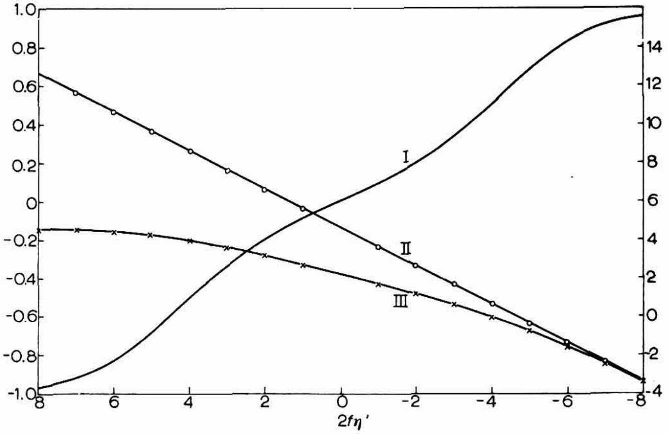


Fig. 4. The current–voltage curve I, for which $n_1 = n_2 = 1$, $p = 0$ and $q = 100$, is referred to the left-hand ordinate. Curves II and III are the plots *vs.* potential of (b) and (a) respectively, and are referred to the right-hand ordinate (see text following eqn. (50)).

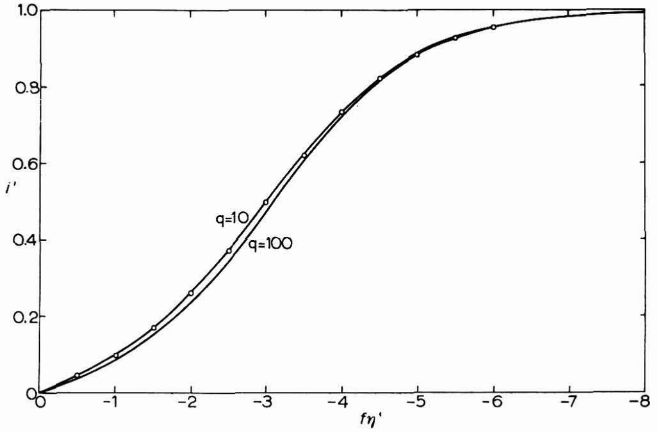


Fig. 5. Cathodic branch of current–voltage curve for which $n_1 = n_2 = 1$, $p = 20$ and for two magnitudes of $q$.

the equation in which the square-root is isolated on one side of the equality sign, and subsequent rearrangement it is found that

$$n_1\, e^{-n_1 f\eta'} \left[\frac{1}{i'} - \frac{1}{n_1} - e^{(n_1+n_2)f\eta'}\left(\frac{1}{i'} + \frac{1}{n_2}\right)\right] = \frac{q}{n_1}\left[\frac{i'\, e^{n_1 f\eta'}}{1 - e^{(n_1+n_2)f\eta'}}\right] + p \tag{50}$$

In the general case, therefore, a linear relationship is expected between the left-hand side, and the square-bracketed term of the right-hand side of eqn. (50); $p$ and $q$ are determined by the slope and intercept of the consequent line. This analysis in practice is likely to be troublesome because of the complexity of the plotted quantities. It might be found convenient to plot in turn

(a) $$\ln\left\{\frac{1}{i'} - \frac{1}{n_1} - e^{(n_1+n_2)f\eta'}\left(\frac{1}{i'} + \frac{1}{n_2}\right)\right\} \text{ vs. potential}$$

(b) $$\ln\left\{\frac{1 - e^{(n_1+n_2)f\eta'}}{i'}\left[\frac{1}{i'} - \frac{1}{n_1} - e^{(n_1+n_2)f\eta'}\left(\frac{1}{i'} + \frac{1}{n_2}\right)\right]\right\} \text{ vs. potential}$$

and (c) the quantities mentioned in connection with eqn. (50), inspecting for linearity at each stage. If (a) were found to be linear with a slope of $n_1 f$, then $q = 0$, there is intermediate formation only, and the intercept determines $p$. Linearity of (b) identifies the case at the other extreme; $p = 0$, dimer formation only, and $q$ determined by the intercept. That (a) and (b) do not both give straight lines under at least one set of circumstances, is evident from the details given in Fig. 4. Finally, if the linearity of neither (a) nor (b) is convincing, the applicability of this model requires that plot (c) be linear.

## GALVANOSTATIC-POTENTIAL–TIME CURVES AT A PLANE ELECTRODE, DUE TO REVERSIBLE CONSECUTIVE REACTIONS

Much of the algebra required for the determination of the potential–time curve resulting from galvanostatic polarisation of an electrode at which multi-electron stepwise reactions occur, has been carried out in the calculations of the preceding sections of this paper. Thus the derivation of expression (40) for the concentration of reduced species $R$ adjacent to the electrode surface in the system of eqns. (35), involved no restriction to constant-potential conditions. On the other hand the method employed in the calculation of the current, assumed time-independence of the surface concentrations functions.

Sacrificing generality we specify a plane electrode here, so that concentration distributions of the reacting species are solutions of the diffusion equation[8]:

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}$$

and enquire into the consequences of the boundary conditions:

$$\frac{i}{FA} = n_2 D_O \frac{\partial C_O}{\partial x} - n_1 D_R \frac{\partial C_R}{\partial x} \quad \text{at} \quad x = 0$$

$$C_O = C_O{}^b, \quad C_R = C_R{}^b \quad \text{at} \quad x \to \infty \quad \text{and} \quad t = 0$$

It is found by manipulation under the Laplace Transform[12] that these conditions are equivalent to the relation:

$$n_2\sqrt{D_O}\,(C_O{}^b - C_O) - n_1\sqrt{D\delta}\,(C_R{}^b - C_R) = \int_0^t \frac{i(t')}{FA}\,\frac{1}{\sqrt{\pi(t - t')}}\,\mathrm{d}t' \quad \text{at} \quad x = 0 \tag{51}$$

which would allow the determination of the functional dependence of potential upon time, for any programmed current $i(t)$. Choosing in this case $i = I$, a constant, the convolution integral on the right-hand side of eqn. (51) is easily evaluated. It is convenient to introduce the previously defined limiting currents $i_1$ and $i_2$ (see eqns. 46 and 47) in this section, remembering that their experimental observation should be at constant potential. Then eqn. (51) may be rewritten with aid of eqns. (45) and (40) in the form:

$$\frac{\dfrac{2I}{\pi} - \dfrac{n_2 i_1 - n_1 i_2}{n_1 + n_2}}{\dfrac{n_2 i_1 + n_1 i_2}{n_1 + n_2}} = i' = \frac{n_1(1 - \mathrm{e}^{(n_1+n_2)f\eta'})}{2q\,\mathrm{e}^{2n_1 f\eta'}}\left\{\sqrt{b^2 + 4q\,\mathrm{e}^{2n_1 f\eta'}} - b\right\} \tag{52}$$

In eqn. (48), $i'$ was independent of time because it was expressed as the ratio of diffusion-controlled currents; $i'$ of eqn. (52) however, depends linearly upon $\sqrt{t}$. Analogous to the limiting currents of polarography, the galvanostatic transition times[13] $\tau_1$ and $\tau_2$ are indicated by extreme polarization of the electrode. Thus at the cathodic transition time $\tau_1$, the electrode potential rapidly falls:

$$\eta \rightarrow -\infty \quad \text{and} \quad i' \rightarrow n_1$$

Expressed in another way this condition means that $i_1(\tau_1) = 2I/\pi$.

$$\text{But } i_1 \propto 1/\sqrt{t}, \text{ so that } i_1 = \frac{2I}{\pi}\sqrt{\frac{\tau_1}{t}} \tag{53}$$

Similarly the anodic transition at $\tau_2$ is indicated by the departure of the electrode potential towards high positive overpotentials $\eta \rightarrow +\infty$ and $i' \rightarrow -n_2$.

Thus

$$i_2 = -\frac{2I}{\pi}\sqrt{\frac{\tau_2}{t}} = \frac{2|I|}{\pi}\sqrt{\frac{\tau_2}{t}} \tag{54}$$

Relations (53) and (54) may now be used to re-express $i'$ in a form more convenient for computation

$$i' = \frac{\sqrt{t} - \dfrac{n_2\sqrt{\tau_1} - n_1\sqrt{\tau_2}}{n_1 + n_2}}{\dfrac{n_2\sqrt{\tau_1} + n_1\sqrt{\tau_2}}{n_1 + n_2}} \tag{55}$$

Analysis of an arbitrary potential–time curve begins with the transformation of the experimental observables $\eta$, $t$, to the derived quantities $\eta'$, $i'$, the reference potential $\eta' = 0$ having been detected from the condition

$$\sqrt{t}_{\eta'=0} = \frac{n_2\sqrt{\tau_1} - n_1\sqrt{\tau_2}}{n_1 + n_2} \tag{56}$$

Subsequent treatment follows the pattern outlined in connection with eqn. (50), yielding the parameters $p$ and $q$ upon which the shape of the transient is essentially dependent.

## THE POLAROGRAPHIC REDUCTION OF PYRAZINE

Current–voltage curves were recorded manually, with a bulb-type dropping mercury electrode having a flow rate of 3.5 mg/sec and a drop-time in the electrolyte on open circuit of about four sec. Temperature control was achieved in an air thermostat which restricted local fluctuations to ±1°. The cell contained only a small volume of electrolyte, and internal resistance was negligible. The solvent medium consisted of 50/50 v/v dimethyl formamide–water mixture, and was buffered with acetic acid and sodium acetate each in $10^{-2}$ *M* concentration. Ammonium nitrate in unimolar concentration served as indifferent electrolyte[14]. Currents were measured at the end of drop life, the apparatus being capable of the detection of $10^{-8}$ A and a potential change of 0.1 mV. Potentials were measured with reference to a saturated potassium chloride–calomel half-cell prepared in the DMF–$H_2O$ mixture. Pyrazine (purchased from L. Light) was adequately soluble in this medium, and was studied in 3 m*M* solution. This produced a limiting current of the order of 20 $\mu$A at the electrode employed, and at room temperature. Maximum suppressor was unnecessary, and the current at constant potential appeared to decay normally. The dependence of $i_1$ upon the square-root of the mercury head, was checked and found to be satisfactory[14].

### *Results*

Current–voltage curves due to pyrazine reduction at four temperatures 16.5°, 30°, 39° and 48°, after conversion to the variables

$$i' = \frac{i - \frac{1}{2}i_1}{\frac{1}{2}i_1} \quad \text{and} \quad \varrho' = E - E_{\frac{1}{2}}$$

are shown in Figs. 6–9. Half-wave potentials and diffusion coefficients, $D$, measured from the original curves are recorded in Table 1.

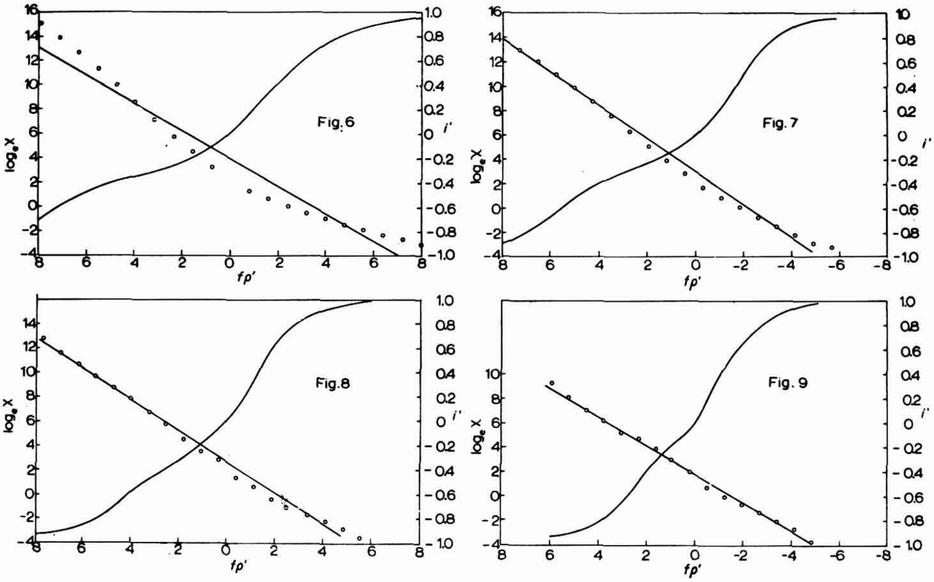
Although the symmetry with respect to inversion through the half-wave point of the waves illustrated is imperfect, their general shape is suggestive of successive single-

TABLE 1

| *Temp.* | *16.5°* | *30°* | *39°* | *48°* |
|---|---|---|---|---|
| $E_{\frac{1}{2}}$ *vs.* S.C.E.[a] | 1.10 | 1.05 | 1.01 | 0.97 |
| $D\,10^6$[b] | 2.35 | 4.02 | 5.01 | 6.25 |
| $\log_e p$ | 3.98 ± 0.25 | 3.02 ± 0.24 | 2.47 ± 0.19 | 1.85 ± 0.19 |
| Slope | 1.24 ± 0.06 | 1.32 ± 0.05 | 1.24 ± 0.05 | 1.28 ± 0.04 |
| $p$ | 53.5 | 20.5 | 11.8 | 6.4 |

[a] Saturated calomel electrode prepared in 50/50 v/v DMF–$H_2O$.

[b] $D$ in $cm^2/sec$.



Figs. 6 to 9. Current–voltage curves for pyrazine reduction referred to the right-hand ordinates. The circled points referred to the left-hand ordinates, record the experimental values of $\log_e \chi$, and the straight lines through these were fitted by the least-squares principle. (Fig. 6), temp., 16.5°; slope, 1.24; log $p$, 3.98; (Fig. 7), temp., 30°; slope, 1.32; log $p$, 3.02; (Fig. 8), temp., 39°; slope, 1.24; log $p$, 2.47; (Fig. 9), temp., 48°; slope, 1.18, log $p$; 1.85.

electron transfer reductions, and provide a suitable test of the equations of the theoretical part of this paper. The polarography of pyrazine itself seems not to have been reported in the literature, but thorough studies of methyl-substituted pyrazines[15], and quinoxaline[16], have indicated that the *para*-dihydro-derivatives are the products of reduction. Hence we assume the reaction mechanism to be

$$\text{Py} + \text{H}^+ + e \rightleftharpoons \text{PyH}$$

$$\text{PyH} + \text{H}^+ + e \rightleftharpoons \text{PyH}_2$$

The buffered medium ensures that no complications arise as a result of the participation of protons in the reaction.

The procedure recommended in connection with eqn. (50), was to examine first of all the plot against potential of

$$\log_e \chi = \log_e \left\{\frac{1}{i'} - 1 - e^{2f\varrho'}\left(\frac{1}{i'} + 1\right)\right\}$$

This function was computed from the $i' - \varrho'$ characteristic for pyrazine reduction, and appears as a set of circled points referred to the left-hand ordinate, in the Figs. 6–9. The straight lines were determined by the least-squares principle. The intercepts at $\varrho' = 0$ ($\log_e p$), and the slope of the straight lines are recorded in Table 1. It is evident that there is improvement of linearity of this function with rise in temperature, and from the concomitant fall in the magnitude of the slope (ignoring the result at 16.5°), which it was predicted should be unity, we conclude that there is approach to reversibility with rise in temperature, and that in other respects this model is applicable.

The fifth line in Table 1 gives the value of the parameter $p$ (eqn. 43), evaluated from the intercepts of the straight lines. Because $p = \sqrt{K_1}$ the square-root of the intermediate-formation equilibrium constant

$$\mathrm{Py} + \mathrm{PyH_2} \rightleftharpoons 2\ \mathrm{PyH}$$

it follows that the radical PyH is quite stable in the medium employed. Furthermore:

$$\log_e p = \tfrac{1}{2} \log_e K_1 = -\frac{\Delta G}{2RT} = -\frac{\Delta H}{2RT} + \frac{\Delta S}{2R}$$

and it is expected that $\log_e p$ should be linearly related to the reciprocal of the absolute temperature. This expectation is realised in practice, and the relevant plot is shown in Fig. 10. The enthalpy change, $\Delta H$, is found to be $-25 \pm 3$ kcal/mole, and the entropy change, $\Delta S$, $= -69 \pm 10$ cal/deg mole.

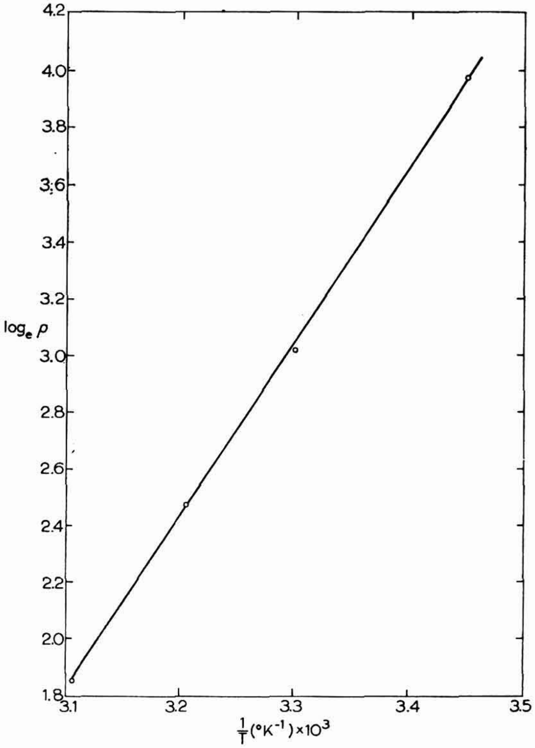


Fig. 10. Enthalpy and entropy determination for formation of the radical PyH.

## CONCLUSIONS

Reversible electrode reactions which involve two consecutive electron-transfer processes, yield polarographic waves and galvanostatic potential–time transients which in principle may be analysed to give intermediate- and dimer-formation constants.

## ACKNOWLEDGEMENT

It is a pleasure to record my gratitude to Dr. ROGER PARSONS of the University of Bristol, for numerous discussions on the theoretical topics and for his direction of the experimental work, of this paper.

## SUMMARY

A theory is presented of diffusion-controlled electrode reactions involving one potential-determining intermediate species, from the point of view of polarographic and chronopotentiometric methods of study. A means of analysis is proposed which utilises directly the current–voltage or potential–time co-ordinates, and allows determination of the equilibrium constant for intermediate formation, and detection of intermediate dimerisation. The method is applied to the polarographic reduction of pyrazine.

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# CHRONOPOTENTIOMETRY OF PLUTONIUM IN MINERAL ACID MEDIA*

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An investigation of the chronopotentiometric behavior of plutonium(III), plutonium(IV), and plutonium(VI) at a platinum electrode in mineral acid media was undertaken for several reasons. Firstly, plutonium is, *a priori*, an exceedingly interesting candidate for chronopotentiometric studies. In aqueous solutions, it may exist in three well-defined oxidation states, plutonium(III), plutonium(IV), and plutonium(VI); a fourth oxidation state, plutonium(V), is also possible. In addition, these species may co-exist under proper solution conditions. Of the several couples which involve these various oxidation states of plutonium, some are thought to be reversible while others are held to be irreversible. Moreover, all the formal potentials for the different plutonium couples in mineral acid media tend to be relatively oxidizing and to have similar values. This latter fact establishes the possibility of co-existence of all four oxidation states of plutonium in the same solution. These characteristics, *in toto*, suggested that a wide variety of chronopotentiometric behavior would be exemplified by plutonium. The experimental results reported below have confirmed this expectation.

Secondly, to our knowledge no chronopotentiometric investigation of any of the oxidation states of plutonium has been reported. Indeed, apart from the potentiometric[1-4] and amperometric[5,6] titration methods and the coulometric procedures[7-9] that are used for the quantitative determination of plutonium, little information concerning the electroanalytical chemistry of plutonium is available. Voltammetric data are scant, probably because the potentials for the various plutonium couples in mineral acid media lie outside the working range of the dropping mercury electrode. HARVEY and co-workers[10], soon after the discovery of plutonium, employed a platinum micro-electrode in conjunction with the voltammetric technique to determine the formal potentials of the plutonium(IV)–plutonium(III) couple in sulfuric, perchloric, and hydrochloric acids. Their results are remarkably good, especially in view

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of the facts that only a few milligrams of plutonium were available and that steady potential measurements were unattainable in certain media. Some ten years later, COOK, FOREMAN AND KEMP[11] published a study of the polarographic reduction of plutonium(VI) to plutonium(V). They used a hydrogen oxalate–oxalate buffer of pH 4.2 in which the plutonium(VI)–plutonium(V) half-wave potential was shifted to a value accessible to study with the dropping mercury electrode, and in which the stability of plutonium(V) was enhanced. The analysis of $10^{-6}$–$10^{-5}$ $M$ solutions of plutonium(IV) in hydrochloric and nitric acid media has been reported recently by KOYAMA[12], who employed the square-wave polarographic technique and platinum electrodes. A survey of these previous studies reveals the need for an investigation of the electrochemical behavior of the various plutonium species in the media which are most frequently encountered, namely, dilute mineral acid solutions.

As a third goal, it was hoped that this investigation would lead to the development of a chronopotentiometric method for the determination of plutonium. For example, because the formal potentials for the plutonium(IV)–plutonium(III) couple in perchloric acid, nitric acid, and hydrochloric acid media are relatively oxidizing, plutonium(IV) undergoes electro-reduction prior to most other ions (especially iron(III)) that interfere with the determination of plutonium. Accordingly, a chronopotentiometric method for the determination of plutonium(IV) might be rather selective. Similarly, a combination of anodic and cathodic chronopotentiometry might permit the determination of each oxidation state in a mixture of oxidation states of plutonium. Although this third goal has not been achieved in the present study, the experimental results indicate the conditions which must be fulfilled for the successful determination of plutonium by the chronopotentiometric technique.

## EXPERIMENTAL

A stock solution of plutonium was prepared by dissolution of the pure (99.93%) metal in 6 $F$ hydrochloric acid. This solution contains predominantly plutonium(IV); small quantities of plutonium(III) and plutonium(VI), however, result from the very slow disproportionation of plutonium(IV). Portions of this solution were used for the preparation of test solutions containing plutonium in a known oxidation state and at a known concentration. The general procedure entailed evaporation of an aliquot of the stock solution with the acid which was to serve as the supporting electrolyte, chemical or electrolytic adjustment of the oxidation state of plutonium, and dilution to a known volume. Controlled-potential coulometry was employed for the determination of the total plutonium content of the test solutions and of the concentration of each oxidation state present.

Solutions of plutonium(IV) of three different concentrations were prepared in 1 $F$ hydrochloric acid, nitric acid, perchloric acid, and sulfuric acid supporting electrolytes. Initially, the adjustment of the oxidation state of plutonium to plutonium(IV) was accomplished chemically by the successive additions of slight excesses of aqueous solutions of hydrazine, sodium nitrite, and sulfamic acid, which is common practice. In later experiments, however, plutonium(IV) was prepared electrolytically to avoid the introduction of these extraneous reagents. To ensure that plutonium(VI) would be absent in the test solutions prepared electrolytically, the plutonium was first reduced quantitatively to plutonium(III). For the electro-generation of plutonium(III), the potential of the working cathode was controlled at +0.525 V *vs.* S.C.E.

(saturated calomel electrode) in 1 $F$ hydrochloric acid, nitric acid, and perchloric acid media and at $+0.300$ V *vs.* S.C.E. in 1 $F$ sulfuric acid medium. This electro-generation of plutonium(III) was followed by the controlled-potential oxidation of plutonium(III) to plutonium(IV) at $+0.895$ V *vs.* S.C.E. in hydrochloric acid, nitric acid, and perchloric acid and at $+0.700$ V *vs.* S.C.E. in sulfuric acid. Pure helium gas was used to de-aerate the solutions prior to and during the electrolyses. The chronopotentiometric results obtained with plutonium(IV) solutions prepared by either the chemical or electrolytic techniques were in good agreement.

Plutonium(III) solutions were prepared electrolytically in 1 $F$ perchloric acid and 1 $F$ sulfuric acid supporting electrolytes according to the procedure described in the preceding paragraph.

Plutonium(VI) was prepared by fuming an aliquot of the stock plutonium solution with concentrated perchloric acid for approximately 15 min. The resulting solution was cooled and diluted to provide a 1 $F$ perchloric acid concentration.

All of the other reagents were analytical reagent-grade and were used without further purification.

An ORNL Model Q-2005-X50 electronic controlled-potential coulometric titrator[13-15] was used both for the adjustment of the oxidation state of plutonium and for the analysis of the test solutions for total plutonium content and oxidation state distribution. The electrolysis cells and procedures have been described in detail and a review of the various applications of controlled-potential coulometry to the analysis of plutonium solutions has been published recently[9].

The electrical circuitry for the chronopotentiometric experiments was essentially the same as that described by LINGANE[16]. The complete chronopotentiograms presented in this paper were recorded with an Electro Instruments Inc. (San Diego, California), Model 500 X-Y recorder. Transition times were measured by means of the manual technique described below. The potential of the working electrode *versus* a saturated calomel reference electrode was followed as a function of time with the X-Y recorder. A double-pole, single-throw relay was employed to start and stop a precision electric clock (Model S-10, Standard Electric Time Co., Springfield, Massachusetts) simultaneously with the closing and opening of the electrolysis circuit. The transition time was measured from the moment the electrolysis circuit was closed to the instant the recorder-pen reached the previously selected transition potential at which point the electrolysis circuit was opened. Comparative measurements made with the recorder and with a cathode ray oscilloscope prior to the present study demonstrated that the pen response of the recorder was fast enough to permit the accurate determination by means of this technique of transition times as short as one second. Furthermore, by observing the complete recorder-pen trace after interruption of the electrolysis, one can ascertain the actual potential at which the electrolysis was stopped. The degree of concordance between this latter potential and the transition potential is a criterion for accepting or rejecting the particular measurement. All of the transition times reported in this paper are averages of from three to six trials.

The chronopotentiometric cell was conventional in design[16] except that it was scaled down in size so that the required volume of solution was only 10 ml. The working electrode consisted of a length of platinum wire which had been coated with Tygon paint (U. S. Stoneware Co., Akron, Ohio) in such a way that a known cylindrical area of platinum was exposed to the solution. The lower edge of the exposed cylinder of platinum was approximately 3 mm above the end of the wire which rested on the bottom of the cell. The radius of the platinum wire was 0.0816 cm, the length of the exposed wire was 0.721 cm, and the geometric area of the electrode was 0.370 cm$^2$.

The platinum wire auxiliary electrode was separated from the test solution by a cracked-glass bridge tube containing the supporting electrolyte solution alone. LINGANE[16] has described the method of construction of such bridge tubes. Electrolytic contact of the saturated calomel reference electrode with the test solution was made through a second cracked-glass bridge tube filled with supporting electrolyte solution.

Pure helium gas was used to remove dissolved air from the solution and to stir the solution between measurements. Before each trial the flow of helium was diverted over the surface of the solution, and the solution itself was allowed one minute or longer to become quiescent.

Because all chemical operations were carried out within sealed glove boxes, it was not feasible to thermostat the test solutions. Although the temperature usually remained constant during a series of measurements, some variations were encountered. Accordingly, the temperature within the glove boxes was monitored regularly so that appropriate corrections for temperature fluctuation could be made.

## DISCUSSION AND RESULTS

In aqueous media, plutonium exhibits four different oxidation states—plutonium(III), plutonium(IV), plutonium(V), and plutonium(VI)—some or all of which may co-exist under the proper solution conditions; each of these oxidation states was observed and studied during the course of work. Formal potentials for various plutonium couples in acid media which are pertinent to the present study are summarized in Table 1. Data for the construction of this table have been obtained from publications by RABIDEAU[17] and by METZ[3].

TABLE 1

FORMAL POTENTIALS FOR VARIOUS PLUTONIUM COUPLES

| *Couple* | *Medium (1 F)* | *Formal potential (V vs. S.C.E.)* |
|---|---|---|
| Pu(IV)–Pu(III) | $H_2SO_4$ | +0.51 |
| | $HNO_3$ | +0.68 |
| | HCl | +0.728 |
| | $HClO_4$ | +0.740 |
| Pu(V)–Pu(IV) | $HClO_4$ | +0.930 |
| Pu(V)–Pu(III) | $HClO_4$ | +0.835 |
| Pu(VI)–Pu(V) | $HClO_4$ | +0.671 |
| Pu(VI)–Pu(IV) | $HClO_4$ | +0.801 |
| Pu(VI)–Pu(III) | $HClO_4$ | +0.780 |

The plutonium(IV)–plutonium(III) and plutonium(VI)–plutonium(V) couples behave more or less reversibly in each medium included in Table 1. In contradistinction, the other four couples listed in Table 1 show generally irreversible behavior because the electrode reactions involve the formation or breakage of plutonium–oxygen bonds and, in three of the four cases, multiple electron changes. The formal potentials for the plutonium(IV)–plutonium(III) couple in nitric, hydrochloric, and perchloric acid media are relatively oxidizing ones. In 1 *F* sulfuric acid, however, the formation of stable complexes of plutonium(IV) with sulfate and hydrogen sulfate ions shifts the plutonium(IV)–plutonium(III) formal potential to a value only 70 mV more oxidizing than that for the iron(III)–iron(II) couple (+0.44 V *vs.* S.C.E.) in the same electrolyte. In 1 *F* perchloric acid, the closeness of the formal potentials for the plutonium(VI)–plutonium(V) and plutonium(IV)–plutonium(III) couples renders possible the simultaneous existence of all four oxidation states of plutonium. The formal potentials for the irreversible couples in Table 1 are not directly measurable, but have been evaluated with data obtained from potential measurements of the reversible plutonium couples and from equilibrium studies involving the various plutonium species[17].

*Chronopotentiometry of plutonium (IV)*

Typical chronopotentiograms appear in Fig. 1 for the reduction of plutonium(IV) to plutonium(III) at the platinum wire electrode in 1 *F* sulfuric acid, nitric acid, perchloric acid, and hydrochloric acid supporting electrolytes. That the electroreduction of plutonium(IV) does proceed to plutonium(III) under chronopotentiometric conditions is confirmed for each medium by the potential at which the chronopotentiometric wave occurs and by the reasonable value for the diffusion coefficient of plutonium(IV) calculated on the basis of a one-electron reduction.

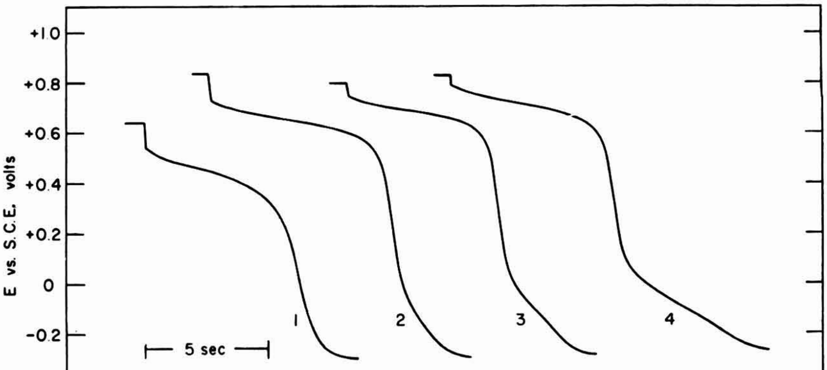

Fig. 1. Chronopotentiograms for the reduction of 0.05 *M* plutonium(IV) to plutonium(III) at a platinum wire electrode in various media. Curve 1: 0.0526 *M* Pu(IV) in 1 *F* $H_2SO_4$ at 25.8°, $i = 1525\ \mu A$; curve 2: 0.0498 *M* Pu(IV) in 1 *F* $HNO_3$ at 25.8°, $i = 1450\ \mu A$; curve 3: 0.0518 *M* Pu(IV) in 1 *F* $HClO_4$ at 26.3°, $i = 1526\ \mu A$; curve 4: 0.0519 *M* Pu(IV) in 1 *F* HCl at 28.9°, $i = 1529\ \mu A$.

In chronopotentiometry with plane electrodes, one criterion for a reversible electrode reaction is that the potential of the working electrode at a time equal to one-fourth the transition time should be very nearly the value of the standard or formal potential for the reaction. This chronopotentiometric quarter-wave potential $E_{1/4}$ is equivalent to the more familiar half-wave potential in polarography. With cylindrical (wire) electrodes the value of $E_{1/4}$ is, theoretically, slightly more reducing for a reduction process and more oxidizing for an oxidation process than the corresponding value for plane electrodes[18]. Moreover, the magnitude of the difference between $E_{1/4}$ for plane and cylindrical electrodes increases with transition time. For the platinum wire electrode used in the present work, the theoretical equation predicts a difference not exceeding 5 mV between $E_{1/4}$ for plane and cylindrical electrodes, which, for practical purposes, is negligible. Therefore, the agreement of the quarter-wave potential with the standard potential is, in this study, a good criterion for reversibility.

TABLE 2

EFFECT OF CURRENT DENSITY ON QUARTER-WAVE POTENTIAL IN REDUCTION OF PLUTONIUM(IV)

| $i(mA/cm^2)$ | $E_{1/4}$(*V vs. S.C.E.*) | $i(mA/cm^2)$ | $E_{1/4}$(*V vs. S.C.E.*) |
|---|---|---|---|
| (a) 0.0526 *M* plutonium(IV) in 1 *F* sulfuric acid | | (c) 0.0518 *M* plutonium(IV) in 1 *F* perchloric acid | |
| 10.50 | +0.42 | 10.50 | +0.69 |
| 7.25 | 0.46 | 7.26 | 0.71 |
| 5.91 | 0.46 | 5.91 | 0.72 |
| 5.04 | 0.48 | 5.05 | 0.72 |
| 4.12 | 0.48 | 4.12 | 0.73 |
| 3.45 | 0.51 | 3.46 | 0.73 |
| 2.54 | 0.51 | 2.54 | 0.73 |
| (b) 0.0498 *M* plutonium(IV) in 1 *F* nitric acid | | (d) 0.0519 *M* plutonium(IV) in 1 *F* hydrochloric acid | |
| 9.30 | +0.61 | 10.51 | +0.72 |
| 6.65 | 0.64 | 7.26 | 0.73 |
| 5.50 | 0.65 | 5.92 | 0.73 |
| 4.74 | 0.66 | 5.05 | 0.73 |
| 3.92 | 0.67 | 4.14 | 0.73 |
| 3.31 | 0.68 | 3.46 | 0.74 |
| 2.46 | 0.69 | 2.54 | 0.74 |

Interesting results are obtained when the effect of current density on the quarter-wave potential is observed for each of the four media. Table 2 presents the data derived from this study. The quarter-wave potential corresponding to each current density was measured from the complete recorded chronopotentiogram. No attempt has been made to correct these potentials for cell resistance; such a correction is small and unimportant for the present discussion. For each of the supporting electrolytes, the quarter-wave potential becomes virtually identical at the lowest current density to the formal potential listed in Table 1. Generally, as the current density is increased, the quarter-wave potential shifts for each medium to more reducing (less positive) values. This behavior is undoubtedly attributable to a decrease in the reversibility of plutonium(IV) reduction. The variation of the quarter-wave potential with current density is most pronounced in sulfuric and nitric acid media and is smaller in the perchloric and hydrochloric acid supporting electrolytes. From this information we conclude that the electro-reduction of plutonium(IV) to plutonium(III) proceeds somewhat less reversibly in 1 *F* sulfuric acid and nitric acid solutions than in perchloric and hydrochloric acid media. Application of the diagnostic criteria suggested by REINMUTH[19] to distinguish totally reversible and totally irreversible electrode reactions indicated, however, that the reduction of plutonium(IV) to plutonium(III) in each of these four media exhibits only quasi-reversible behavior.

*Chronopotentiometry of plutonium(IV) in sulfuric acid.* A family of chronopotentiograms is presented in Fig. 2 for the reduction of 0.05, 0.01, and 0.001 *M* plutonium-

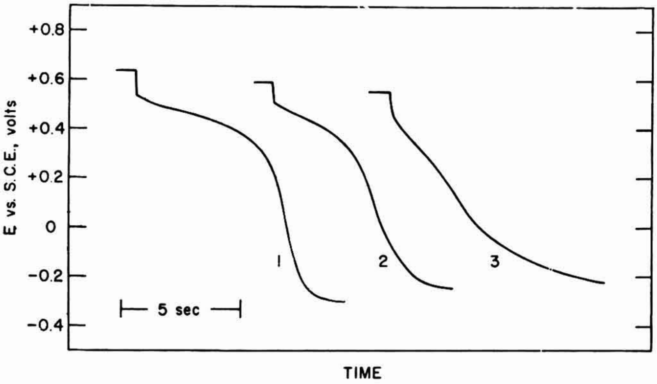

Fig. 2. Family of chronopotentiograms for the reduction of various concentrations of plutonium(IV) to plutonium(III) in 1 *F* sulfuric acid medium. Curve 1: 0.0526 *M* Pu(IV) at 25.8°, $i = 1525$ $\mu$A; curve 2: 0.0105 *M* Pu(IV) at 26.8°, $i = 396\,\mu$A; curve 3: 0.00105 *M* Pu(IV) at 25.8°, $i = 70\,\mu$A.

TABLE 3

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(IV) IN 1 *F* SULFURIC ACID

| $i$ ($\mu A$) | $\tau$ (*sec*) | *Temperature* (°*C*) | $i\tau^{1/2}/AC$ (*A sec*$^{1/2}$ *cm/mole*) |
|---|---|---|---|
| (a) 0.0526 *M* plutonium(IV) | | | |
| 3880 | 1.03 ± 0.01 | 27.0 | 203 |
| 2681 | 2.19 ± 0.01 | 28.5 | 204 |
| 2186 | 3.09 ± 0.01 | 26.0 | 197 |
| 1863 | 4.39 ± 0.02 | 27.2 | 200 |
| 1525 | 6.34 ± 0.04 | 25.8 | 197 |
| 1276 | 9.72 ± 0.03 | 28.0 | 204 |
| 938 | 18.81 ± 0.06 | 28.3 | 209 |
| (b) 0.0105 *M* plutonium(IV) | | | |
| 702 | 1.38 ± 0.01 | 26.5 | 212 |
| 496 | 2.81 ± 0.01 | 26.8 | 213 |
| 396 | 4.46 ± 0.05 | 26.8 | 214 |
| 328 | 6.33 ± 0.00 | 26.5 | 212 |
| 280 | 8.48 ± 0.02 | 26.0 | 209 |
| 235 | 12.55 ± 0.04 | 26.8 | 214 |
| 199 | 17.30 ± 0.04 | 26.0 | 210 |
| (c) 0.00105 *M* plutonium(IV) | | | |
| 111 | 1.46 ± 0.04 | 25.8 | 345 |
| 88.7 | 2.14 ± 0.05 | 25.6 | 334 |
| 70.2 | 3.35 ± 0.03 | 25.8 | 330 |
| 49.5 | 5.88 ± 0.00 | 25.6 | 308 |
| 41.9 | 7.89 ± 0.06 | 25.7 | 302 |
| 35.1 | 10.53 ± 0.08 | 25.5 | 293 |
| 28.9 | 15.61 ± 0.14 | 26.0 | 293 |

(IV) in 1 $F$ sulfuric acid medium at the platinum wire cathode. The initial or open circuit potentials for the chronopotentiograms corresponding to the three concentrations of plutonium(IV) differ because of variations in the plutonium(IV)–plutonium(III) concentration ratio. As mentioned above and as is evident from Fig. 2, the quarter-wave potential in sulfuric acid medium is markedly affected by current density.

Transition-time data for the electro-reduction of 0.05, 0.01, and 0.001 $M$ plutonium(IV) in 1 $F$ sulfuric acid are listed in Table 3. The transition times were measured at +0.05 V *vs.* S.C.E. by means of the manual technique described earlier. Values of $i\tau^{\frac{1}{2}}/AC$ calculated from the experimental data are tabulated and have been plotted *versus* transition time in Fig. 3.

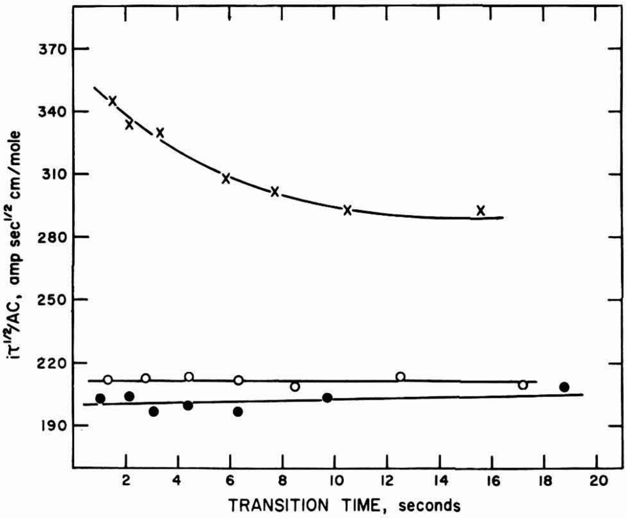

Fig. 3. Plot of $i\tau^{\frac{1}{2}}/AC$ *versus* transition time for the reduction of three concentrations of plutonium(IV) to plutonium(III) in 1 $F$ sulfuric acid solution: ●, 0.05 $M$; ○, 0.01 $M$; ×, 0.001 $M$. The experimental points were taken from Table 3.

Because a platinum wire electrode was used in the present investigation, the experimental values of $i\tau^{\frac{1}{2}}/AC$ in Table 3 should increase with increasing transition time as a result of the cylindricity of the diffusion field[20]. With the particular wire electrode employed, this effect was small and the predicted increase in $i\tau^{\frac{1}{2}}/AC$ was only approximately 6% over a range of transition times from 1–20 sec. Moreover, the experimental values of $i\tau^{\frac{1}{2}}/AC$ for all concentrations of plutonium(IV) should, theoretically, fall on the same curve.

In Fig. 3 it can be seen that the values of $i\tau^{\frac{1}{2}}/AC$ increase as the plutonium(IV) concentration decreases. In addition, the values of $i\tau^{\frac{1}{2}}/AC$ corresponding to 0.01 and 0.001 $M$ plutonium(IV) do not show the expected increase with transition time attributable to the cylindricity of the diffusion field. Several factors combine to produce these effects. First, plutonium(IV) in sulfuric acid solution is a sufficiently strong oxidizing agent to cause spontaneous chemical oxidation of the platinum electrode and the chronopotentiometric reduction of the surface oxide of platinum occurs in the same region of potentials as the reduction of plutonium(IV) in this medium. Second, as the concentration of plutonium(IV) decreases, the quantity of electricity required to charge the electrical double layer becomes a larger and larger fraction of the total amount of electricity in a chronopotentiometric trial. It is of interest to note that the magnitude of the diffusion coefficient of the electroactive species also influences the lower concentration limit in chronopotentiometric analysis. This is because the diffusion coefficient determines in part the thickness of the diffusion layer and, therefore, the quantity of substance which is electrolyzed in an individual experiment. For substances with relatively small diffusion coefficients, such as plutonium(IV), the amount of electrolyzed material is correspondingly small. When the quantity of substance electrolyzed is small, such factors as the charging of the electrical double layer and the surface oxidation or reduction of the working electrode constitute a significant fraction of the total quantity of electricity and limit the lowest concentration for which meaningful chronopotentiometric measurements can be made. For a specific concentration of plutonium(IV), each of these effects is more pronounced at shorter transition times, because the quantity of plutonium(IV) reduced is smaller. These facts explain why, for example, the values of $i\tau^{\frac{1}{2}}/AC$ for the smallest concentration of plutonium(IV) increase rapidly at short transition times (Fig. 3).

The data in Table 3 for the chronopotentiometric reduction of 0.0526 $M$ plutonium(IV) have been used to evaluate the diffusion coefficient of plutonium(IV) in 1 $F$ sulfuric acid medium. For this concentration the above-mentioned effects were negligible. The value of the diffusion coefficient for each of the seven experimental points in Table 3 was calculated from the theoretical equation for chronopotentiometry with a wire electrode[20]. Numerical correction factors for chronopotentiometry with cylindrical electrodes published by EVANS AND PRICE[21] facilitated these calculations. Each calculated diffusion coefficient was corrected for the difference between the actual experimental temperature (Table 3) and 25° on the assumption that the diffusion coefficient increases 2% per degree. The diffusion coefficient of plutonium(IV) in 1 $F$ sulfuric acid at 25° is $5.0 \pm 0.1 \times 10^{-6}$ cm$^2$/sec.

*Chronopotentiometry of plutonium(IV) in perchloric acid.* Three chronopotentiograms for the electro-reduction of 0.05, 0.01, and 0.001 $M$ plutonium(IV) in 1 $F$ perchloric acid supporting electrolyte are shown in Fig. 4. Several differences between the cathodic chronopotentiograms presented in Fig. 4 and the corresponding curves in Fig. 2 for the sulfuric acid medium are noticeable. The initial or open-circuit potentials are approximately 200 mV more oxidizing in perchloric acid than in sulfuric acid because of the difference between the formal potentials of the plutonium(IV)–plutonium(III) couple in perchloric acid and sulfuric acid media (Table 1). As previously observed in sulfuric acid solution, the open circuit potentials for the three chronopotentiograms in Fig. 4 differ somewhat due to variations in the plutonium(IV)–plutonium(III) concentration ratio. In addition, it should be noted that in 1 $F$ perchloric acid medium the reduction of plutonium(IV) will precede the reduction of the spontaneously-formed platinum oxide film. This behavior is particularly evident for the chronopotentiogram for the reduction of 0.001 $M$ plutonium(IV) in 1 $F$ perchloric acid (curve 3, Fig. 4), where the poorly-defined doublet wave corresponds to the successive reductions of plutonium(IV) to plutonium(III) and of the platinum oxide film. Another feature of interest is the small post-wave which appears at approximately 0 V *vs.* S.C.E. in curve (1) of Fig. 4. Such a post-wave has been observed previously by LINGANE[22] and by ANSON[23]. We believe, in agreement with the latter author, that this wave is associated with the formation and adsorption of hydrogen on the finely-divided platinum metal which is produced when a platinum oxide film is

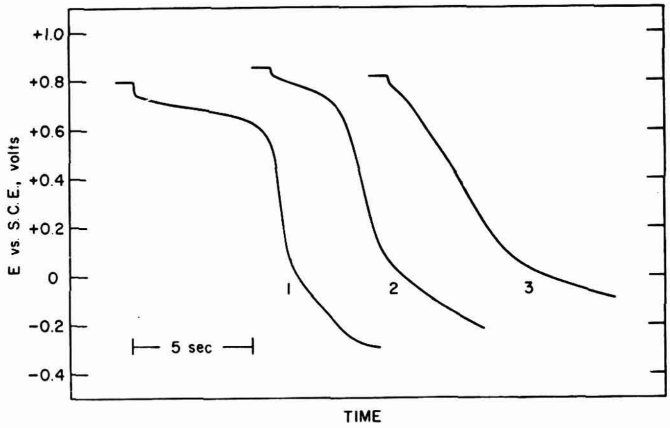

Fig. 4. Cathodic chronopotentiograms for the reduction of different concentrations of plutonium(IV) to plutonium(III) in 1 $F$ perchloric acid medium. Curve 1: 0.0518 $M$ Pu(IV) at 26.3°, $i = 1526$ $\mu$A; curve 2: 0.0104 $M$ Pu(IV) at 26.0°, $i = 397$ $\mu$A; curve 3: 0.00104 $M$ Pu(IV) at 25.4°, $i = 70$ $\mu$A.

TABLE 4

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(IV) IN 1 $F$ PERCHLORIC ACID

| $i$ ($\mu A$) | $\tau$ (sec) | Temperature (°C) | $i\tau^{\frac{1}{2}}/AC$ ($A\ sec^{\frac{1}{2}}\ cm/mole$) |
|---|---|---|---|
| (a) 0.0518 $M$ plutonium(IV) | | | |
| 3890 | 0.92 ± 0.01 | 26.3 | 195 |
| 2685 | 1.85 ± 0.02 | 26.1 | 190 |
| 2189 | 2.90 ± 0.02 | 26.3 | 195 |
| 1866 | 3.84 ± 0.02 | 26.1 | 191 |
| 1526 | 5.99 ± 0.01 | 26.3 | 195 |
| 1278 | 8.03 ± 0.04 | 26.1 | 189 |
| 938 | 15.65 ± 0.09 | 26.1 | 194 |
| (b) 0.0104 $M$ plutonium(IV) | | | |
| 703 | 1.25 ± 0.03 | 26.0 | 205 |
| 496 | 2.51 ± 0.02 | 26.0 | 205 |
| 397 | 3.97 ± 0.02 | 26.0 | 207 |
| 328 | 5.47 ± 0.04 | 26.0 | 200 |
| 281 | 7.36 ± 0.01 | 26.0 | 199 |
| 236 | 10.71 ± 0.02 | 26.0 | 202 |
| 199 | 14.57 ± 0.03 | 26.0 | 198 |
| (c) 0.00104 $M$ plutonium(IV) | | | |
| 111 | 1.64 ± 0.03 | 25.4 | 371 |
| 88.7 | 2.39 ± 0.04 | 25.4 | 358 |
| 70.1 | 3.55 ± 0.02 | 25.4 | 345 |
| 49.3 | 6.27 ± 0.11 | 25.4 | 322 |
| 41.8 | 7.85 ± 0.04 | 25.4 | 306 |
| 35.0 | 10.28 ± 0.07 | 25.4 | 293 |
| 28.9 | 14.01 ± 0.07 | 25.4 | 282 |

reduced. The size of this post-wave usually increases with the strength of the oxidant whose cathodic chronopotentiometry is being studied and with the total number of cathodic polarizations. On the other hand, this post-wave disappears if the electrode is allowed to stand overnight in any of the supporting electrolyte solutions employed in the present work.

Chronopotentiometric data for the reduction of 0.05, 0.01, and 0.001 *M* plutonium(IV) in a 1 *F* perchloric acid supporting electrolyte are presented in Table 4. Transition times were measured manually at +0.30 V *vs.* S.C.E. Fig. 5 is a plot of the experimentally determined values of $i\tau^{\frac{1}{2}}/AC$ *versus* transition time for each concentration of plutonium(IV).

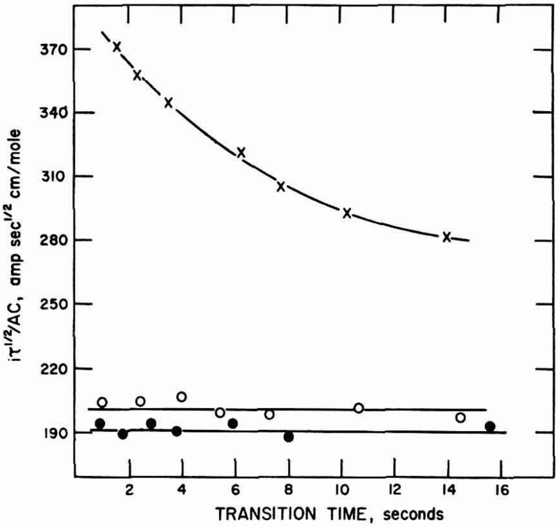

Fig. 5. Plot of $i\tau^{\frac{1}{2}}/AC$ *versus* transition time for the reduction of three concentrations of plutonium(IV) to plutonium(III) in 1 *F* perchloric acid: ●, 0.05 *M*; ○, 0.01 *M*; ×, 0.001 *M*. The experimental data have been taken from Table 4.

It is apparent that the chronopotentiometric behavior of plutonium(IV) in perchloric acid medium resembles that previously described for sulfuric acid supporting electrolyte. The values of $i\tau^{\frac{1}{2}}/AC$ exhibit the dependence on concentration of plutonium(IV) and, for the smallest plutonium(IV) concentration, increase markedly as the transition time decreases (Table 4).

From the data for 0.0518 *M* plutonium(IV) presented in Table 4, the diffusion coefficient for plutonium(IV) in 1 *F* perchloric acid at 25° was found to be $4.7 \pm 0.1 \times 10^{-6}$ cm²/sec. The calculations were performed in the manner described above for sulfuric acid.

*Chronopotentiometry of plutonium(IV) in nitric acid.* The cathodic chronopotentiometry of plutonium(IV) in 1 *F* nitric acid medium resembles the chronopotentiometric behavior of plutonium(IV) in perchloric acid. A typical chronopotentiogram for the reduction of 0.0498 *M* plutonium(IV) in 1 *F* nitric acid at the platinum wire cathode is curve (2) of Fig. 1. This wave was recorded at a current density of 4.74 mA/cm² and at a temperature of 25.8°. As the concentration of plutonium(IV) is decreased, the cathodic chronopotentiograms become less well-defined. This trend parallels the behavior shown in sulfuric acid and perchloric acid supporting electrolytes.

Table 5 presents the chronopotentiometric data obtained at +0.30 V for the reduction of 0.05, 0.01, and 0.001 *M* plutonium(IV) in 1 *F* nitric acid. The increase of $i\tau^{1/2}/AC$ with decreasing plutonium(IV) concentration, previously observed in sulfuric and perchloric acid media, is slightly more pronounced in nitric acid solution than in any of the other three supporting electrolytes employed. It is possible that, in addition to plutonium(IV), nitric acid spontaneously oxidizes a platinum electrode; however, no investigation of the chronopotentiometric behavior of platinum electrodes in nitric acid medium alone has been reported.

TABLE 5

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(IV) IN 1 *F* NITRIC ACID

| $i$ (*µA*) | $\tau$ (*sec*) | *Temperature* (*°C*) | $i\tau^{1/2}/AC$ (*A sec*$^{1/2}$ *cm/mole*) |
|---|---|---|---|
| (a) 0.0498 *M* plutonium(IV) | | | |
| 3441 | 1.24 ± 0.01 | 25.8 | 208 |
| 2460 | 2.53 ± 0.02 | 25.8 | 212 |
| 2034 | 3.66 ± 0.03 | 25.8 | 211 |
| 1751 | 4.97 ± 0.04 | 25.8 | 212 |
| 1450 | 7.32 ± 0.02 | 25.8 | 213 |
| 1223 | 10.71 ± 0.04 | 26.8 | 217 |
| 907 | 20.46 ± 0.10 | 26.8 | 222 |
| (b) 0.00996 *M* plutonium(IV) | | | |
| 684 | 1.53 ± 0.02 | 26.5 | 229 |
| 568 | 2.16 ± 0.04 | 26.2 | 226 |
| 485 | 3.07 ± 0.02 | 27.0 | 230 |
| 390 | 4.92 ± 0.05 | 27.1 | 235 |
| 323 | 6.69 ± 0.02 | 26.5 | 226 |
| 278 | 8.94 ± 0.01 | 26.5 | 225 |
| 233 | 13.43 ± 0.04 | 27.0 | 232 |
| (c) 0.000996 *M* plutonium(IV) | | | |
| 110 | 1.74 ± 0.01 | 27.9 | 393 |
| 88.6 | 2.51 ± 0.03 | 27.3 | 382 |
| 70.1 | 3.87 ± 0.01 | 26.6 | 374 |
| 49.4 | 6.58 ± 0.05 | 27.3 | 343 |
| 41.8 | 8.86 ± 0.04 | 26.6 | 338 |
| 35.1 | 11.79 ± 0.04 | 27.8 | 327 |
| 28.9 | 16.71 ± 0.03 | 27.9 | 321 |

The diffusion coefficient of plutonium(IV) is significantly larger in 1 *F* nitric acid than in sulfuric, perchloric, and hydrochloric acid supporting electrolytes. The value calculated from the data in Table 5 for 0.0498 *M* plutonium(IV) by means of the procedure outlined earlier is $5.8 \pm 0.1 \times 10^{-6}$ cm$^2$/sec at 25°.

*Chronopotentiometry of plutonium(IV) in hydrochloric acid.* The chronopotentiometric reduction of 0.0519 *M* plutonium(IV) to plutonium(III) in 1 *F* hydrochloric acid solution is depicted by curve (4) of Fig. 1. The chronopotentiogram was recorded with a current density of 4.14 mA/cm$^2$ and at a temperature of 29.0°. The cathodic chronopotentiogram exhibits a well-defined wave attributable to the reduction of plutonium(IV), followed by a second wave which is reminiscent of the post-wave described above for the chronopotentiometry of plutonium(IV) in perchloric acid medium.

In a recently reported study[24], evidence was presented that the anodic polarization of a platinum electrode in 1 $F$ hydrochloric acid results in the formation of a surface film of $PtCl_2$. The formal potential of the plutonium(IV)–plutonium(III) couple in 1 $F$ hydrochloric acid (+0.728 V *vs.* S.C.E.) is approximately 200–300 mV more oxidizing than the potential at which platinum is oxidized to $PtCl_2$ (+0.4 to +0.5 V *vs.* S.C.E.). Therefore, a platinum electrode immersed in an hydrochloric acid solution of plutonium(IV) undoubtedly has a $PtCl_2$ film on its surface. The reduction of the $PtCl_2$ film during a chronopotentiometric trial produces a deposit of finely-divided metallic platinum, the presence of which is associated with the post-wave of the chronopotentiogram for plutonium(IV) reduction in hydrochloric acid medium (curve 4, Fig. 1).

The transition-time data which are summarized in Table 6 for the reduction of 0.05, 0.01, and 0.001 $M$ plutonium(IV) in 1 $F$ hydrochloric acid show the already-mentioned increase in $i\tau^{\frac{1}{2}}/AC$ with decreasing plutonium(IV) concentration. In hydrochloric acid medium the more or less concomitant reduction of the $PtCl_2$ film with plutonium(IV) contributes to the increasing $i\tau^{\frac{1}{2}}/AC$ values as the concentration of plutonium(IV) decreases. Transition times were measured at +0.30 V *vs.* S.C.E.

TABLE 6

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(IV) IN 1 $F$ HYDROCHLORIC ACID

| $i$ ($\mu A$) | $\tau$ (*sec*) | *Temperature* (°*C*) | $i\tau^{\frac{1}{2}}/AC$ (*A sec*$^{\frac{1}{2}}$ *cm/mole*) |
|---|---|---|---|
| (a) 0.0519 $M$ plutonium(IV) | | | |
| 3893 | 1.02 ± 0.01 | 29.0 | 205 |
| 2689 | 2.13 ± 0.01 | 29.3 | 204 |
| 2191 | 3.20 ± 0.03 | 29.2 | 204 |
| 1868 | 4.50 ± 0.01 | 29.5 | 206 |
| 1529 | 6.76 ± 0.04 | 29.0 | 207 |
| 1279 | 10.22 ± 0.02 | 29.3 | 213 |
| 939 | 21.17 ± 0.05 | 29.3 | 225 |
| (b) 0.0104 $M$ plutonium(IV) | | | |
| 705 | 1.47 ± 0.02 | 29.3 | 222 |
| 497 | 2.91 ± 0.04 | 29.3 | 220 |
| 397 | 4.42 ± 0.01 | 29.3 | 217 |
| 329 | 6.48 ± 0.01 | 29.3 | 218 |
| 281 | 8.92 ± 0.05 | 29.1 | 218 |
| 236 | 12.68 ± 0.04 | 29.3 | 219 |
| 199 | 18.18 ± 0.03 | 29.0 | 220 |
| (c) 0.00104 $M$ plutonium(IV) | | | |
| 111 | 1.67 ± 0.02 | 28.0 | 374 |
| 88.9 | 2.33 ± 0.02 | 27.5 | 353 |
| 70.4 | 3.57 ± 0.06 | 28.5 | 346 |
| 49.5 | 6.64 ± 0.01 | 28.0 | 332 |
| 41.9 | 9.08 ± 0.02 | 28.0 | 329 |
| 35.1 | 12.40 ± 0.13 | 27.5 | 322 |
| 28.9 | 17.29 ± 0.19 | 27.5 | 313 |

Using the data presented in Table 6 for the reduction of 0.0519 $M$ plutonium(IV) and making the appropriate temperature corrections, we have calculated that the diffusion coefficient of plutonium(IV) in 1 $F$ hydrochloric acid is $5.2 \pm 0.2 \times 10^{-6}$ $cm^2/sec$ at 25°.

*Chronopotentiometry of plutonium(III)*

The anodic chronopotentiometry of plutonium(III) is of special interest because little information is available concerning the electrochemical behavior of this oxidation state of plutonium. Accordingly, the chronopotentiometric behavior of plutonium(III) in sulfuric acid and perchloric acid supporting electrolytes was investigated and the diffusion coefficient for plutonium(III) in each of these media was evaluated. In both sulfuric acid and perchloric acid solutions, the electro-oxidation of plutonium(III) proceeds only to plutonium(IV). In the chronopotentiometric experiments there was no evidence to show that either plutonium(III) or plutonium(IV) undergoes oxidation to plutonium(V) or plutonium(VI).

Whenever a platinum electrode is employed in anodic chronopotentiometry, there is the likelihood that the electrode will undergo surface oxidation and that this will influence the electrode process under study. In sulfuric acid medium, plutonium(III) spontaneously reduces the platinum oxide film after each anodic chronopotentiogram is recorded. In a perchloric acid supporting electrolyte, however, well-defined chronopotentiograms for the electro-oxidation of plutonium(III) to plutonium(IV) may be obtained at either pre-reduced or pre-oxidized platinum electrodes. Surprisingly, no difference in reversibility is observed when this oxidation occurs at pre-reduced or pre-oxidized electrodes. These experimental results are described below in detail.

*Chronopotentiometry of plutonium(III) in sulfuric acid.* The two chronopotentiograms shown in Fig. 6 for the oxidation of plutonium(III) to plutonium(IV) in 1 $F$ sulfuric acid medium provide a comparison of the anodic behavior of this oxidation state of plutonium at a pre-reduced and a pre-oxidized platinum electrode. Curve (1) was recorded after the platinum wire electrode had been cathodized just to hydrogen

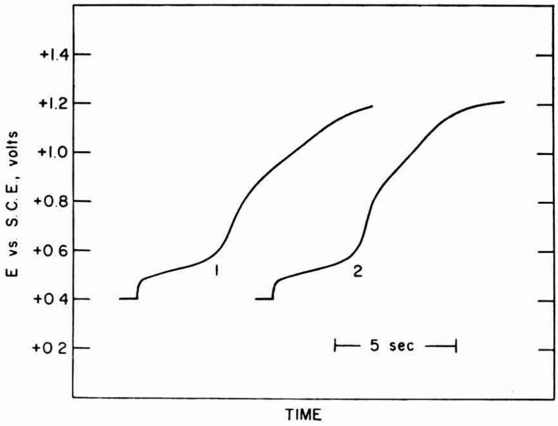

Fig. 6. Chronopotentiograms for the oxidation of 0.0105 $M$ plutonium(III) to plutonium(IV) in 1 $F$ sulfuric acid medium at 25.8°. Each curve was recorded for a current of 394 $\mu$A. Curve 1, pre-reduced platinum electrode; curve 2, pre-oxidized platinum electrode.

evolution to remove any platinum oxide film and after the plutonium(III) solution had been stirred with a rapid stream of helium to remove hydrogen and allowed to become quiescent. Curve (2) corresponds to the chronopotentiogram recorded after the platinum electrode was anodically polarized for 10 sec with a current of 1863 $\mu$A. For each of the two experiments, the concentration of plutonium(III) was 0.0105 $M$, the current density 1.07 mA/cm$^2$, and the temperature 25.8°.

The chronopotentiogram obtained with a pre-reduced platinum electrode (curve 1) differs little from that recorded for a platinum electrode which has been subjected to one or more anodic polarizations (curve 2), except that the potential inflection of the latter is slightly better defined. In each curve, following the wave for the oxidation of plutonium(III) to plutonium(IV) at +0.5 V *vs.* S.C.E., a second poorly-defined wave due to surface oxidation of the platinum electrode commences at approximately +0.8 V *vs.* S.C.E. It is, therefore, concluded that plutonium(III) in sulfuric acid medium chemically reduces the platinum oxide film almost instantaneously after the anodic polarization is interrupted. The chemical reduction of the platinum oxide film by plutonium(III) is not so effective as cathodic polarization for the removal of the oxide film, however, because a cathodic chronopotentiogram recorded after an anodic trial indicates the presence of a very small residual quantity of oxide film. The anodic chronopotentiometry of plutonium(III) in sulfuric acid can be compared to the anodic behavior of hydroquinone[20] and of iron(II)[23] in the same medium.

The quarter-wave potential, $E_{1/4}$, for each chronopotentiogram in Fig. 6 is close to +0.51 V *vs.* S.C.E., which is the value of the formal potential for the plutonium(IV)–plutonium(III) couple in 1 $F$ sulfuric acid medium (Table 1). Such agreement indicates that, under the experimental conditions cited, the electro-oxidation of plutonium(III) to plutonium(IV) fulfils the criterion for reversibility.

Table 7 summarizes the chronopotentiometric data obtained for the electro-oxidation of 0.0105 $M$ plutonium(III) in 1 $F$ sulfuric acid. The transition times were measured from the instant the electrolysis circuit was closed to the moment the potential of the platinum electrode reached +0.70 V *vs.* S.C.E. At this potential the transition time is measurable before any significant quantity of surface oxidation of the electrode occurs. We discovered, however, that 25 $\mu$C of electricity were required to polarize the electrode from the open-circuit potential of +0.40 V *vs.* S.C.E. to the transition potential of +0.70 V *vs.* S.C.E. in blank experiments with the supporting

TABLE 7

ANODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(III) IN 1 $F$ SULFURIC ACID

| $i$ ($\mu A$) | $\tau$ (sec) | Temperature (°C) | $i_{corr}$ ($\mu A$) | $i\tau^{\frac{1}{2}}/AC$ (A sec$^{\frac{1}{2}}$ cm/mole) | $i_{corr}\tau^{\frac{1}{2}}/AC$ (A sec$^{\frac{1}{2}}$ cm/mole) |
|---|---|---|---|---|---|
| 701 | 1.16 ± 0.01 | 25.6 | 679 | 194 | 188 |
| 494 | 2.29 ± 0.01 | 25.6 | 483 | 192 | 188 |
| 394 | 3.67 ± 0.06 | 25.7 | 387 | 194 | 191 |
| 326 | 5.32 ± 0.04 | 25.6 | 321 | 193 | 190 |
| 280 | 7.39 ± 0.04 | 25.6 | 277 | 195 | 193 |
| 234 | 10.50 ± 0.02 | 25.6 | 232 | 195 | 193 |
| 198 | 15.15 ± 0.03 | 25.6 | 196 | 198 | 196 |

electrolyte alone. Under the conditions of these experiments, charging of the electrical double layer rather than oxidation of the electrode comprises the major fraction of this blank quantity of electricity.

LINGANE[16] has devised a simple method to correct for the effect of electrode oxidation and charging of the electrical double layer. The following steps are involved: (i) the quantity of electricity corresponding to electrode oxidation and charging of the double layer is determined in a *blank* experiment without the electroactive species; (ii) this *blank* quantity of electricity is subtracted from the total quantity of electricity in an actual chronopotentiometric experiment to obtain a *corrected* quantity of electricity produced by reaction of the electroactive substance; and (iii) this *corrected* quantity of electricity is divided by the transition time $\tau$ for the actual experiment to obtain a *corrected* current. This approach is tantamount to the requirement of a constant current efficiency of less than 100% for the oxidation or reduction of the electroactive substance during the chronopotentiometric trial. While the postulation of constant current efficiency is not theoretically justifiable, the usefulness of this method of correction has been demonstrated with data for several systems, including the oxidation of oxalic acid[16] and the oxidation of hydroquinone[20] at platinum and gold electrodes in 1 $F$ sulfuric acid medium. This method of correction was applied in the present study. The corrected current was calculated from the relation $i_{\text{corr}} = i - Q/\tau$, where $i_{\text{corr}}$ is the corrected current ($\mu$A), $i$ is the observed current ($\mu$A) in the chronopotentiometric experiment, $Q$ is the quantity of electricity (25 $\mu$C) required to polarize the electrode to the transition potential in a blank experiment, and $\tau$ is the observed transition time (sec) in the actual chronopotentiometric trial.

Values of the corrected current and of $i_{\text{corr}}\tau^{\frac{1}{2}}/AC$ are listed in Table 7. Although the values of $i_{\text{corr}}\tau^{\frac{1}{2}}/AC$ presented in Table 7 are only 2–4% smaller than the observed (uncorrected) values, we believe these corrected data are more meaningful for the purpose of the evaluation of the diffusion coefficient of plutonium(III). The slight increase of $i_{\text{corr}}\tau^{\frac{1}{2}}/AC$ with increasing transition times is due to the cylindricity of the diffusion field.

The diffusion coefficient of plutonium(III) in 1 $F$ sulfuric acid was calculated from the theoretical equation for chronopotentiometry with a cylindrical (wire) electrode for each of the seven values of $i_{\text{corr}}\tau^{\frac{1}{2}}/AC$ included in Table 7. The average of these diffusion coefficient values, corrected for the difference between the experimental temperature and 25°, is $4.7 \pm 0.1 \times 10^{-6}$ cm$^2$/sec at 25°. Each of the seven values of $i_{\text{corr}}\tau^{\frac{1}{2}}/AC$ in Table 7 falls within ± 1% of the value of $i\tau^{\frac{1}{2}}/AC$ calculated for this average diffusion coefficient. This agreement is indicative of the precision attainable in the anodic chronopotentiometry of plutonium(III) in sulfuric acid.

*Chronopotentiometry of plutonium(III) in perchloric acid.* The anodic chronopotentiometry of plutonium(III) in 1 $F$ perchloric acid differs markedly from the behavior in sulfuric acid medium described above. Typical chronopotentiograms for the electro-oxidation of plutonium(III) at the platinum wire anode in 1 $F$ perchloric acid supporting electrolyte solution are presented in Fig. 7. The concentration of plutonium(III) was 0.0105 $M$, the current density 1.07 mA/cm$^2$, and the temperature 25.1°.

Curve (1) represents an anodic chronopotentiogram obtained after the platinum electrode had been previously cathodized to the hydrogen evolution potential in order to remove any platinum oxide film. Prior to the recording of curve (2), the platinum electrode was polarized anodically to produce a platinum oxide film. Therefore, curves (1) and (2) in Fig. 7 provide an interesting comparison of the anodic chronopotentiometry of plutonium(III) in 1 $F$ perchloric acid medium at pre-reduced and pre-oxidized electrodes. Both chronopotentiograms exhibit well-defined waves for the oxidation of plutonium(III) to plutonium(IV). The only discernible difference in these two chronopotentiograms is that the potential inflection in curve (1) is not so sharp as in curve (2). Consequently, the anodic transition time measured at, for example, $+0.90$ V *vs.* S.C.E. is slightly longer for the former than for the latter chronopotentiogram. In order to shed further light on these chronopotentiometric experiments, the following information must be introduced. Firstly, in 1 $F$ perchloric acid medium, the electro-oxidation of plutonium(III) to plutonium(IV) occurs between $+0.7$ and $+0.9$ V *vs.* S.C.E., the same range of potentials as the formation of the platinum oxide film[23]. Secondly, plutonium(III) in perchloric acid does not chemically reduce the platinum oxide film. This second fact was affirmed by the following experiment. If, following an anodic trial (Fig. 7, curve 1), the solution is stirred and de-oxygenated with helium and allowed to become quiescent, the subsequent cathodic chronopotentiogram shows a characteristic wave attributable to the reduction of a platinum oxide film. That this behavior does correspond to the reduction of the oxide film is demonstrated by the observation that, for all succeeding cathodic chronopotentiograms, the potential of the platinum electrode immediately falls to the value at which hydrogen ion is reduced. From these results, we conclude that the differences between the anodic chronopotentiograms recorded with a pre-reduced electrode (curve 1) and a pre-oxidized electrode (curve 2) depend on whether or not the formation of a platinum oxide film accompanies the oxidation of plutonium(III) to plutonium(IV).

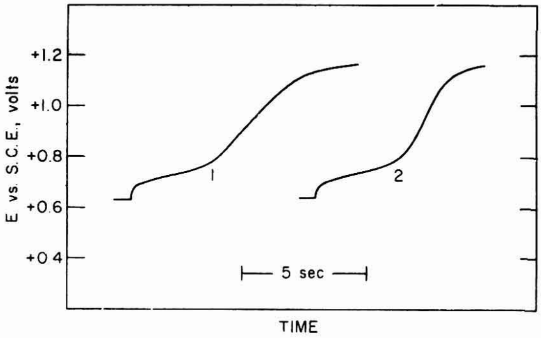

Fig. 7. Anodic chronopotentiograms for the oxidation of 0.0105 $M$ plutonium(III) to plutonium(IV) in 1 $F$ perchloric acid solution at 25.1°. For each curve the current was 395 $\mu$A. Curve 1, pre-reduced platinum electrode; curve 2, pre-oxidized platinum electrode.

One of the interesting discoveries of this phase of the study is that the presence of an oxide film on the platinum electrode does not decrease the reversibility of the oxidation of plutonium(III) in 1 $F$ perchloric acid. This behavior is clearly evident in Fig. 7, which shows no difference in the potential at which plutonium(III) is oxidized for either a pre-reduced electrode (curve 1) or a pre-oxidized electrode (curve 2). Repeated anodic trials have no effect on the chronopotentiogram for plutonium(III) oxidation. However, the possible consequence of more extensive oxidation of the platinum electrode, such as prolonged controlled-potential anodization at oxygen evolution potentials, was not investigated.

These observations contrast markedly with the chronopotentiometric behavior of several systems investigated by other workers. For example, LINGANE[16] found that even a partial oxide film on a platinum electrode increases the overpotential and decreases the transition time for the chronopotentiometric oxidation of oxalic acid in 1 *F* sulfuric acid. Furthermore, a complete oxide film inhibits the oxidation of oxalic acid to such an extent that no chronopotentiogram is observable. Similar results for the electro-oxidation of iron(II) at a platinum electrode in 1 *F* perchloric acid medium were obtained by ANSON[23]. Among other examples of analogous behavior may be mentioned the oxidation of iodide ion in phosphate or borate buffer systems[25] and the oxidation of uranium(IV) in 1 *F* perchloric acid solution[26]. In every case mentioned above, the chronopotentiometric oxidation proceeds less reversibly, *i.e.*, with a larger overpotential, on a pre-oxidized platinum electrode than on a pre-reduced electrode. Hence, plutonium(III) in 1 *F* perchloric acid appears to be unique in that it is oxidized with the same degree of reversibility at both pre-reduced and pre-oxidized platinum electrodes. It is premature to speculate about the reason for this uniqueness. More detailed investigations of the anodic chronopotentiometry of plutonium(III) and of numerous other substances are necessary before an unequivocal interpretation of the effect of surface condition of platinum electrodes on electrochemical processes can be stated.

Transition-time measurements obtained with both a pre-reduced and a pre-oxidized electrode are summarized in Table 8. For the purpose of recording a chronopotentiogram with a pre-reduced electrode, the platinum wire electrode was cathodically polarized to hydrogen evolution before each anodic trial at a constant current of 395 μA for 10 sec. The solution was swept with helium to remove hydrogen and allowed to become quiescent prior to the anodic trial. Chronopotentiograms with a pre-oxidized electrode were recorded after the platinum electrode was anodized at the beginning of each set of trials for 30 sec at a current of 395 μA, after helium was

TABLE 8

ANODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(III) IN 1 *F* PERCHLORIC ACID

| $i$ (μA) | $\tau$ (sec) | Temperature (°C) | $i_{corr}$ (μA) | $i\tau^{1/2}/AC$ (A sec$^{1/2}$ cm/mole) | $i_{corr}\tau^{1/2}/AC$ (A sec$^{1/2}$ cm/mole) |
|---|---|---|---|---|---|
| (a) Pre-reduced electrode; $i_{corr} = i - 248/\tau$ | | | | | |
| 494 | 2.67 ± 0.05 | 25.4 | 404 | 208 | 170 |
| 395 | 4.37 ± 0.04 | 25.4 | 338 | 212 | 181 |
| 326 | 5.99 ± 0.02 | 25.0 | 285 | 206 | 180 |
| 279 | 8.29 ± 0.02 | 25.3 | 249 | 207 | 185 |
| 234 | 12.45 ± 0.01 | 25.4 | 214 | 213 | 195 |
| (b) Pre-oxidized electrode; $i_{corr} = i - 84/\tau$ | | | | | |
| 494 | 2.49 ± 0.02 | 25.4 | 460 | 201 | 187 |
| 395 | 4.01 ± 0.04 | 25.4 | 374 | 204 | 193 |
| 326 | 5.51 ± 0.02 | 25.0 | 311 | 198 | 188 |
| 279 | 7.68 ± 0.06 | 25.3 | 268 | 199 | 192 |
| 234 | 11.56 ± 0.04 | 25.4 | 227 | 205 | 199 |

bubbled through the solution to remove oxygen, and after the solution was allowed at least one minute to achieve quiescence. All transition times were measured from the moment the electrolysis circuit was closed to the instant the potential of the platinum electrode reached +0.90 V *vs.* S.C.E. (Fig. 7). The concn. of Pu(III) was 0.0105 *M*.

During an anodic polarization, the total quantity of electricity produced may originate from four sources: diffusion-controlled electro-oxidation of plutonium(III); charging of the electrical double layer; surface oxidation of the platinum electrode; and, electro-oxidation of water. The transition times for the pre-reduced electrode listed in Table 8 are longer than the corresponding values obtained with the pre-oxidized electrode and this is due almost entirely to the quantity of electricity required to oxidize the surface of the pre-reduced electrode. The other three factors contribute more or less equal amounts of electricity for both the pre-reduced and pre-oxidized electrodes. However, a subtle difference also arises from the fact that a longer electrolysis time, *i.e.*, transition time, allows additional plutonium(III) to diffuse towards the electrode and undergo oxidation. Under the existing experimental conditions, the quantity of electricity required to polarize the pre-reduced electrode in pure 1 *F* perchloric acid from an open-circuit potential of +0.63 V *vs.* S.C.E. to the transition potential of +0.90 V *vs.* S.C.E. was 248 $\mu$C. However, only 84 $\mu$C of electricity were needed to polarize the pre-oxidized electrode to the same transition potential. These quantities of electricity, measured in experiments with the supporting electrolyte solution alone, were used in the calculation of $i_{\mathrm{corr}}\tau^{\frac{1}{2}}/AC$ for the pre-reduced and pre-oxidized electrode according to the procedure of LINGANE[16] already described (*vide supra*). A comparison of the results of these calculations and of the observed (uncorrected) values of $i\tau^{\frac{1}{2}}/AC$ is provided in Table 8. Note that the observed values of $i\tau^{\frac{1}{2}}/AC$ obtained with the pre-reduced electrode are approximately 4% greater than for the pre-oxidized electrode. This is the trend predicted from knowledge of the additional quantity of electricity required to oxidize the surface of the pre-reduced electrode. However, the calculated values of $i_{\mathrm{corr}}\tau^{\frac{1}{2}}/AC$ for the pre-reduced electrode fall 2–9% lower than those for the pre-oxidized electrode. It is apparent, therefore, that the simple method of correction introduces an over-correction. Two sources of error are (i) the inadequacy of the theory of the method of correction and (ii) the incorrectness of the assumption that the quantity of electricity measured in a blank experiment is the same as in an actual trial.

The diffusion coefficient for plutonium(III) in 1 *F* perchloric acid was calculated from the theoretical transition-time equation for chronopotentiometry with a cylindrical (wire) electrode[20] and the values of $i_{\mathrm{corr}}\tau^{\frac{1}{2}}/AC$ for the pre-oxidized electrode listed in Table 8. The value obtained, $4.8 \pm 0.2 \times 10^{-6}$ cm$^2$/sec at 25.0°, is virtually identical with the diffusion coefficient of plutonium(III) in 1 *F* sulfuric acid.

### *Chronopotentiometry of plutonium(VI)*

Throughout these studies of plutonium(VI), the following experimental conditions obtained: the concentration of plutonium(VI) was 0.0103 *M*; the area and the radius of the platinum wire electrode were 0.370 cm$^2$ and 0.0816 cm, respectively; and, with the one exception noted below, the temperature was 25.8°. The platinum electrode was not pre-treated in any unusual way prior to the recording of a chronopotentiogram for plutonium(VI) reduction. Each of the chronopotentiograms and all the data presented for the electro-reduction of plutonium(VI) were obtained after at least one complete cathodic chronopotentiogram was recorded, after helium was bubbled through the solution to remove any hydrogen, and after the solution was allowed to become quiescent. Although plutonium(VI) should, thermodynamically, oxidize a platinum electrode, this possibility was not investigated. We observed, however, that the cathodic chronopotentiogram recorded after the platinum electrode had been deliberately pre-anodized exhibited not the characteristic well-defined doublet wave for plutonium(VI) reduction (*vide infra*), but a single wave the transition time of which is more or less equal to the overall transition time ($\tau_1 + \tau_2$) for the two-step wave.

A family of three chronopotentiograms for the reduction of plutonium(VI) in 1 *F* perchloric acid at a platinum wire electrode is shown in Fig. 8. Curves (1), (2), and (3) were recorded for current densities of 4.66, 3.25, and 1.85 mA/cm$^2$, respectively. The data presented below indicate that, under the experimental conditions, the two-wave chronopotentiograms correspond to the step-wise reduction of plutonium(VI) first to plutonium(V) and then to plutonium(III).

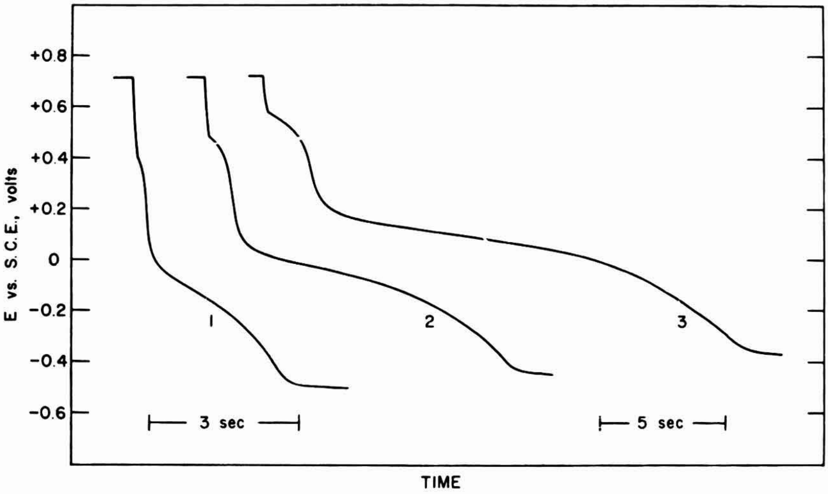

Fig. 8. Family of three chronopotentiograms for the step-wise reduction of 0.0103 *M* plutonium-(VI) in 1 *F* perchloric acid at 25.8°. The 3-sec time scale pertains to curves (1) and (2); the 5-sec time scale applies to curve (3). Curve 1, $i = 1725\ \mu$A; curve 2, $i = 1201\ \mu$A; curve 3, $i = 683\ \mu$A.

To establish the identity of the first step in the chronopotentiometric reduction of plutonium(VI), quantitative measurements of the transition time $\tau_1$ were made over a range of current densities. Experimental data are shown in Table 9. The transition times were measured from the instant the electrolysis circuit was closed to the moment the potential reached +0.40 V *vs.* S.C.E. Selection of this latter transition potential was based on the observation that the inflection for the first wave occurred at +0.40 V *vs.* S.C.E. for each of the chronopotentiograms for which quantitative transition-time measurements were made. The observed values of $i\tau_1^{1/2}/AC$ exhibit the expected increase with $\tau_1$ due to the cylindricity of the diffusion field and have approximately the same magnitude as the values reported earlier for the one-electron reduction of plutonium(IV) to plutonium(III) and the one-electron oxidation of plutonium(III) to plutonium(IV). We conclude, therefore, that the first wave of the chronopotentiograms in Fig. 8 can be attributed to the reduction of plutonium(VI) to plutonium(V).

The formal potential for the plutonium(VI)–plutonium(V) couple in 1 *F* perchloric acid is +0.671 V *vs.* S.C.E. (Table 1). Inspection of the chronopotentiograms in Fig. 8 reveals that the quarter-wave potential for the first wave is considerably more reducing (less positive) than this value and, furthermore, is strongly dependent upon the current density. In curves (1), (2), and (3), the quarter-wave potentials are close to +0.39, +0.47, and +0.56 V *vs.* S.C.E., respectively. Therefore, on the basis of the large overpotential and strong dependence of $E_{1/4}$ on current density, we believe the plutonium(VI)–plutonium(V) couple behaves less reversibly than the plutonium(IV)–plutonium(III) couple in 1 *F* perchloric acid medium.

From the observed values of $i\tau_1^{1/2}/AC$ presented in Table 9, the diffusion coefficient of plutonium(VI), which presumably exists as the $PuO_2^{2+}$ ion, has been calculated to be $7.3 \pm 0.3 \times 10^{-6}$ cm²/sec in 1 *F* perchloric acid at 25.8°. The value of this diffusion coefficient at 25.0° is $7.2 \times 10^{-6}$ cm²/sec.

TABLE 9

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(VI) IN 1 *F* PERCHLORIC ACID

(First wave)

| $i$ ($\mu A$) | $\tau_1$ (sec) | $i\tau_1^{1/2}/AC$ (A sec$^{1/2}$ cm/mole) Observed | Theory[a] |
|---|---|---|---|
| 683 | $1.66 \pm 0.04$ | 231 | 234 |
| 389 | $5.60 \pm 0.04$ | 242 | 238 |
| 324 | $7.42 \pm 0.01$ | 232 | 239 |
| 278 | $10.95 \pm 0.03$ | 242 | 241 |
| 233 | $16.81 \pm 0.16$ | 251 | 243 |

[a] See text.

Theoretical values of $i\tau_1^{1/2}/AC$ calculated by means of the transition-time equation for cylindrical diffusion[20] and using the diffusion coefficient of $7.3 \times 10^{-6}$ cm²/sec at 25.8° agree to within approximately ± 3% with the observed values listed in Table 9. This concordance of theory and experiment indicates that the rate of electro-reduction of plutonium(VI) is diffusion-controlled and, therefore, that the rate of disproportionation of plutonium(V) to plutonium(VI) and plutonium(IV) is insignificant under the experimental chronopotentiometric conditions. If plutonium(V) did disproportionate under these conditions, $i\tau_1^{1/2}/AC$ would increase as the transition time $\tau_1$ increases due to the formation of additional plutonium(VI). Furthermore, any plutonium(IV) formed would undergo electro-reduction to plutonium(III) at the extant potential. These results suggest the possibility that plutonium(V) in 1 *F* perchloric acid could be prepared by the controlled-potential reduction of plutonium-(VI). Indeed, previous work has indicated that the controlled-potential coulometric reduction of plutonium(VI) to plutonium(III) in 1 *F* perchloric acid does proceed through the plutonium(V) oxidation state, but the reaction is too slow to be useful as an analytical method[27]. The preparation of plutonium(V) solutions would afford an opportunity for studies of the electrochemistry and rate of disproportion of this oxidation state of plutonium and this possibility, therefore, warrants further study.

It was determined from quantitative measurements of the overall transition time, $(\tau_1 + \tau_2)$, for the entire doublet wave that the second step of the cathodic chronopotentiograms in Fig. 8 can be assigned to the electro-reduction of plutonium(V) to plutonium(III). It should be emphasized that the actual process which occurs during the interval between the first and second transition times is a combination of the reduction of plutonium(VI) and plutonium(V) to plutonium(III). The theory for diffusion-controlled step-wise processes in chronopotentiometry with cylindrical electrodes predicts, firstly, that the transition times $\tau_1$ and $\tau_2$ for the two waves are governed only by the bulk concentration and the diffusion coefficient of the original parent substance and, secondly, that the ratio $\tau_2/\tau_1$ increases as the magnitudes of the transition times increase[18,28].

Figure 8 reveals that the potential at which the second wave of the two-step reduction of plutonium(VI) occurs is critically dependent upon current density. Consequently, the potential at which the transition time $(\tau_1 + \tau_2)$ was measured had to be determined after first recording a complete chronopotentiogram at each desired current density prior to the actual series of measurements. The transition potentials selected, as well as the other chronopotentiometric data, are included in Table 10. For the present system the second potential inflection is poorly delineated. Therefore, even a slight uncertainty in the selection of the potential at which the transition time is measured markedly affects the chronopotentiometric results. This situation serves to emphasize the care which must be exercised both in the selection of the transition potential and in the interpretation of the transition-time data.

The values of $i(\tau_1 + \tau_2)^{\frac{1}{2}}/AC$ presented in Table 10 are slightly greater than three times the values of $i\tau_1^{\frac{1}{2}}/AC$ of Table 9. Although these experimental data should be interpreted on the basis of the theory of chronopotentiometry for step-wise processes at cylindrical electrodes[18,28], the radius of the platinum wire cathode was large enough (0.0816 cm) that the results may be correctly and more easily interpreted with the theory for semi-infinite linear diffusion. From the theory developed by BERZINS AND DELAHAY[29] for the step-wise reduction of a single electroactive species at a plane electrode, one can derive the relation

TABLE 10

CATHODIC CHRONOPOTENTIOMETRY OF PLUTONIUM(VI) IN 1 $F$ PERCHLORIC AICD

(Double wave)

| $i$ ($\mu A$) | $\tau_1 + \tau_2$ (sec) | *Transition potential* (*V vs. S.C.E.*) | $i(\tau_1 + \tau_2)^{\frac{1}{2}}/AC$ (*A sec*$^{\frac{1}{2}}$ *cm/mole*) |
|---|---|---|---|
| 2413 | 1.50 ± 0.03 | −0.40 | 776 |
| 1725 | 3.02 ± 0.04 | −0.40 | 787 |
| 1201 | 5.80 ± 0.01 | −0.34 | 760 |
| 828 | 12.03 ± 0.04 | −0.30 | 754 |
| 682 | 18.35 ± 0.22 | −0.30 | 766 |

$$\frac{\dfrac{i(\tau_1 + \tau_2)^{\frac{1}{2}}}{AC}}{\dfrac{i\tau_1^{\frac{1}{2}}}{AC}} = \frac{n_1 + n_2}{n_1} \qquad (1)$$

where $n_1$ and $n_2$ are the numbers of electrons per molar unit of electrode reaction for each of the two steps in the reduction or oxidation of the electroactive substance. Since the experimental ratio $(n_1 + n_2)/n_1$ is close to 3 and $n_1 = 1$, it is obvious that $n_2 = 2$ and the second step in the chronopotentiometric reduction of plutonium(VI) must be the electroreduction of plutonium(V) to plutonium(III). It should be noted that, since only integral $n$-values are expected, precise ratios of $(n_1 + n_2)/n_1$ are not strictly necessary.

In 1 $F$ perchloric acid the formal potential for the plutonium(V)–plutonium(III) couple is +0.835 V *vs.* S.C.E. It is apparent from Fig. 8 that the electro-reduction of plutonium(V) to plutonium(III) proceeds with an overpotential of as large as 600–800 mV. This irreversibility of the plutonium(V)–plutonium(III) couple is attributable to the fact that the reduction process requires the transfer of two electrons and the breakage of plutonium–oxygen bonds. This also explains why plutonium(V) is the actual reduction product of plutonium(VI) although the electro-reduction of plutonium(VI) to either plutonium(IV) or plutonium(III) is favored thermodynamically (Table 1). The extreme irreversibility of the plutonium(VI)–plutonium(IV) and plutonium(VI)–plutonium(III) couples favors the reduction of plutonium(VI) to plutonium(V).

The diffusion coefficient of plutonium(VI) in 1 $F$ perchloric acid calculated from the transition time data for the entire doublet wave (Table 10) is larger ($8.4 \pm 0.4 \times 10^{-6}$ cm$^2$/sec at 25.8°) than the value calculated for the first wave ($7.3 \times 10^{-6}$ cm$^2$/sec) and is less precisely determined. This disparity of results is due undoubtedly to the poor definition of the potential inflection for the second wave and the resultant uncertainty in the measurement of the overall transition time. It is evident from Fig. 8 that even a relatively small change in the choice of the transition potential markedly affects the transition time $(\tau_1 + \tau_2)$ and the calculated value of the diffusion coefficient. Therefore, we consider the value based on the first wave, $7.2 \times 10^{-6}$ cm$^2$/sec at 25.0°, to be more reliable.

Current-reversal chronopotentiometry provided additional information regarding the stability of plutonium(V) and the electrochemical behavior of plutonium(VI) and plutonium(V) in 1 $F$ perchloric acid medium. A current-reversal chronopotentiogram is shown in Fig. 9 for the electroreduction of plutonium(VI) to plutonium(V) and the subsequent re-oxidation of plutonium(V) to plutonium(VI) in 1 $F$ perchloric acid solution at a current density of 1.05 mA/cm$^2$. The current was reversed at the moment the potential of the platinum wire electrode reached +0.40 V *vs.* S.C.E. The cathodic branch of the chronopotentiogram can be attributed to the reduction of plutonium(VI) to plutonium(V). The anodic portion of the chronopotentiogram shows two distinct waves, the first of which corresponds to re-oxidation of plutonium(V) to plutonium(VI) and the second of which is caused by surface oxidation of the platinum electrode.

The theory for current-reversal chronopotentiometry has been developed by BERZINS AND DELAHAY[29] for linear diffusion processes and by MURRAY AND REILLEY[30] for diffusion to cylindrical and spherical electrodes. The interpretation of current-reversal chronopotentiograms is straightforward provided the current density remains constant throughout the entire electrolysis and provided the electrode reaction occurring after current reversal is the reverse of the reaction proceeding before current reversal. For a plane electrode, the transition time $\tau_r$ for the current-reversal wave is exactly one-third of the transition time $\tau_1$ for the first wave if both the reactant and product species are soluble. The current-reversal wave is smaller due to the fact that two-thirds of the product species generated prior to current reversal diffuses away from the electrode surface. For the cylindrically-symmetrical diffusion field around a wire electrode, however, the increase in the size of the solution–volume element as the diffusion layer becomes thicker and thicker—or as the radial distance from the electrode surface increases—causes the concentration gradient of the electroactive substance during the current-reversal process to be smaller for a cylindrical electrode than for a plane electrode. Therefore, less than one-third of the product species undergoes the desired electrode reaction upon current reversal and the ratio of the transition times for the first wave and the current-reversal wave, $\tau_1/\tau_r$, is greater than 3 for a wire electrode. Furthermore, for cylindrical diffusion, $\tau_1/\tau_r$ increases as the absolute magnitudes of the transition times increase. Factors which decrease the diffusion-layer thickness relative to the radius of the cylindrical electrode, such as short transition times, small diffusion coefficients for the electroactive species, and a large electrode radius, cause $\tau_1/\tau_r$ to decrease and approach 3 as a limiting value.

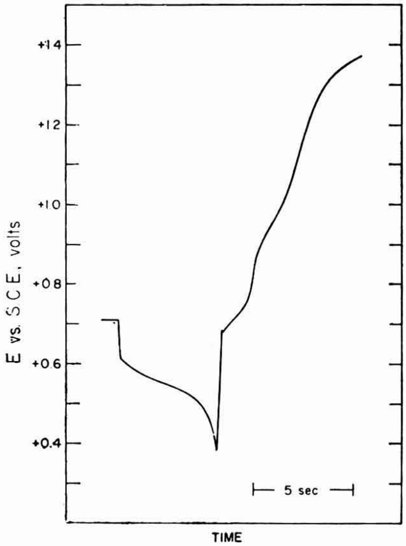

Fig. 9. Current-reversal chronopotentiogram for the reduction of plutonium(VI) to plutonium(V) and the subsequent re-oxidation of plutonium(V) to plutonium(VI) in 1 *F* perchloric acid medium. Concn. of plutonium(VI), 0.0103 *M*; temp., 25.8°; current, 388 $\mu$A.

Table II summarizes the results of three determinations of the ratio $\tau_1/\tau_r$. The transition time $\tau_1$ for the first wave was measured at $+0.40$ V *vs.* S.C.E. according to the manual technique described earlier. The transition time $\tau_r$ for the current-reversal wave was determined by a difference method. Current reversal was accomplished by manipulation of a fast-acting double-pole double-throw switch. Measurements of $\tau_1 + \tau_r$ were obtained by starting simultaneously the electrolysis and the timing clock, reversing the current at the instant the potential of the electrode reached $+0.40$ V *vs.*

S.C.E. (while the timing clock continued to run), and interrupting both the electrolysis and the timing clock when the potential of the electrode reached +0.80 V *vs.* S.C.E. for the current-reversal wave (Fig. 9). The average values of $\tau_1$ were subtracted from the corresponding average values of $\tau_1 + \tau_r$ to obtain the results for $\tau_r$ listed in Table 11. Note that the observed values of $\tau_1/\tau_r$ are constant and do not exhibit the expected increase with transition time attributable to the cylindricity of the diffusion field. The theoretical transition-time ratios included in Table 11 were calculated from the equation for current-reversal chronopotentiometry with a cylindrical electrode derived by MURRAY AND REILLEY[30]. The correct application of the theoretical equation requires knowledge of the diffusion coefficient of the electroactive substance which undergoes the current-reversal electrode reaction, namely plutonium(V). Since such information is not available, the value for the diffusion coefficient of plutonium(VI) determined in the present study, $7.3 \times 10^{-6}$ cm²/sec at 25.8°, was used for the theoretical calculations. In addition, the theoretical transition-time ratios were calculated on the assumption that the observed values of $\tau_1$ were correct. The experimental ratios in Table 11 range from 7–9% smaller than the corresponding theoretical transition-time ratios, but there is no doubt that the theoretical and experimental transition-time ratios are in reasonable agreement.

TABLE 11

CURRENT-REVERSAL CHRONOPOTENTIOMETRY OF PLUTONIUM(VI) IN 1 *F* PERCHLORIC ACID

(First wave)

| $i$ (*μA*) | $\tau_1$ (*sec*) | $\tau_r$ (*sec*) | $\tau_1/\tau_r$ *Observed* | $\tau_1/\tau_r$ *Theory*[a] |
|---|---|---|---|---|
| 388 | 5.18 ± 0.05 | 1.77 ± 0.03 | 2.93 | 3.14 |
| 324 | 7.42 ± 0.01 | 2.54 ± 0.06 | 2.92 | 3.19 |
| 278 | 10.37 ± 0.03 | 3.55 ± 0.07 | 2.92 | 3.21 |

[a] Calculated according to the theoretical equation of MURRAY AND REILLEY[30].

Current-reversal chronopotentiometry corroborates the previous conclusion that the rate of disproportionation of plutonium(V) is too slow to be observed under the extant chronopotentiometric conditions. Disproportionation of plutonium(V) would enhance $\tau_1$ and diminish $\tau_r$, and as a consequence the observed values of $\tau_1/\tau_r$ would be larger than the theoretical ratios. In the present investigation, the experimental values for $\tau_r$ were larger than the values predicted on the basis of the theoretical equation. In attempting to discover the reason for this discrepancy, one should bear in mind that the current-reversal transition time was relatively short in each experiment (Table 11). For short transition times, as discussed previously, surface oxidation of the platinum electrode and charging of the electrical double layer decrease the current efficiency for the electrochemical process of interest and cause the transition times to be larger than expected. In addition, when the timing clock is permitted to run throughout the electrolysis, the inevitable time lag in the manual reversal of the current will cause a positive error in the observed $\tau_r$. However, this same time lag allows some of the product species formed prior to current reversal to diffuse away from the electrode surface and escape electrode reaction; consequently, a negative error for $\tau_r$ results. These factors, coupled with the inherent disadvantage in the use of a difference method to measure $\tau_r$, are probably responsible for the deviations of the experimental results from the theoretical values.

To conclude this phase of the investigation, we determined the effect of current reversal at the potential corresponding to the transition time for the second wave of the cathodic chronopotentiogram for the step-wise reduction of plutonium(VI). These experiments have provided evidence that, following the reduction of plutonium(VI) to plutonium(V) and plutonium(III), current reversal results in the re-oxidation of plutonium(III) to plutonium(IV). A typical chronopotentiogram which illustrates this behavior is shown in Fig. 10; the current density was 3.24 mA/cm².

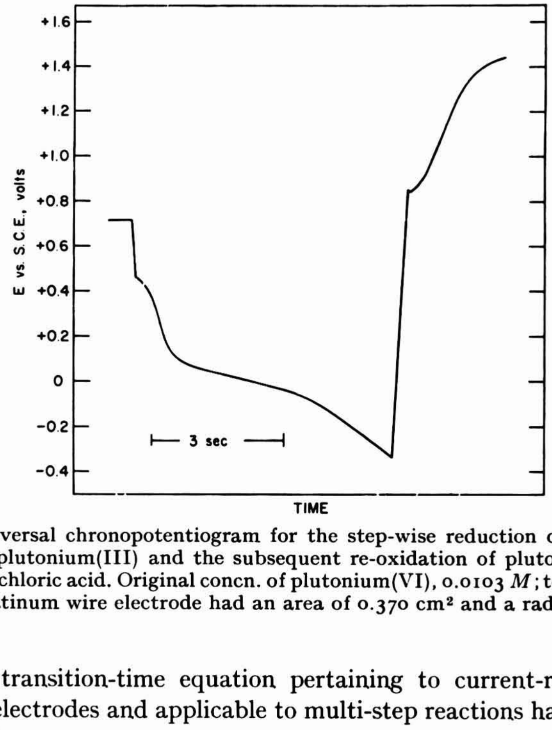

Fig. 10. Current-reversal chronopotentiogram for the step-wise reduction of plutonium(VI) to plutonium(V) and plutonium(III) and the subsequent re-oxidation of plutonium(III) to plutonium(IV) in 1 *F* perchloric acid. Original concn. of plutonium(VI), 0.0103 *M*; temp., 25.8°; current, 1199 μA. The platinum wire electrode had an area of 0.370 cm² and a radius of 0.0816 cm.

A theoretical transition-time equation pertaining to current-reversal processes with cylindrical electrodes and applicable to multi-step reactions has not been reported previously. However, starting with fundamental relations presented by MURRAY AND REILLEY[30], we have derived the general expression for a two-step reduction (or oxidation) process which is followed by current reversal.

$$\frac{\tau_1 + \tau_2}{\tau_r} = \frac{(n_1 + n_2 + n_r)^2}{n_r^2} \frac{\left[1 - \frac{\pi^{\frac{1}{2}} D^{\frac{1}{2}} \tau_r^{\frac{1}{2}}}{4 r_0} + \ldots\right]^2}{\left[1 - \frac{\pi^{\frac{1}{2}} D^{\frac{1}{2}} (\tau_1 + \tau_2 + \tau_r)^{\frac{1}{2}}}{4 r_0} + \ldots\right]^2} - 1 \qquad (2)$$

where $\tau_1 + \tau_2$ is the total transition time for the overall doublet wave, $\tau_r$ is the transition time for the current-reversal wave, $n_1$ and $n_2$ are, respectively, the numbers of electrons per molar unit of electrode reaction for each of the two steps, $n_r$ is the number of electrons for the current-reversal process, $D$ is the diffusion coefficient of the species which undergoes the current-reversal electrode reaction (plutonium(III) in the present situation), and $r_0$ is the radius of the cylindrical (wire) electrode. The two infinite series expansions enclosed within the brackets of the above equation account for the effect of the cylindricity of the diffusion field on the transition times. Additional terms in these expansions can be calculated according to the procedure outlined in a previous communication[20]. One important assumption implicit in the derivation of this equation is that the current density remain constant throughout the duration of the electrolysis.

TABLE 12

CURRENT-REVERSAL CHRONOPOTENTIOMETRY OF PLUTONIUM(VI) IN 1 $F$ PERCHLORIC ACID

(Double wave)

The transition potential *versus* S.C.E. is given in parentheses after the corresponding transition-time measurement.

| $i$ | $\tau_1 + \tau_2$ | $\tau_r$ | $(\tau_1 + \tau_2)/\tau_r$ | |
|---|---|---|---|---|
| *(μA)* | *(sec)* | *(sec)* | *Observed* | *Theory*[a] |
| 1199 | 5.66 ± 0.06 (−0.30 V) | 0.77 ± 0.05 (+1.00 V) | 7.35 | 15.67 |
| 829 | 12.14 ± 0.07 (−0.30 V) | 1.19 ± 0.06 (+0.90 V) | 10.21 | 15.99 |
| 682 | 18.35 ± 0.22 (−0.30 V) | 1.75 ± 0.07 (+0.90 V) | 10.48 | 16.18 |

[a] See text, eqn. 2.

Table 12 summarizes the transition-time data obtained in these current-reversal experiments at 25.5°. The overall transition time $(\tau_1 + \tau_2)$ for the doublet wave was measured by the straightforward manual technique described earlier. Because of the marked effect of current density on the potential at which the second wave of the step-wise chronopotentiometric reduction of plutonium(VI) occurs (*vide supra*), the transition potential for each current density used in the measurements was selected from previously recorded chronopotentiograms. These transition potentials are listed in Table 12. The difference between average values for $\tau_1 + \tau_2$ and $\tau_1 + \tau_2 + \tau_r$ determined the transition time, $\tau_r$, for the current-reversal wave. The measuring technique employed for the evaluation of $\tau_r$ was identical to that mentioned above, and the transition potentials at which measurements of $\tau_1 + \tau_2 + \tau_r$ were made are included in Table 12. Three experimentally-determined values of $(\tau_1 + \tau_2)/\tau_r$ and the corresponding theoretical ratios calculated from eqn. (2) are compared in Table 12. These theoretical ratios were computed using $4.8 \times 10^{-6}$ cm$^2$/sec for the diffusion coefficient of plutonium(III) and assuming that the observed values of $\tau_1 + \tau_2$ were correct.

For purposes of discussion, it is convenient to consider the form of eqn. (2) for an experimental situation in which semi-infinite linear diffusion is closely approximated. Under this condition, the series expansions in eqn. (2) approach unity and the theoretical relation becomes

$$\frac{\tau_1 + \tau_2}{\tau_r} = \frac{(n_1 + n_2 + n_r)^2}{n_r^2} - 1 \tag{3}$$

Equation (3) predicts for a system for which $n_1 + n_2 = 3$ that $n_r = 1$, if $(\tau_1 + \tau_2)/\tau_r$

$= 15$. Similarly, if $(\tau_1 + \tau_2)/\tau_r = 5.25$, $n_r = 2$; and, if $(\tau_1 + \tau_2)/\tau_r = 3$, $n_r = 3$. Obviously, the value of $(\tau_1 + \tau_2)/\tau_r$ is a sensitive indication of the number of electrons, $n_r$, involved in the current-reversal electrode process. The data shown in Table 12 demonstrate that $n_r$ is unity and that the current-reversal reaction is the electro-oxidation of plutonium(III) to plutonium(IV).

### ANALYTICAL IMPLICATIONS

One of the important aims of the present investigation was the determination of experimental conditions suitable for the chronopotentiometric analysis of plutonium solutions. As this study has shown, co-reduction of the spontaneously-formed platinum oxide film limits the concentration range for which the chronopotentiometric determination of plutonium(IV) and plutonium(VI) is practical. Similarly, anodic chronopotentiometry with a platinum electrode for the determination of plutonium(III) is unattractive because the more or less concomitant oxidation of the electrode surface causes an uncertainty in the current efficiency for electro-oxidation of plutonium(III).

Although empirical calibration procedures may be feasible, an important future problem is the search for an electrode which is free from the surface phenomena encountered with a platinum electrode. The use of a gold electrode may be suitable for this purpose, principally because gold is more difficult to oxidize than platinum[16]. Under ideal conditions, knowledge of the diffusion coefficient of the pertinent plutonium species is essential for the calculation of the concentration of that species from theoretical transition-time equations. A summary of the diffusion coefficients for various plutonium species evaluated in this study is presented in Table 13.

TABLE 13

DIFFUSION COEFFICIENTS OF PLUTONIUM SPECIES AT 25°

| *Plutonium species* | *Medium (1 F)* | *Diffusion coefficient $D(\times 10^6\ cm^2/sec)$* |
|---|---|---|
| Pu(III) | $H_2SO_4$ | 4.7 |
| | $HClO_4$ | 4.8 |
| Pu(IV) | $H_2SO_4$ | 5.0 |
| | $HClO_4$ | 4.7 |
| | $HNO_3$ | 5.8 |
| | HCl | 5.2 |
| Pu(VI) | $HClO_4$ | 7.2 |

It is evident from the present work that the chronopotentiometric technique is well suited to (i) the determination of diffusion coefficients, (ii) the identification of electrode reactions, and (iii) the study of the effect of electrode surface condition on electrode processes. Further studies which have been suggested by this investigation should be of interest. These include a thorough study of the electrochemistry and rate of disproportionation of plutonium(V) and the development of analytical procedures for the chronopotentiometric determination of plutonium.

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## SUMMARY

The chronopotentiometric behavior of plutonium(III), plutonium(IV), and plutonium(VI) at a platinum electrode in various mineral acid media has been studied in order to determine the diffusion coefficients of the different plutonium species, the effects of surface oxidation of the platinum electrode, and the possible analytical usefulness of chronopotentiometry for the determination of plutonium.

The reduction of plutonium(IV) to plutonium(III) at a platinum wire cathode in perchloric, sulfuric, nitric, and hydrochloric acid solutions has been investigated. The relatively small diffusion coefficient of plutonium(IV) in each of these media plus the spontaneous chemical oxidation of the platinum electrode by plutonium(IV) result in a significant positive error in chronopotentiometry with concentrations of plutonium(IV) below 0.01 *M*.

Chronopotentiograms for the oxidation of plutonium(III) to plutonium(IV) in sulfuric acid show one wave due to oxidation of plutonium(III) followed by a second wave attributable to the formation of a platinum oxide film. Plutonium(III) in sulfuric acid medium chemically reduces the oxide film. The electro-oxidation of plutonium(III) in perchloric acid medium gives a well-defined chronopotentiogram at either pre-reduced or pre-oxidized electrodes.

The chronopotentiometric reduction of plutonium(VI) in a 1 *F* perchloric acid solution proceeds in a step-wise fashion first to plutonium(V) and then to plutonium(III). For the experimental conditions employed, there was no evidence to show that plutonium(V) undergoes significant disproportionation in the perchloric acid medium.

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# PRE-TREATMENT AND ADSORPTIVE PROPERTIES OF PLATINUM ELECTRODES

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## INTRODUCTION

The strong dependence of hydrogen evolution and ionization and of hydrogen adsorption upon the pre-treatment of the electrode, the purification of the electrolyte, and the experimental conditions of the measurements is a well established fact[1,2] for platinum metal electrodes. While the effect of poisons[2], specifically adsorbed anions or cations[2] or organic molecules[3-6] on hydrogen and oxygen adsorption and on the double-layer capacity have been studied, a systematic study of the major factors which are involved in many procedures of pre-treatment has, to the author's knowledge, not been published.

In the present paper the most usual procedures of pre-treatment were applied to a smooth platinum wire electrode (99.99%, geometric area 0.5 cm$^2$). Cathodic charging curves were used in some cases to determine the initial oxygen coverage of the surface produced by the pre-treatment. The cathodic formation and the anodic removal of an adsorbed layer of hydrogen atoms and the formation and reduction of an oxygen layer were studied after each pre-treatment under equivalent conditions by applying[7] potentiostatically a periodic potential sweep between 0.05 V and 1.4 V in $N$ $H_2SO_4$ and recording the current–potential curves. In addition the capacitive component, $1/\omega C_s$, of the interfacial impedance in a series circuit of resistance $R_s$ and capacitance $C_s$ was determined as a function of potential at 1000 c/sec by voltammetry with superimposed a.c. current. The experiments were carried out in purified solutions so that the effect of pre-treatment could be investigated without interference by effects due to adsorption of impurities from the solution. The change of the surface state with time was followed by measuring the $I$–$U$ curves and $1/\omega C_s$–$U$ curves during the first cycles after the pre-treatment.

## EXPERIMENTAL

The measurements were made in a Pyrex-glass vessel of conventional design. The gases used for stirring and saturating the solution were purified. The electrode potential refers to a hydrogen electrode in the same electrolyte and at the same temperature as the test electrode. All the runs were carried out in quiescent solution saturated with helium. The circuitry has been described[8] in detail elsewhere. If the initial sweeps after the pre-treatment were recorded the electrode was connected to the circuit at about 0.2 V during a cathodic potential sweep. This is easily accomplished since the electrode is grounded[8]. The photographed $I$–$U$ curves exhibit a cathodic current peak at the moment of connecting the electrode to the circuit and this is true for all the pre-treatments which are described here. An initial oxygen layer is quickly[9] reduced at 0.2 V. Nearly a monolayer of hydrogen atoms is present when the cathodic sweep ends at 0.05 V. The expression "monolayer" refers to that part of the surface on which hydrogen atoms adsorb. The initial part of the $I$–$U$ curves during the cathodic sweep between 0.2 V and 0.05 V is omitted for reasons of clarity, and the first sweep after the pre-treatment is defined as starting with the first anodic sweep.

One feature which was a part of all the different procedures of pre-treatment will be described here and abbreviated as Pr. 1 in the subsequent discussions. After each pre-treatment the electrode was transferred under exposure to air to the vessel and immersed in the solution by inserting it in a small glass joint. The solution was stirred intensively with helium. Air could diffuse during the short time (about 30 sec) in which a dummy glass joint was replaced by the electrode against the helium stream into the vessel. Five minutes of intensive stirring after the immersion were chosen to give the electrode time for equilibration and to remove traces of molecular oxygen. Afterwards the solution was left for 1 min to become quiescent. The electrode remained at open circuit during the first 6 min. No noticeable contamination of the electrolyte by repeated immersions was observed with the sensitive technique described in the following paragraph.

The solution was prepared from doubly-distilled water with a specific resistivity of $8 \cdot 10^6$ Ω cm at 25° and analytical reagent sulphuric acid. Pre-electrolysis of the electrolyte did not affect the shape of periodic $I$–$U$ curves at temperatures $T \leqslant 30°$. Evidently the concentration of impurities is negligibly small for measurements at $T \leqslant 30°$. The impurities do not move to the surface to a noticeable amount in about half a cycle (50 sec). The intermediate formation and reduction of the oxygen layer produces[7] a reproducible surface state of "high activity" which is time-independent under the chosen conditions. However, the presence of traces of organic impurities is detectable by $I$–$U$ curves at $T \geqslant 50°$. Curve (a) in Fig. 1 was measured at 70° in the original solution. The characteristic regions are marked. The $I$-$U$ curve, which did not change its shape over several hours, exhibits a small anodic wave at 0.6 V which was not observed during the anodic sweep at $T \leqslant 30°$. After the solution was purified curve (b) was obtained under the same conditions. The comparison of curves (a) and (b) demonstrates the presence of impurities in the original solution by the slight decrease of the height of the two hydrogen waves and by the increase of the oxygen wave during the anodic sweep. The impurities, whose rate of transport to the surface is enhanced with temperature, are oxidized in the oxygen region at higher temperatures. The coincidence of the oxygen reduction waves of curves (a) and (b) indicates that the oxygen layer is formed to the same extent for curves (a) and (b).

The following purification of the electrolyte proved successful. Hydrogen and oxygen were evolved simultaneously for an hour at 1 amp at 70°. A large bright platinum cylinder served as the anode, a platinum wire as the cathode. Hydrogen peroxide was formed to some extent. A potentiostatic $I$–$U$ curve taken at the end of hydrogen and oxygen evolution had a cathodic and an anodic limiting current density of equal size. After the interruption of the current the solution was stirred vigorously for 2 h with purified hydrogen in the presence of the large platinum cylinder at 70°. Two hours were sufficient for the decomposition of the hydrogen peroxide.

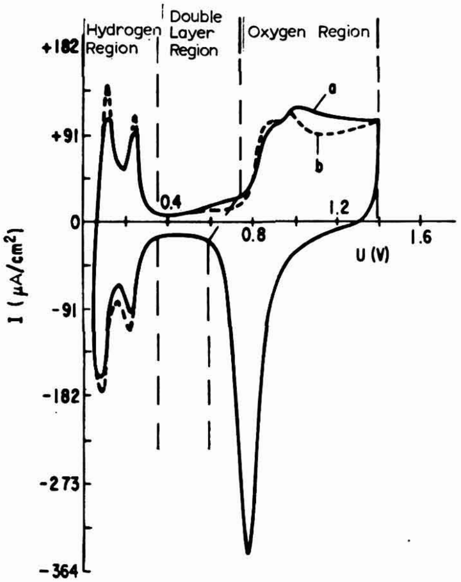

Fig. 1. Periodic current-potential curves at 70° in $N$ $H_2SO_4$. (a), original solution; (b), purified solution.

HOT NITRIC ACID TREATMENT

The electrode was put into hot nitric acid (70%) at 80° for 1 min. It was then washed thoroughly with distilled water. Fig. 2a represents a typical cathodic charging curve which was taken at 30° with 40 μA/cm² at the end of Pr.1. The charging curve ex-

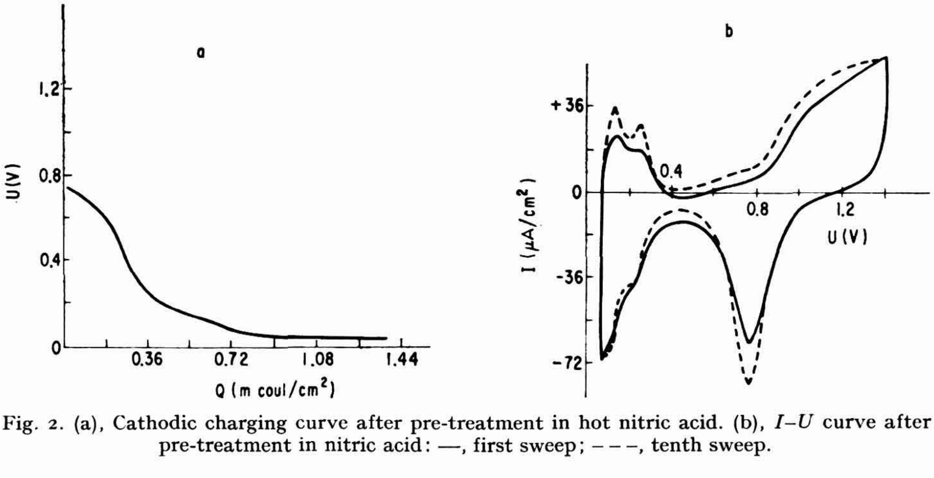

Fig. 2. (a), Cathodic charging curve after pre-treatment in hot nitric acid. (b), $I$–$U$ curve after pre-treatment in nitric acid: —, first sweep; – – –, tenth sweep.

hibits an oxygen branch in which an initial oxygen layer is reduced between 0.8 V and 0.3 V and the hydrogen branch. The oxygen layer does not correspond to a mono-layer since the length of the oxygen branch is shorter than that of the hydrogen branch. It is suggested that the oxygen layer was formed by an electrochemical mechanism in the hot nitric acid. Nitric acid is reduced and the oxygen layer is formed simultaneously at open circuit. The oxygen layer is too large to originate from the interaction between platinum and molecular oxygen in the air during Pr.1 (see the following section).

The *I–U* curves of the first sweep and the subsequent tenth sweep after the described pre-treatment in nitric acid and Pr. 1 are shown in Fig. 2b. The curves at 30° are reproductions of the original ones. The *I–U* curve of the first sweep has not the shape which is characteristic[7,10] for a clean surface (compare curve (b) in Fig. 1). The curve is similar to those which were obtained[11] in the presence of specifically adsorbable halide ions. Hydrogen and oxygen adsorption are inhibited. It is suggested that an intermediate product in the reduction of nitric acid is strongly adsorbed on platinum. It takes several hours of continuous cycling between 0.05 V and 1.4 V before the *I–U* curve regains the regular shape. An intermediate state is represented by the *I–U* curve of the tenth sweep in Fig. 2b. Pre-treatment with hot nitric acid is not recommended on the basis of the results described.

### HOT CHROMIC ACID TREATMENT

The electrode was put for 1 min into hot chromic acid solution (80°). It was then washed thoroughly with distilled water. After Pr. 1 the cathodic charging curve (a) in Fig. 3 was obtained with 40 $\mu A/cm^2$ at 30°. Obviously an oxygen layer was formed during the dipping of the electrode into hot chromic acid. It is approximately an oxygen monolayer under the assumption that the length of the hydrogen branch corresponds to a monolayer of hydrogen atoms. For reasons of comparison a cathodic charging curve (curve b) was also taken with 40 $\mu A/cm^2$ from 1.1 V by switching from the potentiostatic to a galvanostatic circuit when a potential of 1.1 V was reached during the cathodic sweep. As expected, curves (a) and (b) look very similar. Finally the interaction between a platinum surface which is free of an oxygen layer and molecular oxygen in the air was investigated. The electrode was taken out of

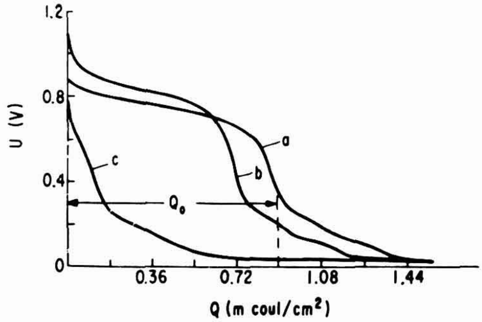

Fig. 3. Cathodic charging curves: (a), after pre-treatment in hot chromic acid solution; (b), from 1.1 V during a cathodic sweep; (c), after 5 min of exposure to air without an oxygen layer on the surface at the beginning of exposure.

the solution while maintaining a potential of 0.5 V where neither hydrogen nor oxygen is adsorbed to a measurable extent. It was washed with distilled water and exposed to air for 5 min. After Pr. 1 curve (c) was found. Obviously oxygen adsorption on platinum from the air is a slow process[12] and cannot account for the oxygen branches of the curve in Fig. 2a and of curve (b) in Fig. 3. It is suggested that the formation of the oxygen layer in hot chromic acid leads to the removal of adsorbed impurities and to the well known cleaning of the surface of platinum.

After the treatment in chromic acid solution and Pr. 1 the *I–U* curves and the $1/\omega C_s$–*U* curves do not differ during the first initial cycles at 30° (see curves (a) and (a′) in Fig. 4). The shape of the $1/\omega C_s$–*U* curves, which also reflect the three characteristic regions, was described in more detail in a previous communication[8]. If the electrode is exposed to air after the treatment in chromic acid and washing in distilled water, a slight change in shape takes place between the first and second sweep (curves (b) and (b′) in Fig. 4). It takes between 5–10 cycles before the shape of curves (a) and (a′) is approached. The difference between the first sweep and the second

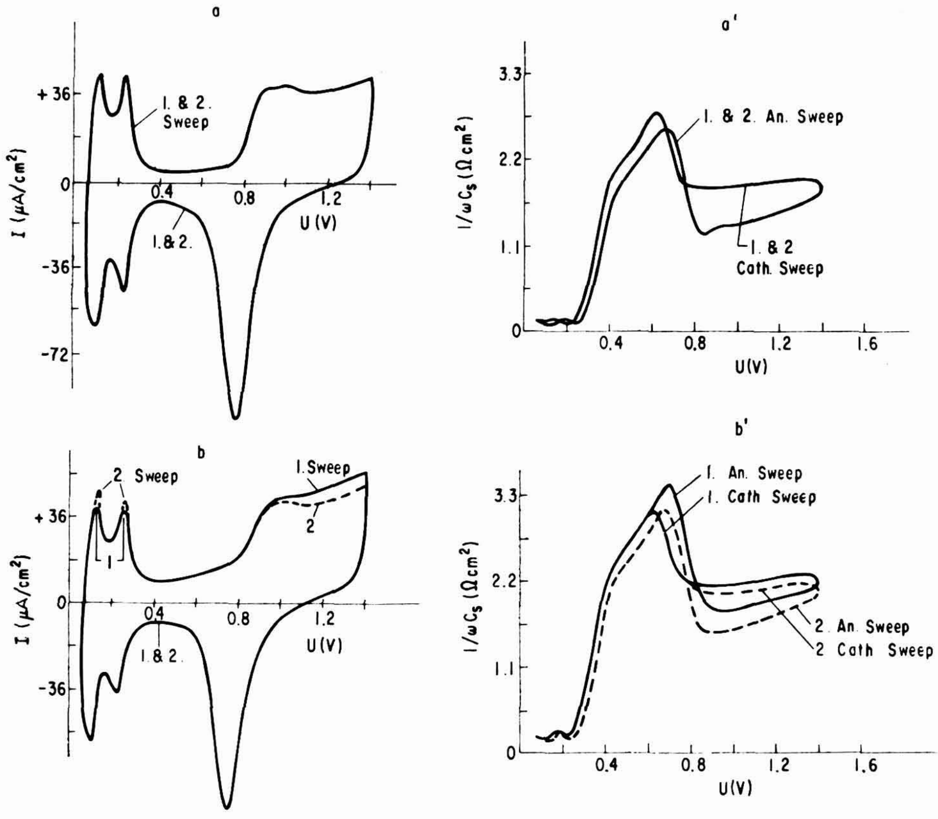

Fig. 4. *I–U* curves (a and b) and $1/\omega C_s$–*U* curves (a′ and b′) after pre-treatment (a and a′) and after 65 h of exposure to air (b and b′) at 30°.

sweep increases very slowly with the time of exposure to air. No difference could be detected after 1 h. The electrode had been exposed to air for 65 h in the case of curves (b) and (b′). Evidently the oxygen layer which is formed by the pre-treatment with chromic acid protects the electrode surface effectively against adsorption of hydrocarbons and other impurities. The removal of adsorbed impurities is demonstrated in curve (b′) by the increase of the height of the hydrogen waves and by the decrease of the oxygen wave during the second sweep. Evidently the first anodic formation of the oxygen layer removed most of the adsorbed impurities. The $1/\omega C_s$–$U$ curves confirm this conclusion. The double-layer capacity which decreases with adsorbed organic particles[3,5] becomes larger in the double layer and in the oxygen region with each sweep and tends towards the values corresponding to curve (a′).

## MECHANICAL ABRASION

The electrode which was used in the experiments of Fig. 4 was abraded mechanically with fine emery paper. Afterwards treatment with hot chromic acid and Pr. 1 were applied. As expected from this rough treatment, impurities are introduced to the surface (curves (a) and (b) in Fig. 5). It takes about 10 cycles before the shape of the $I$–$U$ curve (a) in Fig. 4 is approached. Then the current at a given potential during the anodic sweep is two to three times larger than that at the same potential of curve (a). The roughness factor of the surface was increased by the abrasion. The $1/\omega C_s$–$U$ curves show the occurrence of an additional effect which did not disappear over several hours of cycling. There are two maxima of $1/\omega C_s$ in the double-layer region. The hump in the $1/\omega C_s$–$U$ curves of Fig. 4 at about 0.4 V developed into a maximum after the abrasion. The interpretation of the latter phenomenon requires additional experimental work.

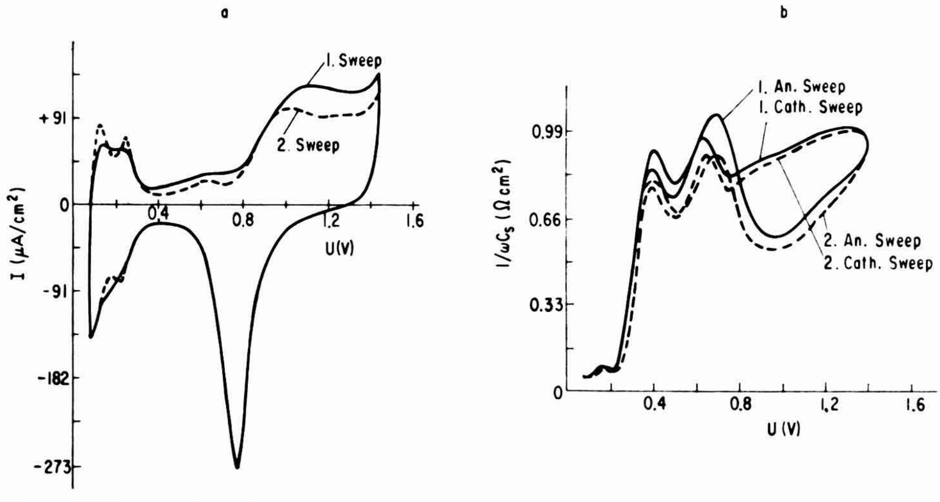

Fig. 5. $I$–$U$ curves (a) and $1/\omega C_s$–$U$ curves (b) during the first and second cycle after mechanical abrasion at 30°.

## GLOWING IN A GAS FLAME

After washing in distilled water the electrode was glowed in the blue flame of natural gas in a bunsenburner. Pr. 1 followed. The results were very similar to those in Fig. 4 and figures are not shown for this reason. The hydrogen peaks are slightly smaller and the oxygen wave is slightly larger during the first than during the second anodic sweep. A small amount of impurities is produced on the surface as confirmed by the capacity data in the double-layer region. These traces of impurities are removed by the first anodic formation of the oxygen layer. The results are in agreement with earlier work[13].

The same procedure was repeated with a hydrogen flame. The results were similar to those described for the glowing in the blue flame of natural gas. A passivation of the surface was not observed.

A spectacular poisoning of the electrode surface resulted from glowing in a small yellow flame of natural gas in a torch. This poisoning did not disappear with time during cycling between 0.05 and 1.4 V over 3 h and withstood treatment in hot chromic acid. Strong mechanical abrasion was necessary to remove it. It is suggested that residues of hydrocarbons or carbon itself were burned into the surface.

## SUMMARY

The nature of the major factors which are involved in the common methods of pretreament and their influence on the adsorptive properties were studied for smooth platinum electrodes by cathodic charging curves, cyclic voltammetry, and voltammetry with superimposed a.c. current. The differences of the current–potential curves and the capacitive component–potential curves during the first cycle and the subsequent cycles are discussed. It is shown to what extent these differences result from a contamination of the surface, introduced by the pre-treatment.

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# POLAROGRAPHY OF TITANIUM

## IV. SALICYLATE AND SULPHOSALICYLATE COMPLEXES OF TETRAVALENT TITANIUM

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The work previously carried out on the organo-titanium complexes had a purely analytical purpose, *i.e.*, to find some stable forms of complex which could yield a well-shaped polarographic wave[1,2]. The difficulty in estimating titanium as a free ion is due to its rapid hydrolysis in solution; the stabilisation of the titanyl ion using organic reagents has opened the way to a proper study of organic complexes[3,4,5]. According to PECSOK[3], a reversible wave having a half-wave potential of $-0.351$ V *vs.* S.C.E. is obtained in a saturated salicylic acid solution.

Titanium salicylate complexes[6] were studied using JOB's method[7]. Although this method for complexes with a hydrolysable cation has the advantage over any other electrochemical method based on potential measurements, it must be borne in mind that the variation method of JOB is preferably used in systems showing a simple equilibrium which is not the case in the Ti–salicylate or Ti–sulphosalicylate systems, as it will be explained in the discussion. The results obtained by DUTT AND GOSWAMI[6] show the presence of a Ti–salicylate complex in the ratio of 1:3. SOMMER[8] made a study of the analytical reaction of salicylate and its derivatives with titanium; he also made a spectrophotometric study of the complexes of tetravalent titanium with sulphosalicylate where he claims the identification of relatively unstable TiR and $TiR_2$ complexes. No definite polarographic work has been reported in the literature and the present study was made with a view to elucidate the possible complexes which could be formed at different concentrations of complexing agents and different pH values.

An electrode reaction is proposed which accounts for the different polarographic waves obtained.

### EXPERIMENTAL

The various polarographic techniques and apparatus and the preparation of the depolariser have been previously described[9]. Current–time curves on the first drop were recorded according to the method of SMOLER AND NĚMEC[10]. The salicylic and

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sulphosalicylic acid used were chemically-pure reagents; salicylic acid was brought into solution by the cautious addition of NaOH, and sulphosalicylic acid solution was prepared by direct dissolution of the acid in distilled water.

Blank polarograms were registered to test the purity and the possibility of the reduction at the D.M.E. of the two organic acids used; no wave was obtained before the evolution of hydrogen, however. According to a paper published by HALE[11] a reduction wave is obtained at $-2.39$ V *vs.* S.C.E. in neutral and alkaline salicylate solution with certain quaternary ammonium compounds as supporting electrolytes. KORSHUNOV *et al.*[12] stated that salicylic acid was found not to be reducible in alkaline solutions of tetramethyl ammonium hydroxide.

Acetate buffer was used when salicylate was the complexing agent, while an appropriate mixture of a solution of sulphosalicylic acid and its salt acted as a buffer in this complexing solution. In most cases the ionic strength was kept constant.

## RESULTS AND DISCUSSION

### *A. Tetravalent titanium in salicylate solutions*

The single reduction wave of the titanyl ion which is normally obtained in a non-complexing electrolyte like perchloric acid is split into two by the addition of salicylate ions (Fig. 1).

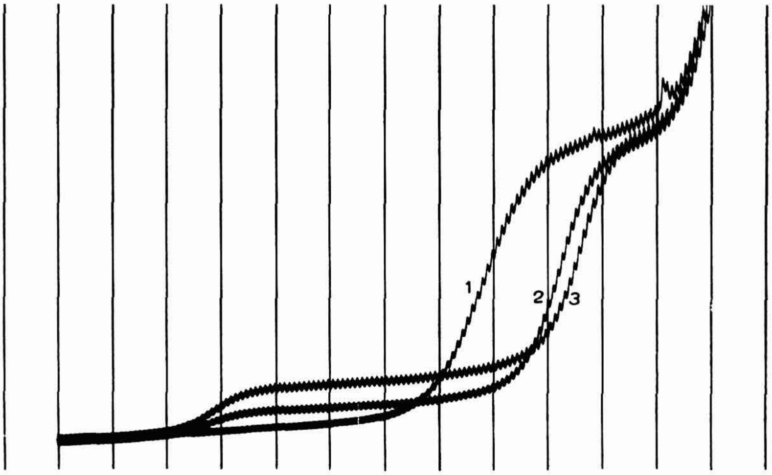

Fig. 1. Addition of salicylate to 0.1 *N* perchloric acid solution as supporting electrolyte. Ti(IV), $2.2 \times 10^{-3}$ *M*; start, 0 V *vs.* S.C.E.; 100 mV/absc.; S, 1/20. Salicylate: (1), 0 *M*; (2), $9.8 \times 10^{-3}$ *M*; (3), $1.93 \times 10^{-2}$ *M*.

In a recent work by the author[13] the pre-wave was proved to have a kinetic character, its height being independent of the height of the mercury reservoir while the total limiting current is diffusion-controlled.

Examination of Fig. 1 shows that waves 2 and 3 are shifted towards more negative potentials as the concentration of salicylate is increased; this shift denotes the reduction of a tetravalent titanium compound different from that found in $HClO_4$ medium.

The negative shift of the main wave and the appearance of a small pre-wave are explained as follows. The free tetravalent titanium ion is assumed to undergo a step-wise hydrolysis ending in the formation of a precipitate of $TiO_2$.

$$Ti^{4+} \overset{(OH)^-}{\rightleftharpoons} \left[Ti(OH)\right]^{3+} \overset{(OH)^-}{\rightleftharpoons} \left[Ti(OH)_2\right]^{2+} \overset{(OH)^-}{\rightleftharpoons} \left[Ti(OH)_3\right]^{+} \qquad (1)$$

The relative concentrations of the intermediate species, depend on the hydrogen ion concentration.

In dilute acid medium, as it is in the case in the experiment represented in Fig. 1, the majority of tetravalent titanium ions are in the form, $[Ti(OH)_2]^{2+}$, in equilibrium with small amounts of $[Ti(OH)]^{3+}$; both species in presence of salicylate ion form stable complexes, which reduce to give a double cathodic wave. The equilibrium thus proposed is:

$$\begin{tikzcd}
{[Ti(OH)]^{3+}} \arrow[r, shift left, "(OH)^-"] \arrow[d, shift left, "nR"'] & {[Ti(OH)]^{2+}} \arrow[l, shift left] \arrow[d, shift left, "nR"'] \\
{[Ti(OH)R_n]^{(3-n)+}} \arrow[r, shift left, "(OH)^-"] \arrow[u, shift left] & {[Ti(OH)_2R_n]^{(2-n)+}} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd} \qquad (2)$$

Complex of the type $[Ti(OH)R_n]$ are more easily reduced at the D.M.E. than $[Ti(OH)_2R_n]$[14]. The reduction of the former complex gives rise to the less negative wave and the height of this wave will ultimately depend on the rate with which the complex $[Ti(OH)R_n]$ is formed. This rate, according to the above scheme, will increase when the acidity of the solution increases and a shift towards the left hand side would be expected. It was difficult, however, to carry out a study of pH-dependence due to the precipitation of salicylic acid at lower pH values and a series of experiments were carried out at pH which does not cause precipitation.

The increase in the salicylate concentration was accompanied by an increase in the less negative wave at the expense of the second wave; Fig. 2 shows the result of this experiment. This increase can be understood if we assume that the unstable $[Ti(OH)]^{3+}$ ions are stabilized in the complex, $[Ti(OH)R_n]^{(3-n)+}$; the equilibrium

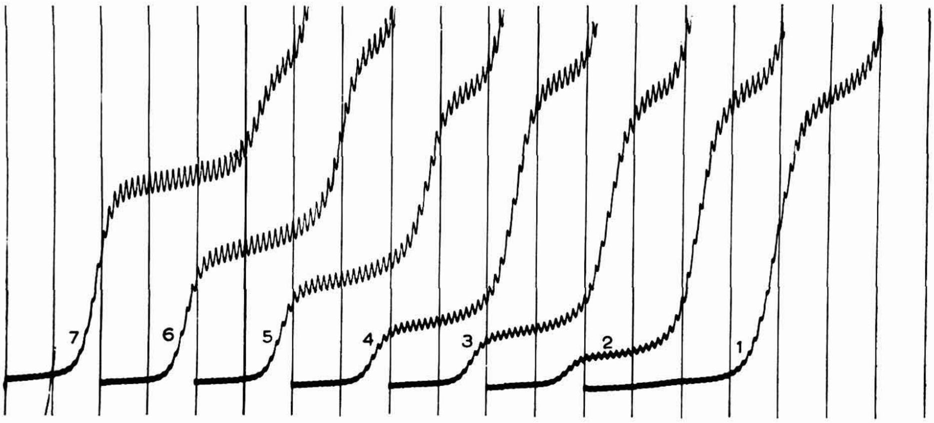

Fig. 2. Effect of concn. of salicylate ions. Acetate buffer pH 2.6; $\mu$ 0.25; start, 0 V *vs.* S.C.E.; Ti(IV), $2.2 \times 10^{-3}$ *M*; S, 1/30; 200 mV/absc. Salicylate: (1), 0; (2) 1.85; (3) 3.98; (4), 5.66; (5), 10.7; (6), 15.1; (7), 26.8 × $10^{-3}$ *M*.

represented in scheme (2) being disturbed, will be restored by the production of more $[Ti(OH)]^{3+}$ which in its turn combines with a salicylate molecule and enriches the system with $[Ti(OH)R_n]^{(3-n)+}$.

The salicylate concentration represented in curve 7 of Fig. 2 was the highest that could be reached without precipitation of salicylic acid. A concentration dependence of salicylate at different pH values was tested. It was found that at pH 4.6 a concentration ratio of salicylate: $Ti^{4+}$ equal to 10:1 was enough to form a stable complex; if this ratio is decreased, hydrolysis starts and is shown by a strong decrease in the cathodic wave and the appearance of a turbidity in the electrolysis vessel.

### *B. Tetravalent titanium in sulphosalicylate solutions*

The behaviour of the titanyl ion in the presence of sulphosalicylate was more easily studied because of the ease of solubility of sulphosalicylic acid and the fact that a mixture of the acid and its salt acts as a buffer solution. It was possible, at a relatively high and constant concentration of sulphosalicylate and by careful control of pH to obtain three different forms of complex on one polarogram (Fig. 3). This figure shows their positions with respect to each other and the transition of one state to another. At pH 1.2 one form of complex, (A), predominates and is reduced by a single wave, Fig. 3, curve 1. As the pH increases from 1.2 to 1.75, the wave splits into two giving rise to a second form of complex labelled (B), curve 2; the intensity of the yellow colour increases at the same time. The wave which is due to the reduction of complex (A) decreases with increasing pH and moves towards more negative potentials (see Table 1) until at pH 3.75 the predominant species in the solution is the form (B) and this is reduced by a single wave, curve 3. As the pH is further increased to 6.6, a third wave, (C), appears. At the same time the half wave potential of wave (B) shows a shift towards the negative. When the pH reaches 9.0, the solution becomes colourless and a single cathodic wave (Fig. 3, curve 5) is obtained due to the

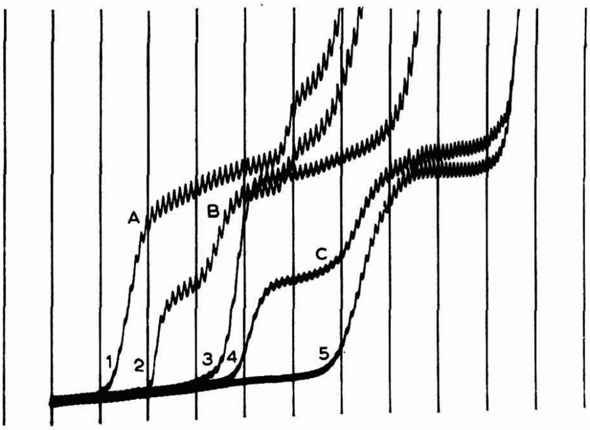

Fig. 3. Polarogram showing the reduction of three different titanium–sulphosalicylate complexes. Sulphosalicylate, 0.215 *M*; Ti(IV), 1,32 × $10^{-3}$ *M*; start, 0 V *vs.* S.C.E.; 200 mV/absc.; S, 1/20. pH: (1), 1.2; (2), 1.75; (3), 3.75; (4), 6.6; (5), 9.0.

reduction of a colourless complex of titanium–sulphosalicylate, which then becomes the predominant species. The successive appearance of these waves and the change in the intensity of the colour with changing pH reveal the presence of different complexes which could not be adequately studied by JOB's method. The results obtained by DUTT AND GOSWANI[6] probably give the overall stability constant of the different complexes in solution; the value of the dissociation constant will be correct only when the conditions favour the formation of one complex only. At pH values higher than 9, a precipitate of $TiO_2$ appears in the cell.

TABLE 1

HALF-WAVE POTENTIALS OF THE DIFFERENT POLAROGRAPHIC WAVES

| *Composition of the soln.* | *pH* | *$E_{\frac{1}{2}}$ vs. S.C.E.* | | |
|---|---|---|---|---|
| | | *Wave (A) (V)* | *Wave (B) (V)* | *Wave (C) (V)* |
| 0.1 *N* $HClO_4$ | 0.08 | | −0.785[a] | |
| 0.1 *N* $HClO_4$, $1.93 \times 10^{-2}$ *M* salicylate | 0.10 | −0.308 | −0.945 | — |
| Acetate buffer, 0.298 *M* salicylate | 0.46 | — | −0.893 | — |
| Acetate buffer, 0.018 *M* salicylate | 0.46 | — | −0.735 | −0.900 |
| Satd. sulphosalicylate | — | — | −0.785 | — |
| 0.125 *M* sulphosalicylate | 1.2 | −0.325 | — | — |
| | 1.75 | −0.443 | −0.665 | — |
| | 3.75 | — | −0.767 | — |
| | 6.6 | — | −0.820 | −1.270 |
| | 9.0 | — | — | −1.290 |

[a] Simple titanyl ion

The nature of waves (A) and (B), was closely examined by measuring the *i–t* curves on the first drop[10]. The curves were registered by applying a potential of −0.6 V and −1.0 V for waves (A) and (B) respectively *i.e.*, at their plateau (see Fig. 3). The exponent, $\alpha$, calculated by WEBER[15] for the equation relating the current with the time (*viz.* $i = kt^{\alpha}$) should have a value of 0.66 for a kinetic process and approximately 0.190 for a diffusion process. In the present case, the value for wave (A) when it forms a small portion of the total wave is 0.55, and for wave (B) 0.29, which shows that the first wave is kinetic while the second wave is diffusion-controlled.

The most suitable explanation for the results obtained in the presence of an excess of sulphosalicylate is the step-wise hydrolysis of the complex formed by the combination of tetravalent titanium ion and sulphosalicylate which can be illustrated as follows:

$$\begin{tikzcd}
{[Ti(OH)]^{3+}} \arrow[r, phantom, "\overset{(OH)^-}{\rightleftharpoons}"] \arrow[d, shift left] & {[Ti(OH)_2]^{2+}} \arrow[r, phantom, "\overset{(OH)^-}{\rightleftharpoons}"] \arrow[d, shift left] & {[Ti(OH)_3]^{+}} \arrow[d, shift left] \\
{[Ti(OH)R_n]^{(3-n)+}} \arrow[u, shift left, "nR"] \arrow[r, phantom, "\overset{(OH)^-}{\rightleftharpoons}"] & {[Ti(OH)_2R_n]^{(2-n)+}} \arrow[u, shift left, "nR"] \arrow[r, phantom, "\overset{(OH)^-}{\rightleftharpoons}"] & {[Ti(OH)_3R_n]^{(1-n)+}} \arrow[u, shift left, "nR"] \\
\text{(A)} & \text{(B)} & \text{(C)} \\
\text{Bright yellow} & \text{Dark yellow} & \text{Colourless}
\end{tikzcd} \qquad (3)$$

The above three complexes when reduced at the D.M.E. give rise to waves (A), (B) and (C) respectively.

From scheme 3, the hydrolysis process and its rate will play an important role in the determination of the nature of the polarographic wave. At high concentrations of hydrogen ions this rate becomes very slow and gives rise to a kinetic reduction wave; however, as the pH increases the rate of hydrolysis gradually increases until it becomes greater than the rate of diffusion, in which case the reduction of the hydrolysed complex will be governed by its diffusion to the electrode surface.

It was proved that complex (B) changes to (C), instantaneously at higher pH values by the drop-wise addition of 0.1 *N* NaOH when the yellow colour of complex (B) changes to colourless (complex C); the yellow colour was rapidly restored on the addition of dilute perchloric acid.

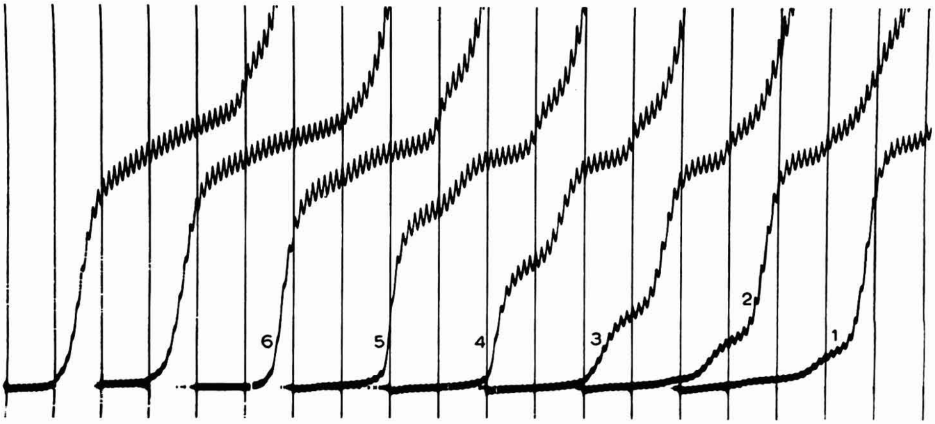

Fig. 4. Effect of pH at constant sulphosalicylate concn. Sulphosalicylate, 0.25 *M*; Ti(IV), 1.53 × $10^{-3}$ *M*; start, 0 V *vs.* S.C.E.; 200 mV/absc. pH: (1), 2.9; (2), 2.65; (3), 2.4; (4), 2.15; (5), 1.95; (6), 1.85.

The effect of pH on the equilibrium between complexes (A) and (B) was investigated. It is a decisive fact that between pH 1.5 and 3.5 two waves appear (Fig. 4); their ratio shows the dependence on pH according to a formula similar to that of Henderson–Hasselbach:

$$\mathrm{pH} = \mathrm{p}K + \log \tfrac{\mathrm{A}}{\mathrm{B}}$$

where (A) and (B) are two different forms of titanium–sulphosalicylate complex. The problem could be regarded as a simple dissociation and recombination of an organic acid[16]. If the rate of hydrolysis were very slow, the height of the wave at which the complex $[\mathrm{Ti(OH)R}_n]^{(3-n)+}$ is reduced, would be an exact measure of its concentration; if the rate of hydrolysis were infinitely fast, the reduction would take place by a single wave which would then indicate the total concentration of the hydrolysed species (complex B) and in this case there would be no pre-wave.

The value of the pH at which both polarographic waves are equal gives therefore only the apparent hydrolysis constant, *K′*, which differs more from the true hydrolysis constant, *K*, the greater the rate of hydrolysis. The plot of $i_k/i_l$ *vs.* pH gives a curve similar to the dissociation curves of the acids[14] (Fig. 5) with a $pK' = 2.2$.

The exact composition of the different complexes (ratio of Ti(IV) : sulphosalicylate) could not be identified using polarography. Polarographic methods can only be used when the equilibrium in the solution is between a free ion and its complex form[17]. An attempt was made to calculate the number of sulphosalicylate radicals in the complex by potentiometric titration using the method of BANK AND SINGH[18] in their study of the 5-sulphosalicylate complexes of Be and Cu. If the measurement in the presence of sulphosalicylate and titanyl ion had differed from that carried out in the absence of the titanyl ion, this difference would have enabled the number of sulphosalicylates radical in the complex to be calculated. Unfortunately the measurements were unsuccessful.

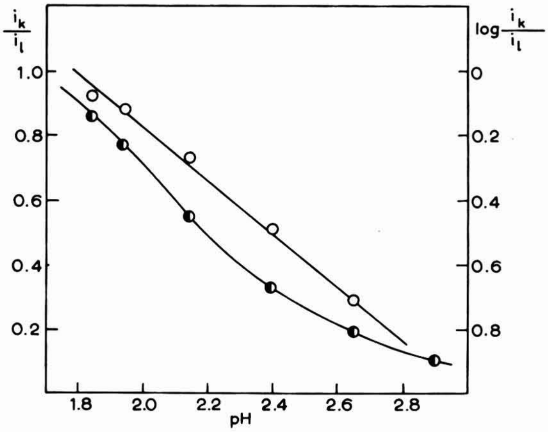

Fig. 5. Graphical representation of $i_k/i_l$ *vs.* pH.

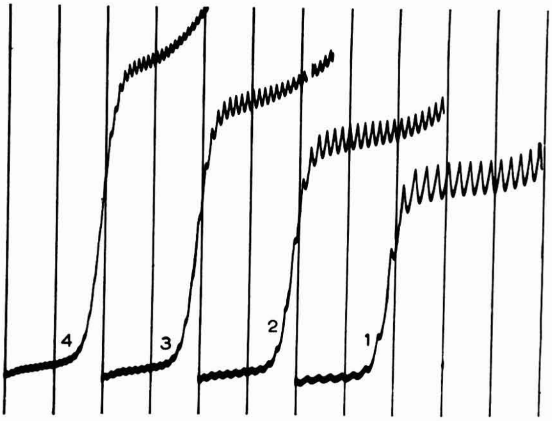

Fig. 6. Effect of the height of the mercury reservoir. Satd. soln. of potassium sulphosalicylate; Ti(IV), $1.53 \times 10^{-3}$ *M*; start, −0.4 V *vs.* S.C.E.; 200 mV/absc. Height: (1), 36 cm; (2), 49 cm; (3), 64 cm; (4), 81 cm.

## ANALYTICAL APPLICATION

As hydrolysis of the titanyl ion is prevented either by a high concentration of hydrogen ion or by a high concentration of complexing agent, attempts were made to reduce the titanyl ion in a saturated solution of sulphosalicylate. A single wave which is diffusion-controlled was obtained (Fig. 6); its half-wave potential is about $-0.785$ V *vs.* S.C.E.which classifies the wave as complex (B) (see Table 1). The graph of log $[i/(i_d - i)]$ *vs.* $E_{de}$ is a straight line. The inverse slope of the curve is 0.062, which approaches to the theoretical value of 0.059 for a reversible one-electron process. This wave could be used for the analytical estimation of Ti since a plot of $i_d$ *vs.* concentration is linear in the range of $7.5 \times 10^{-4}$ to $3.9 \times 10^{-3}$ *M* Ti(IV).

## SUMMARY

Polarographic studies of tetravalent titanium in salicylate and sulphosalicylate media revealed the successive appearance of different titanium–salicylate or titanium–sulphosalicylate complexes.

The complexes are derived from each other by a process of hydrolysis. Two salicylate complexes were detected and three sulphosalicylate complexes.

In the presence of excess complexing agent and in the pH range of 1–9 the equilibrium of the different species could be represented as follows:

$$[\mathrm{Ti(OH)R}_n]^{(3-n)+} \xrightleftharpoons{(\mathrm{OH})^-} [\mathrm{Ti(OH)_2R}_n]^{(2-n)+} \xrightleftharpoons{(\mathrm{OH})^-} [\mathrm{Ti(OH)_3R}_n]^{(1-n)+}$$

A mechanism is proposed which accounts for the different polarographic waves.

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# Short Communications

## A.c. polarography of complex metal ions

The conventional polarographic method can be applied advantageously to the study of complex metal ions since the half-wave potentials of metal ions are shifted usually to more negative values by complex formation. Quantitative information regarding the formula and dissociation constant of the complex can be obtained by measuring this shift as a function of the concentration of the complexing agent provided the reduction or oxidation of the metal ion complex takes place reversibly at the dropping mercury electrode[1]. However, no data is available in the literature for such quantitative studies regarding the formula and dissociation constant of complexes by a.c. polarography.

The purpose of the present investigation is, therefore, to ascertain if a.c. polarography can be applied to determine the formula and dissociation constant of the ammino-cadmium complex.

Cadmium sulphate ($3\ CdSO_4 \cdot 8H_2O$) used was B.D.H., A.R. quality. Standard solutions of ammonia (B.D.H.) were used as the complexing agent. Mercury for the dropping electrode was purified by passing it through Meyer's column, after which it was washed several times with distilled water, dried, passed through a sintered-glass filter and finally distilled under vacuum.

The technique was the same as that described earlier[2,3], the only modification being that the series resistance was made as small as possible. This consists in applying to the D.M.E., a 50 c/sec. a.c. ripple of 20 mV (r.m.s.) on the d.c. potential and observing the alternating component of the resulting pulsating current.

A 0.1 $M$ potassium nitrate (B.D.H., A.R.) solution in conductivity water was the supporting electrolyte. Negative d.c. potentials were applied to the D.M.E. with respect to the saturated calomel electrode. The experiments were carried out at a constant temperature of $30 \pm 0.5°$. The constants of the D.M.E. were: $m = 4.564$ mg/sec and $t = 1.8$ sec per drop in 0.1 $M$ KCl, open circuit.

The technique of the alternating current polarography is based on the investigation of electrode processes by the use of a small (of the order of millivolts or tens of millivolts) sinusoidal alternating potential superimposed on the steady polarising potential. The alternating current produced under these conditions is measured and recorded as a function of the applied steady potential, and the resulting graph is called an "a.c. polarogram". When a reversible redox process is being studied, the main characteristic of an alternating current polarogram is that a maximum alternating current can be observed at steady potentials. This is referred to as $E_p$ (peak potential) and corresponds to $E_{\frac{1}{2}}$ (half-wave potential) in the conventional polarogram.

According to Kolthoff and Lingane[1] the formula and dissociation constant of the complex ion of a metal that is soluble in mercury may be given by the following relations:

$$\frac{\Delta(E_{\frac{1}{2}})_C}{\Delta \log C_X} = -p\,\frac{0.0591}{n} \tag{1}$$

$$(E_{\frac{1}{2}})_C - (E_{\frac{1}{2}})_S = \frac{0.0591}{n}\log K_C - p\,\frac{0.0591}{n}\log C_X \tag{2}$$

where $(E_{\frac{1}{2}})_C$ and $(E_{\frac{1}{2}})_S$ refer to the reversible half-wave potentials of the complex metal ion and simple metal ion respectively; $C_X$ is the concentration of the complexing agent; $p$ is the co-ordination number of the complex metal ion; $n$ is the number of electrons involved in reduction to metal amalgam and $K_C$ refers to the dissociation constant of the complex.

The above equations can be applied for deriving the formula of the complex by a.c. polarography as well as its dissociation constant if $(E_{\frac{1}{2}})_C$ and $(E_{\frac{1}{2}})_S$ are replaced by $(E_p)_C$ and $(E_p)_S$, *i.e.*, their peak potentials, respectively.

Figure 1 gives a straight line on plotting $(E_p)_C$ *vs.* log ammonia concentration with a slope of $-0.121$ V. From this slope, using eqn. (1), the value of $p$ is found to be 4.1 with $n = 2$ showing that the formula of the complex is $Cd(NH_3)_4^{2+}$.

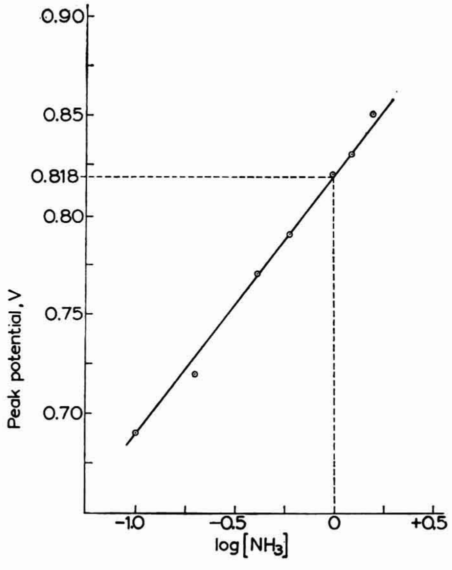

Fig. 1. Effect of ammonia concn. on the peak potential of the ammino–cadmium complex in 0.10 $M$ $KNO_3$.

From the equation for the straight line through the experimental points, it is found that $(E_p)_C$ is $-$ 0.818 V at an ammonia concentration of 1.00 $M$. From this value and the measured peak potential of the simple cadmium ion in 0.1 $M$ $KNO_3$ containing no added ammonia ($-0.60$ V *vs.* S.C.E.), the value of $K_C$ was calculated from eqn. (2) as $0.397 \times 10^{-7}$ which agrees fairly well with the value of $1 \times 10^{-7}$ for $K_C$ obtained from conventional polarography[4].

The complexes of cadmium with thiocyanate, iodide and oxalate ions have also been studied by a.c. polarography and the details will be published elsewhere.

It may, therefore, be concluded that a.c. polarography can be successfully used for the quantitative study of complex metal ions. The method has the following advantages over the conventional polarographic method.

(i) It is unnecessary to analyse the polarogram for its reversibility as in conventional polarography, since a.c. polarograms will be obtained only for reversible oxidation and reduction processes.

(ii) Oxygen need not be removed from the solution as it does not interfere in a.c. polarography provided it does not react chemically with the reducible species as in the case of lead[5].

(iii) Peak potentials can be determined more conveniently and accurately than half-wave potentials.

(iv) Measurement can be made more rapidly and with an improved all round reproducibility.

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## The analysis of cathodic waves

In a recent paper SATHYANARAYANA[1] has presented an analysis of cathodic polarographic waves which differs somewhat from ours[2]. This difference may be summarized by saying that our method of analysis applies to a purely cathodic (or purely anodic) wave of a moderately fast electrode reaction where the concentration of the product of the electrode reaction in the bulk of the solution is zero, for example, as a result of decomposition after diffusion from the immediate neighbourhood of the electrode surface. On the other hand, SATHYANARAYANA's analysis concerns what might be termed an 'impure' cathodic wave, *i.e.*, one in which there is a trace of the product in the bulk of the solution. This is evident from Fig. 2 of his paper and also from his use of eqn. (2). If this equation is applied to the situation envisaged in our paper, exp

$nf\eta$ is zero since $\eta$ is very large and negative at all points in the wave because the zero concentration of the product substituted in the Nernst equation gives an infinite value for the reversible potential. Clearly each method is valid for the prescribed circumstances, but they are not interchangeable.

We should also like to point out that SATHYANARAYANA's "approximate method" is valid only for the particular case when the diffusion current is proportional to the square root of the diffusion coefficient (eqn. 9 in his paper) and thus is incorrect for example, for convective mass transport in general, in particular for the rotating disc electrode. It is in fact possible to use a single method of analysis for the stirred systems as well as polarographic systems and we present this briefly below, including also the application to the corresponding chronopotentiometric case[3].

It is well known that the current–voltage relationship for a reaction

$$O + n\,e \rightarrow R \tag{1}$$

at dropping mercury or plane unstirred electrodes may be expressed as

$$i/i_\infty = F(\mathcal{X}) \tag{2}$$

where $i$ and $i_\infty$ are the observed and diffusion-controlled currents at the given potential $\varrho'$ and time $t$

$$\mathcal{X} = (k_f \delta_o / D_o)\ (1 + \exp nf\varrho') \tag{3}$$

and

$$\varrho' = E - E_s' = E - E_s + (nf)^{-1} \ln (D_o \delta_R / \delta_o D_R) \tag{4}$$

$f = F/RT$, $D$ is the diffusion coefficient and $\delta$ the 'thickness' of the diffusion layer for the species given as a subscript. (The appropriate values of $\delta$ and $F(\mathcal{X})$ for semi-infinite diffusion to the plane and d.m. electrodes may be inferred from the review by DELAHAY[4].)

For a pure cathodic wave

$$\frac{i_\infty - i_l/2}{i_l/2} = \tanh\ (nf\varrho'/2) \tag{5}$$

where the limiting current is given by

$$i_l = nFA\, D_o C_o^b / \delta_o \tag{6}$$

The extension to chronoamperometry is direct, if it is noted that $\delta$ is proportional to $\sqrt{t}$.

For a stirred system, the steady-state current–voltage curve may also be expressed by eqns. (2) and (3) with

$$F(\mathcal{X}) = \mathcal{X}/(1 + \mathcal{X}) \tag{7}$$

and

$$\delta_o = \int_o^\infty e^{\int^x (V/D_o \, dx}\ dx \tag{8}$$

for one-dimensional convective diffusion to a plane electrode (*e.g.*, a rotating disc); $V$ is the velocity of the solution perpendicular to the plane of the electrode.

Similarly, the galvanostatic potential–time curve[3] at a plane electrode may be expressed

$$\sqrt{t/t_\infty} = F(\chi) = 2\chi/(\pi + 2\chi) \tag{9}$$

$t_\infty$ and $t$, respectively, are the times required to reach a potential $\varrho'$ when the reaction is purely diffusion-controlled and when it is also controlled by the electrode process. The analogue of eqn. (5) is

$$\frac{\sqrt{t_\infty} - \sqrt{\tau_1}/2}{\sqrt{\tau_1}/2} = \tanh\,(nf\varrho'/2) \tag{10}$$

where $\tau_1$ is the cathodic transition time.

The condition of electrochemical irreversibility means that the inequality exp $nf\varrho' \ll 1$ is satisfied for an appreciable range of variation of the experimental observable ($i$ or $t$ in the cases discussed above). Thus, eqns. (5), (9) and (3) lead to

$$\begin{gathered} i < i_\infty = i_1 \\ t < t_\infty = \tau_1 \\ \chi = k_f \delta_o / D_o \end{gathered} \tag{11}$$

Using eqns. (2) or (9) we may determine $F(\chi)$ in this region and a plot of log $\chi$ against potential will be linear if

$$k_f = k_s \exp\,\{-\alpha nf(E - E_s)\} \tag{12}$$

At $E_s'$, the reference potential (see eqns. 3, 4, 5, 10)

$$\begin{gathered} i_\infty = i_1/2 \quad \text{or} \quad \sqrt{t_\infty} = \sqrt{\tau_1}/2 \\ \chi = 2\, k_f \delta_o / D_o \end{gathered} \tag{13}$$

Thus, if $F(\chi)$ is equated to $2\, i/i_1$ or $2\sqrt{t}/\sqrt{\tau_1}$ in place of (2) or (9) respectively, near to $E_s'$ and the resulting value of log $(\chi/2)$ is plotted against potential, this curve cuts the previously plotted line at the point with co-ordinates $E_s'$ and log $(k_s \delta_o / D_o)$.

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## Polarographic cell with permanent external reference electrode

A great number of polarographic cells for different purposes has been described in the literature[1-4]. Some of them use an internal electrode (mercury pool, silver wire), many others are equipped with an external electrode separated from the solution under analysis by a porous membrane (sintered glass[5,6], cellophane[7-9]) or by a stopcock[10,11]. The most widely used cell of the former type is the H-cell of Lingane and Laitinen[6], and of the latter type is Kalousek's cell[10] and its modifications.

The cell described in this paper is shown in Fig. 1; the term "compact" cell has been proposed for it. The upper cylindrical part, K, containing the solution under study is separated from the lower part containing the reference (saturated calomel) electrode, A, by a sintered-glass disc, D, of medium porosity (diameter about 15 mm). In order to eliminate the mixing of the solution with the reference electrode solution, a 1-mm layer of 1% agar gel, G, saturated with potassium chloride is placed on the disc from the side of the reference electrode. The solution can be poured out through the joint $P_1$, the stopper of which is of a length to form part of the wall of the cell. The second joint, $P_2$, serves for filling of the reference electrode. Both joints were not ground until the cell was otherwise finished. If the joint $P_1$ is carefully ground, the danger of the stopper falling out is minimised. Dissolved oxygen is removed from the solution by bubbling nitrogen through the narrow tube $V_1$, which passes through the rubber stopper together with the polarographic capillary C. The inert gas leaves the cell through an outlet capillary $V_2$, which prevents any re-solution of air into the test solution. External connection with the mercury-pool electrode can be made by means of a platinum wire sealed in the glass-wall of the lower part of the cell. A clamp was cemented to this contact. When a constant temperature was required a plastic tube was pulled on the clamp and the whole cell was immersed into a thermostat.

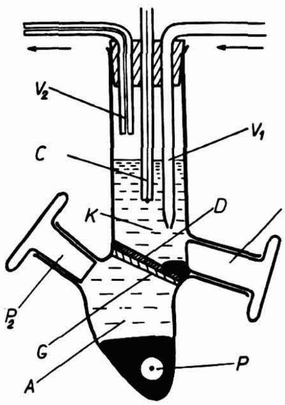

Fig. 1. "Compact" cell. K, test solution; A, reference electrode; D, glass disc; G, layer of 1% agar; $P_1$ and $P_2$, joints with stoppers; $V_1$ and $V_2$, inlet and outlet tubes for inert gas; P, external connection; C, polarographic capillary.

The resistance of the "compact" cell and of five other cells — when filled with 1

*N* KCl — was measured either with the mercury drop hanging at the end of the silver wire (MICKA electrode[12]) or with a platinum electrode as one electrode and a 1 *N* calomel reference electrode as a second electrode. The resistances were measured with a conductance bridge (RCL bridge TESLA) at 1000 c.p.s. (Table 1).

TABLE 1

RESISTANCE OF POLAROGRAPHIC CELLS FILLED WITH 1 *N* KCl (at 19°)

| *Cell* | $R_{Hg}$ *(ohm)*[c] | $R_{Pt}$ *(ohm)*[d] |
|---|---|---|
| "Compact" cell with agar plug | 60 | 30 |
| without agar | 45 | 25 |
| H-cell (LINGANE AND LAITINEN) | 53 | 30 |
| KALOUSEK cell[a] | 320 | 310 |
| DOUSEK-KALOUS cell[a] | 360 | 340 |
| HEYROVSKÝ cell[b] | 20 | 8 |
| Cell with mercury pool electrode | 30 | 11 |

[a] Cell with external electrode with a stop-cock.
[b] Conical cell with mercury pool electrode.
[c] Resistance with mercury hanging drop electrode of area 4.7 mm².
[d] Resistance with platinum electrode of area 33 mm².

From conductivity measurements it was found that the resistance of the "compact" cell is distinctly lower than that of cells with the stop-cock and can be compared with that of mercury pool cells. The resistances of the agar plug and of the porous disc are surprisingly low and therefore no correction for the *iR* drop is necessary.

The possibility that constituents from the solution which had diffused into the porous disc or agar plug could diffuse back into and contaminate a succeeding test solution was checked with solutions of cadmium sulfate and potassium chromate. The extent of such contamination was proved to be negligible. The "compact" cell was constructed using the experience gained with cells in which porous discs were used. Its construction resembles that of the cell with an oblique disc recommended by SEIDEL[2] and the arrangement for removing the air to that used by VON STACKELBERG[2].

All instructions for experimental work with the "compact" cell are summarised in books by KOLTHOFF AND LINGANE[1], by MEITES[3] and by VON STACKELBERG[2]. First of all it is necessary to prevent the agar plug from drying out and to rinse out the cell promptly and thoroughly before each analysis. When a set of experiments is finished or when the reference electrode is changed, the whole cell should be rinsed out with hot water and the porous disc cleaned by suction.

In comparison with other cells the "compact" cell offers some advantages. Work with it is very rapid and easy; the joint facilitates the washing and emptying. It can easily be constructed in a variety of sizes. Because of the constant known potential of the reference electrode, low resistance and versatility, the "compact" cell can be recommended for precise experimental work especially when studying the influence of a systematic change of some variable such as concentration of the substance, pH, ionic strength or height of the reservoir.

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# Announcement

## I.U.P.A.C CONFERENCE ON THE PROPERTIES AND USES OF PLASMA

The *Sub-commission on Gaseous State* (*Commission on High Temperatures and Refractories*) of the *International Union of Pure and Applied Chemistry* is organizing in Moscow, on the 19th, 20th and 21st July 1965, an International Symposium on plasma; this symposium will follow immediately the IUPAC XXth Congress.

The promoters of this meeting intend essentially that the papers should cover plasma above the normal flame temperature range so that for the purposes of this conference a working definition of plasma can be used when there is substantial ionisation, for example more than 1%. Alternatively, an arbitrary temperature limit of approximately 2500°K could be set.

It has been obviously not possible to draw up a detailed programme. Very broadly, however, the conference would be divided into the physics and chemistry of plasma and the potential ways in which plasma can serve mankind.

The titles of proposed papers are to be received by December 15th, 1964; the abstracts would have to be received by February 1st and the final paper by May 15th 1965.

The scientists interested by this symposium or who whish to present a paper are requested to acquaint Dr. LOUIS DEFFET — member of the said commission — who has been appointed to get this information for Belgium, Holland and Luxemburg.

The "Provisional Registration Form" should be forwarded in duplicate to Dr. L. DEFFET, Director of the *Centre de Recherches pour l'Industrie des Produits Explosifs*, Val du Bois, Sterrebeek (Brabant), Belgium.

Following the receipt of this application further details concerning the programme of papers and the organization of the symposium, will be forwarded as soon as possible.

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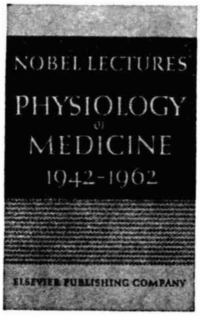

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