

TABLE I  
OXIDATION OF ISOBORNEOL WITH CHROMIC ACID  
Temperature was held below 30° for all oxidations

Run	Isoborneol, g.	CrO <sub>3</sub> , g.	H <sub>2</sub> O, ml.	gl. AcOH, ml.	Addn. time, hr.	Yield, % camphor	Yield, % OH-acid	Yield, % $\alpha$ -campholenic acid	Material balance, %
1	77.12	30	18	80	3.5	96.0	0.28	0.3	96.6
2	154.24	60	160	160	4.6	96.3	1.7	1.7	99.7
3	154.24	65	175	175	5.75	91.4	2.1	2.2	95.7
4	154.24	65	175	175	7.0	88.1	0.8	0.9	89.7

91.4% (139 g.) of camphor, 2.1% (3.9 g.) of hydroxydi-hydro- $\alpha$ -campholenic acid, and 2.2% (3.7 g.) of  $\alpha$ -campholenic acid.

Check runs 2, 3 and 4 were made and the results are given in Table I

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NEWARK, DEL.

RECEIVED SEPTEMBER 12, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

## A Polarographic Study of the Oxalato Complexes of Titanium

BY ROBERT L. PECSOK

Titanium(III) and -(IV) yield reversible polarographic waves in oxalic acid solutions with pH less than 3. The half-wave potential is independent of the concentration of titanium, and is expressible as  $E_{1/2} = -0.25 - 0.080 \text{ pH} + 0.020 \log [\text{H}_2\text{C}_2\text{O}_4]$  in volts vs. the saturated calomel electrode. Data are given from which this equation is derived and its form explained by a treatment of the equilibria involved. The yellow oxalato-titanium(III) ion has been investigated spectrophotometrically.

The polarographic reduction of titanium(IV) in oxalate solutions has been used by Adams<sup>1</sup> in the analysis of clays and clay products. He reported that the half-wave potential was a function of the concentrations of sulfuric acid, titanium, and iron. Lingane and Vandenbosch<sup>2</sup> questioned the dependence of the half-wave potential on the concentrations of titanium and iron, and gave data showing that it was independent of both.

The titanium waves have been studied in tartaric acid<sup>3,4,5</sup> and citric acid<sup>4,5</sup> solutions. This paper presents the results of a systematic study of the polarography of the titanium(III) and -(IV) oxalate complexes. An electrode reaction is proposed to account for the behavior of the half-wave potential of the system.

### Experimental

All polarograms were taken with a Sargent Model XXI Polarograph utilizing an H-cell with an external saturated calomel electrode. No damping was employed for any polarograms. The cell was maintained at  $25.0 \pm 0.1^\circ$  in a grounded water-bath. The internal resistance of the several cells used was assumed to be negligible since the half-wave potential of lead ion was found to be independent of its concentration.

Purified nitrogen was used to remove dissolved oxygen from the test solutions and from the supporting electrolyte before adding the titanous chloride reagent. Residual currents were measured and the proper corrections applied where necessary. In most cases, since the waves were so well defined with horizontal plateaus, residual current corrections were made by extrapolation.

The pH of the solutions was measured with a Beckman model G pH meter, in most cases, after the polarogram had been taken.

Solutions of titanous and titanic chloride made up from the commercially available 20% titanous chloride reagent were found to contain an approximately equivalent amount of zinc and thus were not suitable for this work. A stock solution of titanous chloride was prepared by distilling titanic chloride reagent in the presence of sodium, collecting only the water-white fraction, dissolving in redistilled hydrochloric acid, and reducing electrolytically between carbon electrodes under nitrogen. This stock solution was approximately 0.1 M in hydrochloric acid. The titanic chloride stock solution was prepared by oxidation of the titanous solution after increasing its hydrochloric acid content to 3 M. The titanous solution was standardized by pipeting an aliquot into an excess of ferric sulfate and subsequent titration with standard dichromate solution. The titanic solution was standardized by passage of an aliquot through a Jones reductor into an excess of ferric sulfate, followed by titration as above.

Supporting electrolytes were made up from reagent grade chemicals as required. No maxima were observed in any of the polarograms and therefore no suppressor was added.

### Results and Discussion

Titanium(IV) forms complexes with many organic hydroxy acids. In preliminary work, re-

TABLE I  
HALF-WAVE POTENTIALS OF TITANIUM(IV) IN ORGANIC ACIDS

Supporting electrolyte	$E_{1/2}$ , v. vs. S.C.E.	Type of wave
0.2 M tartaric acid	-0.38	Reversible
Satd. tartaric acid	- .42	Reversible
0.2 M citric acid	- .37	Reversible
Satd. citric acid	- .49	Irreversible
Satd. salicylic acid	- .35	Reversible
0.2 M succinic acid	- .85	Poorly defined
0.2 M formic acid	- .79	Poorly defined
3.5 M lactic acid	- .40	Reversible
0.2 M acetic acid	- .85	Poorly defined
0.1 M hydrochloric acid	- .81	Irreversible
Satd. phthalic acid	- .93	Irreversible

(1) D. F. Adams, *Anal. Chem.*, **20**, 891 (1948).

(2) J. J. Lingane and V. Vandenbosch, *ibid.*, **21**, 649 (1949).

(3) V. Caglioti and G. Sartori, *Gazz. chim. ital.*, **66**, 741 (1936).

(4) R. Strubl, *Collection Czech. Chem. Commun.*, **10**, 475 (1938).

(5) M. Kalousek, *ibid.*, **11**, 592 (1939).

versible or nearly reversible reduction waves were found for titanium(IV) in tartaric, citric, oxalic, salicylic and lactic acids. The half-wave potentials are indicated in Table I.

Complexes yielding waves of this type are not formed in formic, acetic or succinic acids, where the polarographic waves are similar in shape and half-wave potential to those in hydrochloric acid.

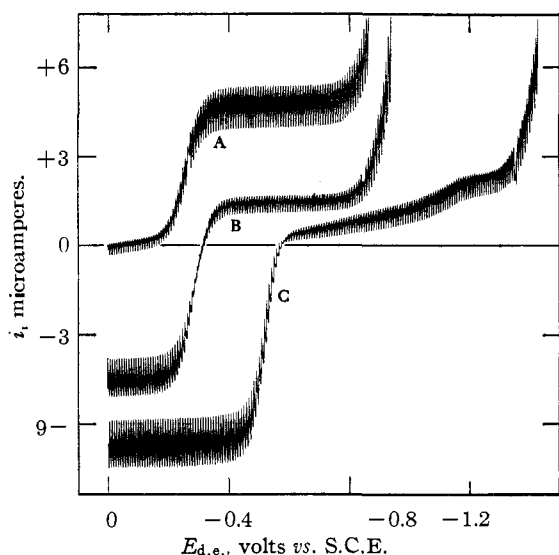


Fig. 1.—Typical polarograms: A, 1.19 millimolar titanium(IV) in 0.2 M oxalic acid, pH 0.60; B, 0.345 millimolar titanium(IV) and 1.35 millimolar titanium(III) in 0.2 M oxalic acid, pH 1.00; C, 0.509 millimolar titanium(IV) and 1.99 millimolar titanium(III) in 0.2 M oxalate, pH 4.20.

Typical polarograms of titanium in 0.2 M total oxalate are reproduced in Fig. 1. Several polarograms were obtained with a voltage span of 0.5 volt/13.5 in., and accurate measurements made of the current and potential at selected points in the wave. The graphs of  $\log [i - (i_d)_s] / [(i_d)_e - i]$  vs.  $E_{d.e.}$  are plotted in Fig. 2, where the symbols have their usual meanings.<sup>6</sup> The inverse slope of curve A is 0.0596 and that of curve B is 0.0640, corresponding to the theoretical value of 0.059 for a reversible one-electron process. All polarograms used in this study were checked for reversibility by the method of Tomes.<sup>7</sup> The values for the difference,  $E_{3/4} - E_{1/4}$ , varied from 0.055 to 0.065 volt, indicating near reversibility in each case and that theoretical equations for the half-wave potential should apply.<sup>8</sup>

Equilibrium is apparently attained immediately upon mixing the solutions. Polarograms of a solution of 1 millimolar titanium(IV) in 0.05 M oxalic acid run immediately after preparation and after two weeks standing were identical.

A solution of 1.61 millimolar titanium(IV) in 0.2 M oxalic acid was polarographed twice, first with the column of mercury standing at 61.5 cm. above the capillary tip, and secondly at 30.7 cm. above the tip. In the first case,  $m = 2.459$  mg./sec.,  $t_d = 3.30$  sec./drop,  $i_d = 6.06$   $\mu$ a.,  $I = 1.69$ , and  $E_{1/2} = -0.250$  v. In the second case,  $m = 1.205$  mg./sec.,  $t_d = 6.85$  sec./drop,  $i_d = 4.08$   $\mu$ a.,  $I = 1.62$ , and  $E_{1/2} = -0.247$  v. These data show that the Ilkovic equation for the diffusion current is obeyed to within 4%, and that therefore the current is diffusion controlled and not rate controlled.

**Effect of pH.**—In the earlier studies of the titanium(IV) oxalate complex,<sup>1,2</sup> a buffer consisting of 1 N sulfuric acid saturated with sodium oxalate was used. In making up this buffer, the first precipitate observed is sodium binoxal-

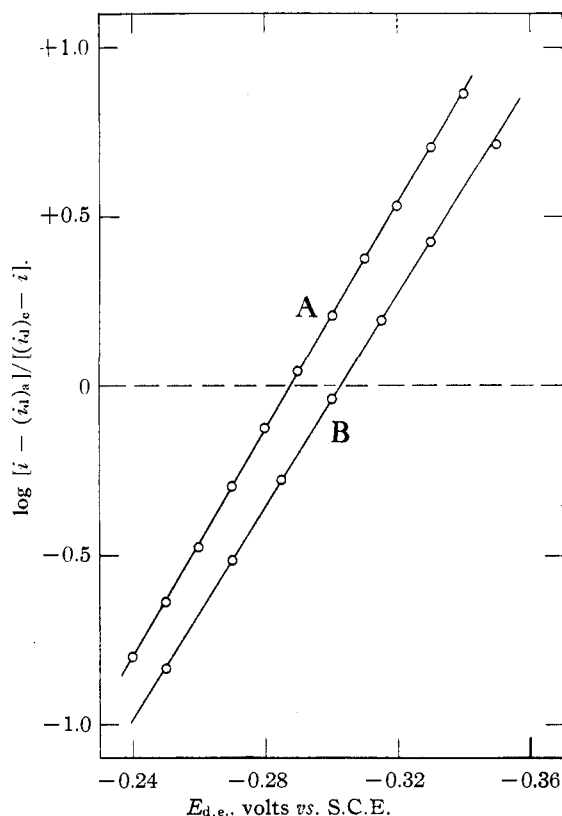


Fig. 2.—Test of reversibility of titanium system in oxalate medium: A, 1.61 millimolar titanium(IV) in 0.25 M oxalic acid, pH 0.50; B, 2.13 millimolar titanium(III) in 0.10 M oxalic acid, pH 1.15.

ate at a pH of ca. 0.7. This buffer then contains 0.5 M oxalic acid and 0.1 M binoxalate ion. The solution cannot become saturated with sodium oxalate until all of the original acid has been neutralized to binoxalate ion and the pH increased to greater than 3. Presumably the previous authors used a buffer saturated with sodium binoxalate and not sodium oxalate.

A series of solutions was prepared all containing 0.1 M total oxalate and 1.47–1.79 millimolar titanium(IV). The pH of the solutions was varied by using different ratios of oxalic acid and sodium oxalate, adding excess sulfuric acid or sodium hydroxide. Above pH 3 the wave decreases in height and becomes irreversible. Above pH 4, no reduction occurs although the titanium remains in solution as an oxalate complex.

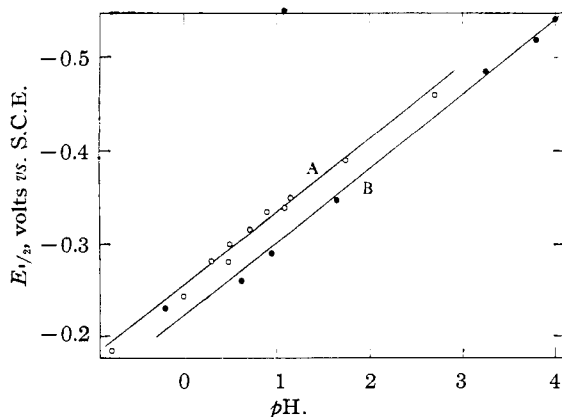


Fig. 3.—Effect of pH on the half-wave potential: A, 1.79 millimolar titanium(IV) in 0.2 M total oxalate; B, 2.13 millimolar titanium(III) in 0.1 M total oxalate.

(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 158.

(7) J. Tomes, *Collection Czech. Chem. Commun.*, **9**, 12, 81, 150 (1937).

(8) Ref. 6, pp. 167 ff.

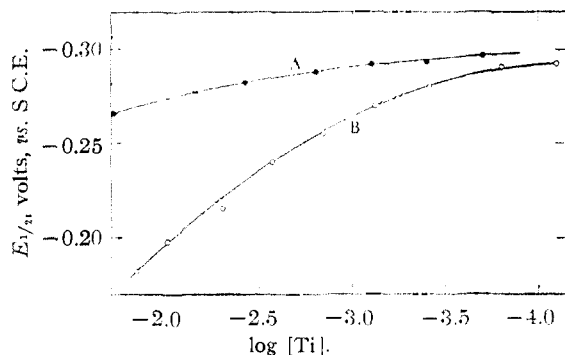


Fig. 4.—Effect of the concentration of titanium on the half-wave potential: A, titanium(III) in 0.2 *M* oxalic acid; B, titanium(IV) in 0.2 *M* oxalic acid.

A second series of solutions was prepared similar to the first but containing 2.13 millimolar titanium(III). The titanous chloride reagent was added after the solution had been deaerated in the polarographic cell. The *pH* of these solutions were measured after the polarogram had been recorded. The oxidation wave of the titanium(III) oxalate complex remains reversible up to a *pH* of 4.2, where there is no corresponding reduction wave for titanium(IV). Similar behavior has been reported for the oxidation of chromium(II) in alkaline salicylate solutions.<sup>9</sup>

The half-wave potentials as a function of *pH* for both series are plotted in Fig. 3. The reciprocal slopes of the curves are 0.079 and 0.080 volt/*pH* unit. There is a constant difference in the potentials of the two series of about 35 millivolts at a given *pH*. This is accounted for in part by the difference in oxalic acid concentrations (see below). The remaining difference must result from the slight deviation from reversibility of the titanium(III) wave, as noted above.

**Concentration of Titanium.**—Adams reported that the half-wave potential of titanium(IV) in an oxalate buffer of unstated *pH* became about 0.5 volt more negative as the concentration of titanium was increased from 0.063 to 9.26 millimolar.<sup>1</sup> This behavior is undoubtedly due to the high resistance of his reference electrode and the lag in his recorder. This was pointed out by Lingane and Vandenbosch,<sup>2</sup> who found that the half-wave potential was independent of the concentration of titanium and equal to  $-0.285$  v. vs. the saturated calomel electrode in the same buffer.

In the present study a series of polarograms of increasing amounts of titanous chloride in 0.2 *M* oxalic acid yielded a marked shift in a positive direction for the half-wave potential. A less pronounced shift, but in the same direction, was obtained for a similar series of titanous chloride. These results are plotted in Fig. 4. The *pH* of all solutions were measured or estimated from the hydrochloric acid content of the reagent, and found to decrease slightly with additions of titanous chloride and considerably with additions of titanous chloride. This is to be expected because of the excess acid present in the reagents in order to prevent hydrolytic precipitation. Since the *pH* of the solution of high titanium(IV) was negative and not accurately known, it was not feasible to convert the half-wave potentials to a common *pH* value. This was possible with the titanous solutions, using the previously determined dependence of the half-wave potential on *pH*. These corrected values showed that the half-wave potential is indeed independent of the concentration of titanium(III). Since all waves for both series are reversible, the same must follow for titanium(IV) solutions.

It is interesting to note that both curves in Fig. 4 appear to approach a value of  $-0.30$  v. vs. the saturated calomel electrode at low concentrations of titanium, when the *pH* effect can be neglected. Thus, the half-wave potential of titanium in 0.2 *M* oxalic acid, *pH* 1.2 is  $-0.30$  v. vs. the saturated calomel electrode.

**Concentration of Oxalic Acid.**—Several series of solutions were prepared containing 0.332, 1.61 and 8.05 millimolar

titanium(IV) and 2.13 millimolar titanium(III) in variable concentrations of oxalic acid. The half-wave potentials shifted in a positive direction with increasing concentrations of oxalic acid as shown in Fig. 5. Here, too, there is a change in *pH* with additions of oxalic acid and this positive shift is partially explained in this manner. Correcting the half-wave potentials to the same *pH* value leaves a net effect of approximately  $+0.02$  volt per tenfold increase in the concentration of oxalic acid. The same numerical effect was obtained in a supporting electrolyte containing 1 *N* excess sulfuric acid where the change in *pH* is relatively negligible.

Thus there is a definite positive shift in the half-wave potential with increasing concentration of oxalic acid which is independent of the *pH*, the concentration of titanium and its oxidation state.

**Diffusion Current Constants.**—Since the diffusion current, like the half-wave potential, is a function of *pH* and the concentration of oxalic acid, and therefore in these experiments not strictly proportional to the concentration of titanium, it was not considered useful to make highly accurate measurements of the diffusion current constant. For analytical purposes it is necessary to prepare calibration curves under the same conditions. The approximate values obtained for the value  $i_d/Cm^{2/3}t^{1/6}$  are: 1.75 for titanium(IV) in 0.2 *M* oxalic acid, *pH* 0.5, and 1.60 for titanium(III) in 0.2 *M* oxalic acid, *pH* 0.8 ( $m^{2/3}t^{1/6}$  2.222).

**Spectrophotometric Investigation of the Oxalato-Titanium(III) Complex.**—The oxalato-titanium(III) complex is yellow and therefore it should be possible to establish the

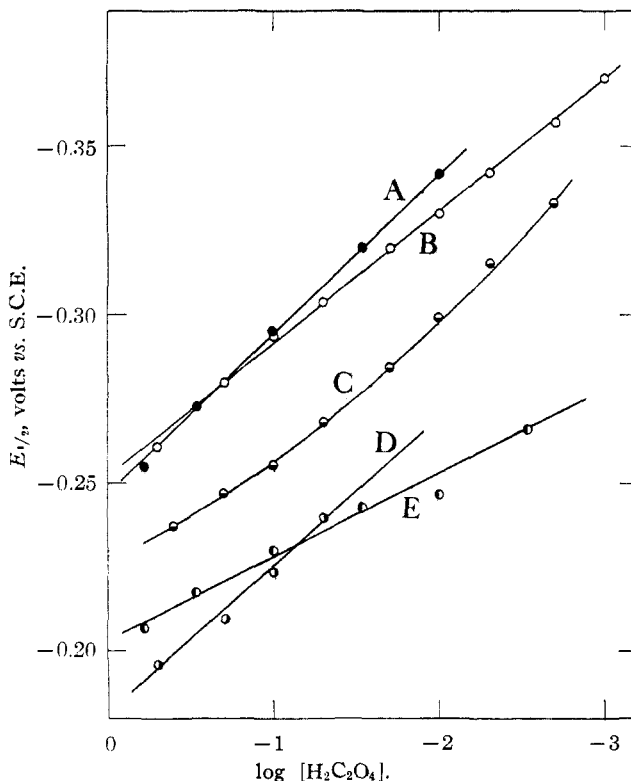


Fig. 5.—Effect of concentration of oxalic acid in half-wave potential: A, (solid circles) 2.13 millimolar titanium(III); B, (open circles) 0.332 millimolar titanium(IV); C, (lower half solid) 1.61 millimolar titanium(IV); D, (right half solid) 8.05 millimolar titanium(IV); E, (left half solid) 0.332 millimolar titanium(IV) plus 1 *N* sulfuric acid.

ratio of titanium to oxalate by use of the method of continuous variations.<sup>10</sup> The absorption spectra of both the complexed and uncomplexed species were obtained with a Beckman model DU spectrophotometer. The curves are shown in Fig. 6. Note that the scale for the molar extinc-

(9) R. L. Pecsok and J. J. Lingane, *THIS JOURNAL*, **72**, 189 (1950).

(10) W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941); **64**, 1630 (1942).

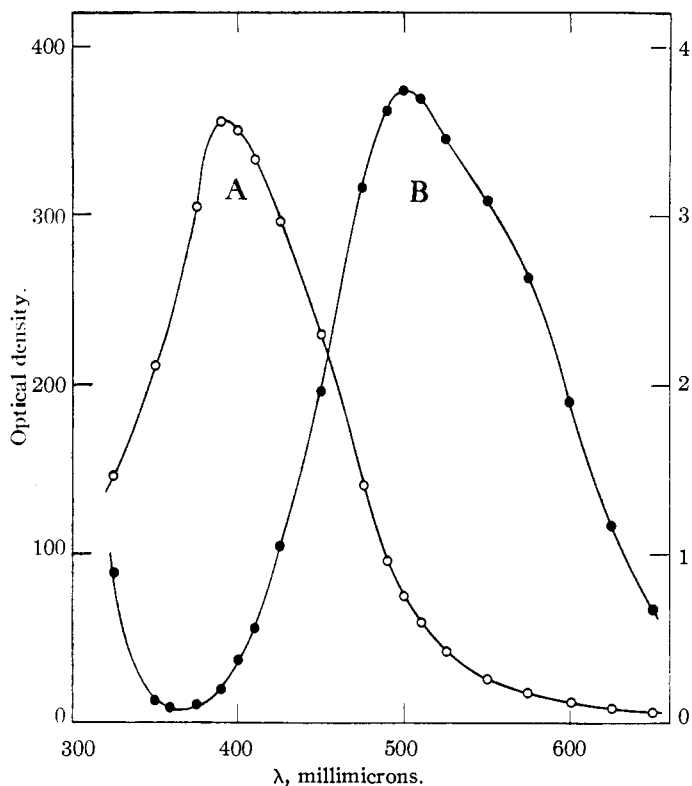


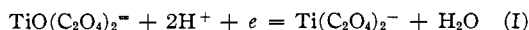
Fig. 6.—Absorption spectra: A (left marginal scale), 4.90 millimolar titanium(III) and 18.9 millimolar oxalic acid; B (right marginal scale), 0.0549 M titanium(III) chloride.

tion coefficient of the uncomplexed titanium has been increased 100-fold. The wave length 390 mμ was selected for measurement of the mixtures. At this wave length the absorption of the uncomplexed titanium is negligible and the optical density is essentially a direct measurement of the concentration of the complex.

A series of solutions was made up by measuring appropriate amounts of stock solutions of titanous chloride, air-free oxalic acid and air-free water into special 5-ml. absorption cells equipped with special standard taper ground-glass stoppers. The operations were conducted under carbon dioxide to minimize air oxidation. The solutions all contained a total of 10 millimolar oxalic acid plus titanium(III), but in various proportions. The optical densities measured at 390 mμ vs. the concentrations of titanium are plotted in Fig. 7. A maximum occurs at 3.2 millimolar titanium, indicating that there is a ratio of 1 titanium(III) to 2 oxalates in the complex ion.

Since the oxalato-titanium(IV) complex is colorless, it is not possible to establish its formula by this method. Nor were conductometric measurements feasible because of the excess hydrochloric acid in the reagent. However, Brintzinger and W. Eckardt,<sup>11</sup> have reported a complex with the formula  $TiO(C_2O_4)_2^-$  from dialysis experiments. For the tervalent ions, ferric, cobaltic, manganic and chromic, they report complexes of the type  $M(C_2O_4)_3^-$  which do not correspond to the above formula for the oxalato-titanium(III) complex obtained in these experiments. The dialysis experiments were carried out in solutions containing 0.01–0.05 N complex and 2 N ammonium oxalate.

**Proposed Electrode Reaction.**—The electrode reaction which most nearly fits the data obtained is



(11) H. Brintzinger and W. Eckardt, *Z. anorg. allgem. Chem.*, **224**, 93 (1935).

From this equation one predicts that

$$E_{1/2} = E^\circ - 0.059 \times 2pH$$

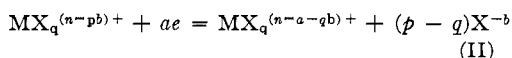
where  $E^\circ$  is the standard potential of reaction (I). The observed equation for the half-wave potential is

$$E_{1/2} = -0.25 - 0.080pH + 0.02 \log [H_2C_2O_4]$$

volts vs. the saturated calomel electrode.

Since the polarographic waves upon which the observed dependence is based have been shown to be reversible and diffusion controlled, the discrepancies must have some other cause. This situation represents a case where the equations developed by Lingane<sup>12</sup> are not applicable.

Consider the reaction



If the concentration of X is large relative to that of the complex ions and  $p = q$ , then the half-wave potential must be independent of the concentration of X. In this case, although the concentrations of oxalic acid and hydrogen ion are large, the concentration of oxalate ion is extremely small relative to that of the complex ions. It must, however, remain constant at surface of the electrode during the growth of the drop.

The equilibria are maintained

$$[Ti(C_2O_4)_2^-]/[Ti^{+3}] = [C_2O_4^{2-}]^2/K_3 \quad (III)$$

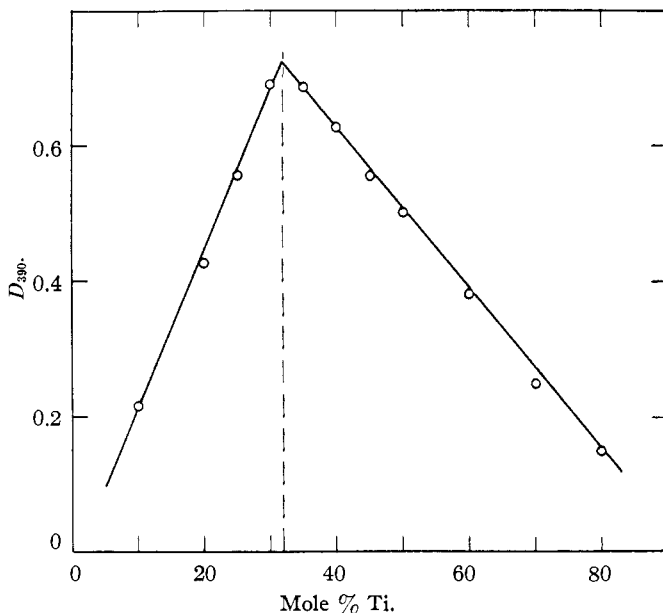


Fig. 7.—Optical densities of solutions containing 10 millimolar total concentration of titanium(III) and oxalic acid.

and

$$[TiO(C_2O_4)_2^-]/[TiO^{++}] = [C_2O_4^{2-}]^2/K_4 \quad (IV)$$

where  $K_3$  and  $K_4$  are the dissociation constants of the complex ions. Adding one to each side of equations III and IV, and inverting, we obtain

$$\frac{[Ti^{+3}]}{[\Sigma Ti^{+3}]} = \frac{K_3}{K_3 + [C_2O_4^{2-}]^2} \quad (V)$$

(12) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

and

$$\frac{[\text{Ti}^{+4}]}{[\Sigma \text{Ti}^{+4}]} = \frac{K_4}{K_4 + [\text{C}_2\text{O}_4^{2-}]^2} \quad (\text{VI})$$

where  $[\Sigma \text{Ti}^{+3}]$  represents  $[\text{Ti}^{+3}] + [\text{Ti}(\text{C}_2\text{O}_4)_2^-]$ , etc.

It is the ratio  $[\text{Ti}^{+3}]/[\text{Ti}^{+4}]$  which determines the standard potential (or polarographic half-wave potential) of reaction I. Dividing V by VI, one obtains

$$\frac{[\text{Ti}^{+3}]}{[\text{Ti}^{+4}]} = \frac{K_3}{K_4} \times \frac{K_4 + [\text{C}_2\text{O}_4^{2-}]^2}{K_3 + [\text{C}_2\text{O}_4^{2-}]^2} \times \frac{[\Sigma \text{Ti}^{+3}]}{[\Sigma \text{Ti}^{+4}]} \quad (\text{VII})$$

If the square of the concentration of oxalate ion is large compared to the values of  $K_3$  and  $K_4$ , the latter can be neglected in the center fraction of the right-hand side of equation VII, in which case the ratio is independent of the concentration of oxalate ion. If, however, the square of the concentration of oxalate ion is of the same order of magnitude as  $K_3$  and/or  $K_4$ , then the ratio  $[\text{Ti}^{+3}]/[\text{Ti}^{+4}]$ , and the corresponding potential, must be a function of the concentration of oxalate ion. The latter is a function of the concentration of oxalic acid in the present discussion at constant pH.

The positive shift of potential with increasing concentration of oxalic acid indicates that the numerator of equation VII increases less rapidly than the denominator; therefore,  $K_4$  is larger than  $K_3$ . It is not possible to determine the values of  $K_3$  and  $K_4$  from the present data alone and no values have been reported in the literature.

The half-wave potential of this system extrapolated to 1 M oxalic acid and 0 pH is  $-0.25$  v. vs. the saturated calomel electrode or 0 v. vs. the

standard hydrogen electrode. The standard potential of the uncomplexed species is  $-0.04$  v. vs. the standard hydrogen electrode<sup>13</sup> which is not measurable polarographically because of irreversible electrode reactions. This slight shift in potential of 0.04 v. indicates that the +3 and +4 complexes have dissociation constants of the same order of magnitude with the trivalent being slightly more stable, in agreement with the preceding paragraph.

The above discussion also resolves the discrepancy noted for the dependence of half-wave potential on pH. If the total oxalate concentration is maintained constant and the pH altered, two effects result. First, the potential is changed because hydrogen ions are involved in reaction I. Second, the concentration of oxalate ion is changed. The two effects are in opposite directions and qualitatively in accord with the observed facts.

An increase of pH of one unit will increase the concentration of oxalate ion 100-fold. Since the observed dependence of potential for the latter is 0.02 volt per tenfold increase, the observed discrepancy of 0.04 volt for the pH dependence is exactly accounted for.

**Acknowledgment.**—The author is indebted to Mr. C. E. Johnson for furnishing a solution of purified titanous chloride, and to Professor J. B. Ramsey for valuable discussion.

(13) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 483.

LOS ANGELES 24, CALIFORNIA RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

## The Emission Spectrum of Curium<sup>1</sup>

BY JOHN G. CONWAY, MILTON F. MOORE AND W. W. T. CRANE

The wave lengths of the most prominent lines in the arc and spark spectra of curium have been measured. The region covered extended from 2516–5000 Å. The wave lengths of the lines are given, together with a discussion of methods of spectrographic analysis of curium samples.

### Introduction

In August of 1947 L. B. Werner<sup>2</sup> isolated a sufficient amount of curium to permit a spectrochemical analysis to be performed. At that time the wave lengths of 54 lines were measured and these assigned to curium.<sup>3</sup> More recently W. W. T. Crane isolated additional quantities of curium and a portion was made available for further wave length measurements.

The handling of active elements such as curium requires many special protective techniques and equipment. A controlled atmosphere chamber mounted in a gloved box and a filter system were developed and constructed (Fig. 1) to meet these requirements. The controlled atmosphere chamber is made air tight before sparking, so that during

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. B. Werner, U. S. Atomic Energy Commission Declassified Document AECD-2729 (July, 1948).

(3) J. G. Conway and M. F. Moore, University of California Radiation Laboratory Report UCRL-78 (April, 1948).

TABLE I

WAVE LENGTHS OF CURIUM

Wave length	In-tensity spark	Wave length	In-tensity spark	Wave length	In-tensity spark	Wave length	In-tensity spark
2516.0	2	2727.7	3	2909.1	2	2998.8	2
2562.3	1	2736.8	3	2913.1	4	3000.8	2
2585.8	2	2748.0	1	2929.0	2	3037.4	2
2616.8	2	2773.5	2	2933.2	3	3044.7	6
2617.2	3	2792.0	1	2934.9	3	3046.6	5
2625.4	2	2796.2	1	2935.4	3	3047.5	2
2628.2	2	2796.4	1	2944.5	2	3050.8	2
2636.2	3	2811.5	5	2953.0	3	3059.0	2
2651.1	4	2817.4	4	2955.6	2	3081.6	4
2653.7	4	2821.5	4	2957.5	4	3092.8	4
2677.0	1	2833.7	4	2961.8	2	3096.4	1
2693.8	1	2862.2	2	2963.0	2	3101.5	1
2704.8	1	2862.8	2	2968.9	4	3104.9	1
2707.1	1	2872.0	3	2984.5	3	3118.3	3
2710.1	1	2882.3	1	2996.2	3	3143.9	1
2725.6	2	2888.1	1	2998.3	3	3161.8	3