[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Potentiometric Titration of +4 and +6 Selenium and Tellurium with Chromous Ion

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This paper presents the results of a potentiometric investigation of the reduction of selenium and tellurium from the +6 and +4 oxidation states by chromous ion. Tomicek,[1] and Willard and Fenwick,[2] studied the reduction of selenium and tellurium compounds with titanous ion, but titrimetric reduction with chromous ion has not previously been investigated.

This study has led to the development of new methods for the accurate determination of Se(IV) and Te(IV), both separately and in mixtures of these two elements.

Preparation of Materials

Tellurium Dioxide.—This was prepared from U. S. P. elementary tellurium by the method of Schuhmann.[3,4] Finely granulated tellurium was added slowly to excess concentrated nitric acid at 70°. When the metal had all dissolved the solution was allowed to evaporate at 80° until crystallization of the basic tellurium (IV) nitrate, $2TeO_2 \cdot HNO_3$, began. The crystals obtained by cooling were air dried and then ignited strongly in a platinum crucible to convert to TeO_2. The latter was dissolved in concentrated hydrochloric acid, the acidity was adjusted to approximately 10 *M*, and the solution was saturated with sulfur dioxide to precipitate any selenium. Tellurium is not easily reduced at this acid concentration. The solution was then filtered, diluted until the hydrochloric acid concentration was about 2 *M*, and treated again with sulfur dioxide to precipitate elementary tellurium. This was converted to the basic nitrate, and the latter was ignited for four hours in a muffle furnace at 400° to obtain pure TeO_2 which was stored in a desiccator.

When assayed by oxidation to the +6 state with excess potassium dichromate and potentiometric titration of the excess dichromate with ferrous ion, as recommended by Shrenk and Browning,[5] a purity factor of 99.87 ± 0.06% was obtained. Gravimetric assay by precipitation as the element from a boiling hydrochloric acid solution with sulfur dioxide and hydrazine hydrochloride[6] gave a purity factor of 99.90 ± 0.06%.

Since tellurium dioxide is only very slightly soluble in water, standard solutions were prepared in dilute hydrochloric acid.

Telluric Acid.—The method of Meyer and Franke,[7] involving oxidation of elemental tellurium with chloric acid solution, was used. The crystals of orthotelluric acid, H_6TeO_6, obtained by evaporating the solution were purified by two further recrystallizations from water.

A stock solution in water was prepared and standardized by the method of Gooch and Howland[8] which employs the reaction $H_6TeO_6 + 2Br^- + 2H^+ = H_2TeO_3 + Br_2 + 3H_2O$ in dilute sulfuric acid. The bromine produced was distilled with the aid of pure carbon dioxide or nitrogen into an excess of potassium iodide solution, and the liberated iodine was titrated with thiosulfate.

Selenium Dioxide.—This was prepared from U. S. P. elementary selenium by the method described by Biltz, Hall and Blanchard.[9] The finely pulverized selenium was dissolved by treatment with excess concentrated nitric acid, the solution was evaporated to dryness, and the resulting selenium dioxide was sublimed. The sublimate was dissolved in 10 *M* hydrochloric acid and reduced to elementary selenium with sulfur dioxide in the cold. To prevent the formation of Se_2Cl_2 it was necessary to partially neutralize the solution with sodium hydroxide near the end of the reduction. The precipitated selenium was washed free of chloride ion, converted to the dioxide with nitric acid, and the selenium dioxide was finally sublimed.

A stock solution was prepared in water. Acidimetric titration with carbonate-free sodium hydroxide using the glass electrode[5] showed a molarity of 0.05093. A molarity of 0.05097 was found by precipitation as elemental selenium from a tartaric acid solution with hydroxylamine hydrochloride.[10]

Selenic Acid.—Following the procedure outlined by Gilbertson and King[11] selenic acid solution was prepared by oxidizing a solution of the previously purified selenium dioxide with 30% hydrogen peroxide. The solution was standardized by titration with sodium hydroxide, which yielded a molarity of 0.02024, and also by the method of Gooch and Howland[8] which led to a molarity of 0.02026.

Titration Technique

Titrations were performed with standard 0.1000 *M* solutions of chromous sulfate, prepared in either 0.1 or 1 *N* sulfuric acid by the method described by Lingane and Pecsok.[12]

A 250-cc., three-necked balloon flask served as titration vessel.[12] A bright platinum indicator electrode was used, in conjunction with the saturated calomel electrode. The salt bridge contained dilute sulfuric acid. Carbon dioxide or nitrogen, purified by passage through a wash bottle containing chromous sulfate solution, was bubbled rapidly through the solution to remove air for at least ten minutes before a titration was started, and at a slower rate during the titration. Magnetic stirring was employed. The solutions were adjusted to an initial volume of 150 cc.

Potentials were read on a Leeds and Northrup potentiometer in the usual manner.

Results and Discussion

+4 Selenium.—In solutions acidified with hydrochloric or sulfuric acid +4 selenium is reduced to the elemental state by chromous ion, according to

$$H_2SeO_3 + 4Cr^{++} + 4H^+ = Se + 4Cr^{+++} + 3H_2O$$

Typical titration curves for titrations in various concentrations of hydrochloric acid are shown in Fig. 1.

Steady potentials are reached in two or three minutes at room temperature, and somewhat more rapidly at 70°. It was necessary to clean the platinum indicator electrode with concentrated nitric acid before each titration to obtain repro-

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* Allied Chemical and Dye Corporation Fellow, 1947–48.

(1) O. Tomicek, *Bull. soc. chim.*, **41**, 1389 (1927); *Rec. trav. chim.*, **43**, 793 (1924).

(2) H. H. Willard and F. Fenwick, THIS JOURNAL, **45**, 933 (1933).

(3) R. Schuhmann, *ibid.*, **47**, 356 (1925).

(4) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 312.

(5) W. T. Shrenk and B. L. Browning, THIS JOURNAL, **48**, 139 (1926).

(6) V. Lenher and A. W. Homberger, *ibid.*, **30**, 387 (1908).

(7) J. Meyer and W. Franke, *Z. anorg. Chem.*, **193**, 191 (1930).

(8) F. A. Gooch and J. Howland, *Am. J. Sci.*, [3] **48**, 375 (1894).

(9) H. and W. Biltz, W. T. Hall and A. A. Blanchard, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1928.

(10) V. Lenher and C. H. Kao, THIS JOURNAL, **47**, 2454 (1925).

(11) L. I. Gilbertson and G. B. King, *ibid.*, **58**, 180 (1936).

(12) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

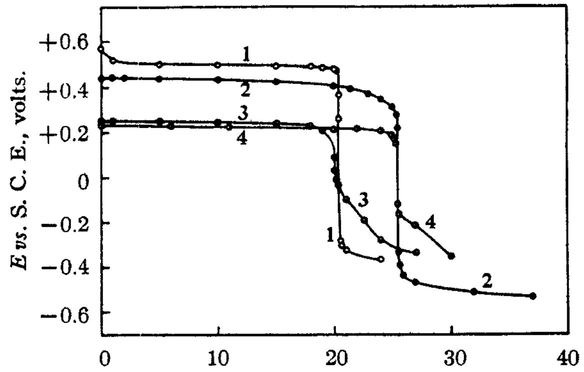

Fig. 1.—Titration of +4 selenium in hydrochloric acid media: (1) 9 *N* acid at 70°; (2) 6 *N* acid at 25°; (3) 0.1 *N* acid at 25°; (4) 1 *N* acid at 25°.

ducible potentials; when this was omitted the potential values before the equivalence point were abnormally low, although the e. p. could be determined without difficulty.

In 0.1 and 1 *N* hydrochloric acid the shape of the curves immediately after the e. p. suggests the partial reduction of Se to hydrogen selenide, and the characteristic odor of this gas could be detected. The formation of H_2Se was most pronounced in titrations in 9 *N* hydrochloric acid at 70°. The standard potential of the half reaction $Se + 2H^+ + 2e = H_2Se$ is −0.36 v. *vs.* N. H. E., which is only slightly more oxidizing than that of the chromic–chromous couple (−0.40 v.) and consequently complete reduction to hydrogen selenide cannot be expected.

From the data in Table I it is seen that titration in 0.1 *N* hydrochloric acid yields low results. In 1 to 9 *N* hydrochloric acid accurate results are obtained at both 25° and 70°. The higher acid concentrations are preferable because of the very large potential change at the e. p., and because the reaction is more rapid the higher the acidity.

TABLE I

TITRATION OF SELENIUM (IV) WITH CHROMOUS SULFATE

Initial volume of solution was 150 cc. Calculated volume of chromous sulfate required was 25.52 cc. Solutions swept with CO_2

Initial acidity	Temp., °C.	Cr_2SO_4 required	Error, cc.
0.1 *N* HCl	25	25.35	−0.17
	70	25.26	− .26
1.0 *N* HCl	25	25.49	− .03
	70	25.47	− .05
6.0 *N* HCl	25	25.52	.00
		25.45	− .07
		25.57	+ .05
	70	25.48	− .04
		25.56	+ .04
		25.53	+ .01
9.0 *N* HCl	70	25.55	+ .03
		25.55	+ .03
1.0 *N* H_2SO_4	70	25.48	− .04
6.0 *N* H_2SO_4	70	25.48	− .04
		25.52	.00
		25.62	+ .10
		25.67	+ .15

Titration curves in 1 to 6 *N* sulfuric acid are very similar to those in the same concentration of hydrochloric acid. Titration in sulfuric acid solution is not as satisfactory as in hydrochloric acid because the reaction is slower, although it is feasible if the titration is performed at 70°. The data in Table I show a somewhat poorer precision in sulfuric acid than in hydrochloric acid.

+4 Tellurium.—Typical titration curves in various concentrations of hydrochloric and sulfuric acids are shown in Fig. 2. The titration reaction is

$$TeOOH^+ + 4Cr^{++} + 3H^+ = Te + 4Cr^{+++} + 2H_2O$$

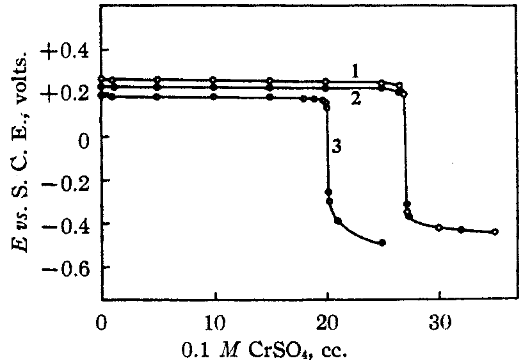

Fig. 2.—Titration of +4 tellurium: (1) 0.3 and 1 *N* hydrochloric acid, and 1 and 6 *N* sulfuric acid, at 25°; (2) 6 *N* hydrochloric acid at 25°; (3) 9 *N* hydrochloric acid at 70°.

The potential change at the e. p., although quite large, is smaller than that in the titration of +4 selenium. This is understandable from the following potential data[13] (referred to the standard hydrogen electrode). The standard potential

$$H_2SeO_3 + 4H^+ + 4e = Se + 3H_2O;\ E^0 = +0.74\text{ v.}$$
$$TeOOH^+ + 3H^+ + 4e = Te + 2H_2O;\ E^0 = +0.529\text{ v.}$$
$$TeCl_6^- + 4e = Te + 6Cl^-;\ E^0 = +0.55\text{ v.}$$

of the half reaction $Te + 2H^+ + 2e = H_2Te$ (−0.69 v.) is more reducing than that of the chromic–chromous couple (−0.40 v.), which precludes reduction to hydrogen telluride.

The reduction of +4 tellurium proceeds more rapidly than that of +4 selenium; at 70° establishment of the potential is almost instantaneous.

The data in Table II show that the titration is very accurate in all concentrations of hydrochloric acid between 0.3 and 9 *N*, and in 1 and 6 *N* sulfuric acid.

+6 Tellurium.—The standard potential of the half reaction

$$H_6TeO_6 + 3H^+ + 2e = TeOOH^+ + 4H_2O;\ E^0 = +0.96\text{ v.}$$

is 0.43 v. greater than that of the $TeOOH^+$–Te

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(13) W. M. Latimer, "Oxidation Potentials," Prentice–Hall, Inc., New York, N. Y., 1938.

TABLE II

TITRATION OF TELLURIUM (IV) WITH CHROMOUS SULFATE

Initial volume of solution was 150 cc. Calculated volume of chromous sulfate required was 26.99 cc. All titrations at room temperature. Solutions swept with carbon dioxide

Initial acidity	Cr_2SO_4 required, cc.	Error, cc.
0.3 *N* HCl	26.94	−0.05
	26.91	− .08
1.0 *N* HCl	26.96	− .03
	26.97	− .02
6.0 *N* HCl	26.98	− .01
	26.96	− .03
	26.96	− .03
	27.03	+ .04
9.0 *N* HCl	26.97	− .02
	27.06	+ .07
1.0 *N* H_2SO_4	26.94	− .05
	26.96	− .03
	27.09	.00
	27.03	+ .04
6.0 *N* H_2SO_4	26.86	− .13
	26.86	− .13
	27.04	+ .05
	26.96	− .03

couple, so that a two stage reduction of telluric acid, first to the +4 state and then to the element, is possible. However, the reduction of telluric acid by chromous ion in either hydrochloric or sulfuric acid medium is so slow that a determination of tellurium based on reduction from the +6 to the +4 state is not feasible.

The first addition of chromous ion produces elemental tellurium which is only slowly reoxidized to the +4 state by the remaining telluric acid. In 6 *N* hydrochloric acid at 70° it is possible to obtain a titration curve with two inflection points if a long time is allowed for establishment of equilibrium between each addition of chromous ion until the first end-point has been reached. However, under these conditions a considerable part of the telluric acid is reduced by chloride ion

$$H_6TeO_6 + 2Cl^- + 3H^+ = TeOOH^+ + Cl_2 + 4H_2O$$

and since much of the resulting chlorine escapes from the solution, too little chromous solution is required. In a typical case, 9.75 cc. of chromous solution was required to reach the first end-point, compared to a theoretical 10.04 cc.

Titration of telluric acid to the elemental state is not feasible in any concentration of either hydrochloric or sulfuric acid up to 6 *N* at room temperature, nor in hot sulfuric acid solutions, because of the slow reduction. Although the reduction of telluric acid to the element proceeds at a more rapid rate in hot hydrochloric acid, the reduction by chloride ion precludes the use of this medium during the first stage of the titration. It is possible to obtain accurate results in the titration to the element by starting the titration in 6 *N* hydrochloric acid at room temperature, gradually heating the solution to 70° over a period of about ten minutes as the chromous solution is slowly added, and finally completing the titration at 70°. About one-half the total required volume of chromous solution should be added during the heating period. In five such titrations the volumes of chromous solution required ranged from 30.09 to 30.22 cc., the average being 30.14 ± 0.04 cc., in good agreement with the theoretical volume 30.13 cc. In this procedure the only oxidized form of tellurium that remains near the end-point is the +4 state, and the titration can be completed quickly.

+6 Selenium.—The titration of selenic acid is more difficult than telluric acid because the reaction is slower. Titration to the elemental state in 6 *N* hydrochloric acid at 70° led to results that were about 5% low, apparently because of partial reduction of the selenic acid by chloride ion. Starting the titration in 6 *N* hydrochloric acid at room temperature, slowly heating to 70° as the chromous solution was added, and finally completing the titration to the elemental state at 70°, yielded results accurate to about 0.5%. However, the titration requires such a long time that it is not practical.

Simultaneous Determination of Selenium and Tellurium.—Since in strongly acid solutions the oxidation potential of the Se(IV)–Se couple is about 0.3 v. greater than that of the Te(IV)–Te couple it is possible to determine both elements by a single titration with chromous ion.

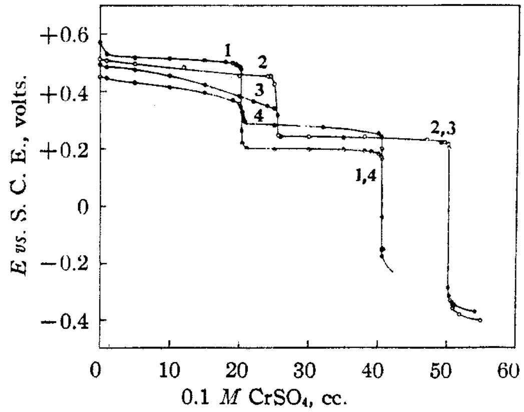

Fig. 3.—Titration of mixtures of +4 selenium and +4 tellurium under various conditions: (1) 9 *N* hydrochloric acid at 70°; (2) 6 *N* hydrochloric acid at 70°; (3) 6 *N* hydrochloric acid at 25°; (4) 6 *N* sulfuric acid at 70°.

Titration curves of mixtures of +4 selenium and +4 tellurium under various conditions of acidity and temperature are shown in Fig. 3. In all cases the first inflection point corresponds to the reduction of Se(IV) to the elemental state, and the second occurs after the reduction of Te(IV) to the metal. Since the reduction of Te(IV) by chromous ion is more rapid than that of Se(IV), addition of chromous ion causes some transient precipitation of elemental tellurium during the selenium stage of the titration, and equilibrium is established via the reduction of Se(IV) by the elemental tellurium.

In 6 *N* sulfuric acid at 70°, and in 6 *N* hydrochloric acid at room temperature the potential change at the selenium equivalence point is small and a long time is required for the attainment of equilibrium. In 9 *N* hydrochloric acid at 60° to 70° the titration is very satisfactory; a large potential break occurs at the selenium e. p. and equilibrium is established quickly. Under these conditions the titration yields accurate results. In three titrations, 25.55 ± 0.05 cc. of 0.1 *M* chromous sulfate solution was required to titrate the selenium, and 25.29 ± 0.09 cc. was used to titrate the tellurium, compared to theoretical values of 25.52 cc. and 25.30 cc., respectively.

Fairly accurate determinations of selenium may also be obtained in the presence of a large amount of tellurium. In two titrations in which 1.2 g. of tellurium (as TeO_2) was present, the selenium titration required 25.64 ± 0.02 cc. of 0.1 *M* chromous sulfate solution, compared to a theoretical 25.52 cc. The amount of selenium present was 6% of the amount of tellurium.

Selenium in Presence of Copper.—Since selenium frequently occurs in association with copper, the possibility of simultaneously determining both elements by titration with chromous ion was investigated.

Titration curves of solutions containing approximately equimolar concentrations of Se(IV) and Cu(II) are shown in Fig. 4. In all cases the Se(IV) is reduced first. In sulfuric acid medium the cupric copper is reduced to the metal, but in hydrochloric acid the copper exists as a chlorocuprate ion (probably $CuCl_4^{=}$) which is reduced to a chlorocuprite complex (probably $CuCl_2^{-}$).[12]

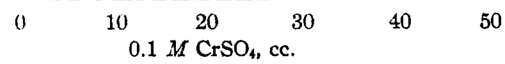

Fig. 4.—Titration of mixtures of +4 selenium and copper: (1) 9 *N* hydrochloric acid at 70°; (2) 6 *N* hydrochloric acid at 25°; (3) 6 *N* sulfuric acid at 70°.

In 6 *N* sulfuric acid at 70° (Curve 1 in Fig. 4) co-reduction of the copper takes place along with the reduction of the Se(IV), and the small gradual inflection in the titration curve occurs when only about half the Se(IV) is reduced.

In 6 *N* hydrochloric acid at room temperature (Curve 2) there is no distinct inflection at the completion of the Se(IV) reduction, although the completion of the reduction of both the Se(IV) and the Cu(II) is marked by a large potential change.

The optimum conditions appear to be 9 *N* hydrochloric acid and a temperature of 70°, as shown by curve 3. Under these conditions a small but distinct potential change occurs when the Se(IV) has been reduced, and both elements can be determined with fair accuracy. In one such titration, 20.8 cc. of 0.1 *M* chromous solution was used to reach the first inflection point, which was 2% greater than the theoretical 20.38 cc., and 22.5 cc. was required to titrate the copper, compared to a theoretical 22.71 cc.

Summary

In solutions acidified with sulfuric or hydrochloric acid Se(IV) and Te(IV) can be titrated accurately with standard chromous solution. The optimum conditions are 6 to 9 *N* hydrochloric acid and a temperature of about 70°. In both cases reduction proceeds to elemental selenium and tellurium.

Although it is quite possible to obtain titration curves for the stepwise reduction of both Se(VI) and Te(VI), first to the +4 states and then to the elements, the slow establishment of equilibrium renders impractical the determination of these elements by titrimetric reduction to the +4 states.

Accurate determinations of Se(IV) and Te(VI) in mixtures were obtained by a single titration with chromous ion in 9 *N* hydrochloric acid at 60° to 70°. A small amount of selenium can be determined accurately in the presence of large amounts of tellurium under these conditions.

Se(IV) and Cu(II), in mixtures containing approximately equal amounts of the two, can be determined with an accuracy of about 2% when the titration is performed in hot 9 *N* hydrochloric acid.

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