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THE FREE ENERGY AND HEAT CONTENT OF TELLURIUM DIOXIDE AND OF AMORPHOUS AND METALLIC TELLURIUM. THE REDUCTION POTENTIAL OF TELLURIUM

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Purpose of the Research

In two previous articles[1] researches were described in which the free energy and heat content of arsenious oxide and the reduction potential of arsenic were determined from the results of electromotive-force measurements at two different temperatures and the free energy of antimony trioxide and the reduction potential of antimony were determined from the results of like measurements at 25°. The object of the present investigation was to determine in a similar manner (1) the free energy and heat content of tellurium dioxide; (2) the free energy of and heat relations between "amorphous" and "metallic" tellurium;[2] and (3) the reduction potential of tellurium. These quantities and relations were derived from measurements at 25° and 45° of the electromotive force of the cells, Te(s) + TeO_2(s), $HClO_4$ (0.10–0.74 *N*), H_2(g), and from solubilities of tellurium dioxide in perchloric acid. Several electromotive-force measurements were made at each temperature with the "amorphous" form of tellurium and one measurement at each temperature with the "metallic" form.

Le Blanc[3] first measured the electromotive-force of tellurium cells, but obtained very variable results. Kasarnowsky[4] has recently measured at 25° the cells, Te(s), $TeCl_4$ (0.003–0.031 *N*) + HCl (2.5 *N*), (KCl satd.), HCl (0.128 *N*), H_2(g), with concordant results; and assuming that the tellurium in 2.5 *N* hydrochloric acid solution is completely in the form of the elementary ions Te^{++++}, he calculated the molal electrode-potential to be -0.549 ± 0.001 volt. This is in reality only a molal reduction potential calculated for the total tellurium for the case that H^+ and Cl^- are at the activities which they have in 2.5 *N* hydrochloric acid.

The present investigation was undertaken at the suggestion of Professor A. A. Noyes, to whom I wish to express my indebtedness for much valu-

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[1] Schuhmann, This Journal, **46**, 52, 1446 (1924).

[2] For convenience in this article the material obtained from a hydrochloric acid solution of tellurium dioxide by reduction with sulfur dioxide is called "amorphous," and the material obtained by fusion is called "metallic," as has been generally done in the past.

[3] Le Blanc, *Z. Elektrochem.*, **12**, 652 (1906).

[4] Kasarnowsky, *Z. anorg. allgem. Chem.*, **128**, 28 (1923).

able advice. It was aided on the financial side by a grant made to him by the Carnegie Institution of Washington.

Preparation of Materials

The perchloric acid used was obtained from the same source as that used in the previous investigations; and the solutions were prepared in the same manner. All concentrations are expressed in moles per 1000 g. of water.

The tellurium dioxide and the two forms of elementary tellurium were prepared by the following procedure. The metal, obtained from a domestic source and containing small quantities of copper and selenium, was dissolved in nitric acid (d., 1.250) at about 70°, as recommended by Norris, Fay and Edgerly for preparing the basic nitrate.[5] The solution was evaporated on a steam-bath at about 80° until a considerable quantity of crystals had formed in the bottom of the vessel. It was then allowed to cool overnight and filtered. After careful washing, the salt was dried in air at 110° and ignited, giving tellurium dioxide.[6] This procedure freed the material from copper, but did not free it from selenium. The oxide was therefore dissolved in 10 N hydrochloric acid; and the solution was saturated with sulfur dioxide and heated to boiling. The latter process was repeated until no further reduction took place. The selenium, with a small part of the tellurium, was thus reduced and precipitated. After filtering, the solution was diluted by adding four volumes of water and was again saturated with sulfur dioxide and heated to boiling, the saturation and heating being repeated until no further reduction occurred. This procedure precipitates all of the tellurium in a form which can be filtered readily. The precipitated tellurium was washed many times by decantation and then on a filter, until the wash water showed no chloride. It was dried in air at 110°. This material, free from copper and selenium, was the amorphous tellurium used in the experiments.

The metallic form was obtained by fusing the amorphous material in a glass tube, of which one end was connected to a nitrogen gasometer and the other had a capillary tube sealed to it. A current of nitrogen was passed through the tube before and during the process of fusion. The fused mass was cooled slowly and then ground fine for use in the experiments.

The dioxide for the experiments was prepared by treating the amorphous elementary tellurium previously prepared in just the same manner as the original metal. That is, it was dissolved in nitric acid (d., 1.250), the basic nitrate was obtained by crystallization and this salt was ignited. The ignition, at a low red heat just below fusion, was continued for about three hours, until the material gave no test for nitrate with brucine solution. As was shown by Norris, Fay and Edgerly, this procedure gives tellurium dioxide, TeO_2.[6]

Apparatus and Methods of Measurement

The apparatus, including the cell and hydrogen generator, was the same as that used in the investigation on the free energy and heat content of arsenious oxide.[1]

The cell was prepared for the experiments in essentially the same manner as the arsenic cell. A mixture of tellurium dioxide and elementary tellurium (amorphous or metallic depending on the cell to be measured) in a solution of perchloric acid was rotated at the proper temperature for

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[5] Norris, Fay and Edgerly, *Am. Chem. J.*, **23**, 107 (1900).

[6] Ref. 5, p. 109.

two or three days. A few drops of this solution were then used to moisten some elementary tellurium sufficiently to form a mush and the platinum spiral used for the electrode was coated with this mush. The electrode was then placed in position in the bottom of the tellurium half-cell and was completely covered with dry elementary tellurium of the same form that was used in preparing the mixture and the electrode. The half-cell was then completely filled from the remaining portion of the rotated mixture and was sealed. The hydrogen half-cell and the connecting part of the cell were filled with the same perchloric acid solution that was used in preparing the mixture to be rotated. Such cells reached a constant electromotive force in from three to four hours and remained constant for many hours with variations of less than 0.1 mv.

The Measured Electromotive Forces

The electromotive-force measurements were made on cells with three different concentrations of perchloric acid. The values obtained for the individual cells are tabulated with the molalities of the perchloric acid solutions and the hydrogen pressures in Table I. The hydrogen pressures were obtained by subtracting from the corrected barometric readings the vapor pressures of the solutions at that temperature, which were taken as equal to those of pure water at the same temperature (24 mm. at 25°, and 71 mm. at 45°).

TABLE I

ELECTROMOTIVE FORCES OF THE CELL, Te(s) + TeO_2(s), $HClO_4$, H_2(g)

Kind of Te	Temperature °C.	Molality of $HClO_4$	Pressure of hydrogen	E.m.f. observed	E.m.f. for H_2 at 1 atm.
"Amorphous"	25	0.7370	712	−0.52774	−0.52857
		.2924	711	− .52771	− .52856
			712	− .52772	− .52855
		.1028	712	− .52776	− .52859
				Mean	− .52857
	45	.7370	665	− .51945	− .52128
		.2924	664	− .51940	− .52125
		.1028	666	− .51952	− .52133
				Mean	− .52129
"Metallic"	25	.1028	715	− .52795	− .52873
	45	.1028	668	− .51940	− .52112

The Free Energy and Heat Content of Tellurium Dioxide

In calculating the free energy of formation of tellurium dioxide only those values of the electromotive force that refer to "amorphous" tellurium will be used. By multiplying the mean values of the electromotive force of the cell (—0.5286 at 25°, and —0.5213 at 45°) by 4 × 96,500/4.182, the free-energy decreases for the cell reaction are found to be those expressed by the equations:

$$Te(s) + 2H_2O(l) = TeO_2(s) + 2H_2(g) - 48{,}000 \text{ cal. at } 25°, \quad —48{,}120 \text{ cal. at } 45°$$

Substituting in the first of these equations the value[7] (—113,120 cal.) of the free energy of $2H_2O(l)$ at 25°, we get $Te(s) + O_2(g) = TeO_2 + 64{,}323$ cal. That is, the free energy of formation of tellurium dioxide (1 TeO_2) from tellurium and oxygen at 25° is —64,320 cal.

The heat-content decrease $—\Delta H$ for the cell reaction was calculated by substituting the two free-energy values just calculated and the respective temperatures in the familiar Gibbs-Helmholtz equation integrated under the assumption that the heat content ΔH is constant for this temperature interval. This calculation gives $—\Delta H$ equal to —58,840 cal. for the cell reaction at 35°. The heat content of $2H_2O(l)$ at 25° is given by Lewis and Randall[8] as —2 × 68,270 cal.; and this value combined with the heat-content change of the cell gives for the heat content of $1TeO_2$ the value —77,700 cal. Thomsen[9] calculated the heat of formation of solid tellurous acid ($1H_2TeO_3$) to be —77,176 cal. His value was derived from the heat of decomposition of tellurium tetrachloride by water and he assumes that solid tellurous acid, H_2TeO_3, was formed in this reaction. The practical identity of these two values and the experiments on the hydration of the solid phase described below make it probable that solid tellurium dioxide precipitates instead of tellurous acid. Mixter[10] obtained —87,100 cal. for the heat of formation of solid tellurium dioxide ($1TeO_2$).

Mr. Warren P. Baxter of this Laboratory has kindly made experiments to determine whether the tellurium dioxide in the solid phase is present as (anhydrous) TeO_2, or as a hydrate of this, such as H_2TeO_3. Known weights of ignited tellurium dioxide were rotated with 120 cc. of 0.75 *N*

	0.75 *N* $HClO_4$ Mg.	0.10 *N* $HClO_4$ Mg.
Ignited TeO_2 taken	744	458
Dissolved by the $HClO_4$ (calcd. from Table II)	96	14
Undissolved by the $HClO_4$ (by difference)	648	444
After standing in air for one hour	658	446
After standing in evacuated desiccator for 1/2 hour	653	442
After standing in evacuated desiccator for 2 1/2 hours	651	439
After standing in non-evacuated desiccator for 5 days	651	440
Calcd., assuming the TeO_2 changed to H_2TeO_3	726	497

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[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, p. 485.

[8] Ref. 7, p. 483.

[9] Thomsen "Thermochemistry" (translated by Burke), Longmans Green and Co., London, **1920**, p. 216.

[10] Landolt-Börnstein-Roth-Scheele, "Tabellen," Julius Springer, Berlin, **1923**, p. 1495.

and 0.10 N $HClO_4$ for three days; the solid residue was filtered on a weighed filter-paper and washed with cold water, then quickly with a little 95% alcohol and a little ether. The paper containing the solid was then dried, first in the air, then in a desiccator containing sulfuric acid and weighed. The results are shown above.

It is evident from these results that the solid phase, even after several days' contact with the acid solutions, is still the anhydrous dioxide.

The Identity in Free Energy and Heat Content of "Amorphous" and "Metallic" Tellurium

The electromotive-force values given in Table I for "metallic" tellurium will be seen to differ from those given for "amorphous" tellurium by an amount which may be readily ascribed to experimental error. That is, the electrode potential of the "metallic" tellurium is identical (within ± 0.0002 volt) with that of "amorphous" tellurium at both temperatures. Hence their free energies and heat contents are the same.

This conclusion is not in accord with that of previous investigators. It is generally asserted that an amorphous form is obtained by reduction with sulfur dioxide in hydrochloric acid solution and that metallic tellurium is obtained by reduction with metals (zinc, tin, etc.) in acid solution, by oxidation in alkaline solution with air, by distillation, by reduction of solid tellurium dioxide with hydrogen, or by fusion. Berthelot and Fabre,[11] who prepared the metallic form in several ways, determined the heat of transition of the amorphous to the metallic form, and found it to be —24,000 cal. Damiens[12] investigating anew the allotropy of tellurium came to the conclusion, in agreement with Berthelot and Fabre, that there are two distinct forms; but on redetermining the heat of transition of the amorphous form he found it to be + 2630 cal.[13] Cohen and Kröner,[14] from measurements of the electrical conductivity of the "amorphous" form at a series of temperatures below the fusion point and of the specific gravity of the "metallic" and of the "amorphous" forms after heating for periods of time at various temperatures below fusion, concluded that the two forms are always present together, dissolved in each other in definite proportions depending on the temperature.

The identity of the two forms was further demonstrated by X-ray photographs made by Dr. M. L. Huggins in this Laboratory, using the powder method. Comparative photographs were taken of the "amorphous" form, of the "metallic" form, and of crystals which separated on exposing to the air a potassium telluride solution that had been prepared by fusing tellurium with potassium cyanide. The "amorphous"

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[11] Berthelot and Fabre, *Ann. chim. phys.*, [6] **14,** 98 (1888).

[12] Damiens, *Compt. rend.*, **174,** 1344 (1922).

[13] Damiens, *ibid.*, **174,** 1548 (1922).

[14] Cohen and Kröner, *Z. physik. Chem.*, **82,** 597 (1913).

form was prepared by precipitating it by sulfur dioxide gas from a cold 2.5 *N* HCl solution of tellurous nitrate, filtering out the precipitate immediately, washing it with cold dilute acid, water, alcohol and ether and exposing it to the X-rays during the following 48 hours. The "metallic" form was produced by fusing the "amorphous" powder in a current of hydrogen. All these preparations were made by Mr. Richard Pomeroy in this Laboratory. All three powders were found to give identical patterns—all showing the same lines and without any additional ones in any of the three cases.

Solubility of Tellurium Dioxide in Perchloric Acid Solutions and the Reduction Potential of Tellurium

The solubility of tellurium dioxide in each of three concentrations of perchloric acid was determined as follows. A volume of perchloric acid solution (about 130 cc. for the two higher concentrations and about 300 cc. for the lowest concentration) was mixed with an excess of tellurium dioxide and some of the "amorphous" tellurium and was rotated in the thermostat at 25° for three to six days. The mixture was rapidly filtered in air at about 25° and the filtrate was weighed. Enough hydrochloric acid was then added to bring the acid concentration up to about 2.5 *N*. The solution was then saturated with sulfur dioxide and heated to boiling. This was repeated until no further reduction could be observed. The precipitated tellurium was collected in a perforated crucible, dried in air at 110° for two to three hours and weighed.[15]

TABLE II

SOLUBILITY OF TELLURIUM DIOXIDE IN PERCHLORIC ACID SOLUTIONS AT 25°

Molality of $HClO_4$	At. wts. of Te(Σ Te) $\times 10^3$ per 1000 g. of water				Activation of $HClO_4$	$\frac{(\Sigma \text{ Te}) \times 10^3}{(H^+)}$
	I	II	III	Mean		
0.7370	5.27	5.24	5.09	5.20	0.787	9.0
.2924	1.97	1.94	1.96	1.96	.768	8.7
.1028	0.74	..	..	0.74	.814	8.9

Values were obtained both from the undersaturated and from the supersaturated side for the two higher concentrations of acid; but for the lowest concentration of acid only one value was obtained (from the undersaturated side). The experimental values are given in Table II.

In the last column of Table II are given the ratios of the total dissolved

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[15] As was shown by Brauner [*J. Chem. Soc.*, **55**, 392 (1889)] and again pointed out by Norris and Fay [*Am. Chem. J.*, **20**, 278 (1898)] this method of analysis is not absolutely accurate, but involves small compensating errors. During the process of filtering and washing, a small part of the tellurium is oxidized by the oxygen of the air and is redissolved, resulting in a small negative error. During the subsequent process of drying also some oxidation takes place, resulting in a small positive error. In practise these two errors generally balance each other. The result may be in error by ±0.5%, according to these authors.

tellurium to the hydrogen-ion activity (H^+) for each concentration of acid. The values of (H^+) were obtained by multiplying the molalities of perchloric acid by its activations (or activity coefficients). In a previous article[16] its activations were shown to be equal to those of hydrochloric acid, for which values have been tabulated by Lewis and Randall.[17] These are the values here employed.

It will be seen that the ratios of the last column of Table II are substantially constant. From this it must be inferred from the mass-action law that the tellurium in solution exists as a univalent ion, such as $Te(OH)_3^+$ or $TeO(OH)^+$, at these concentrations of acid.

Correspondingly, the electrode reactions of the cell may be expressed as follows: $Te(s) + 2H_2O = TeO(OH)^+ + 3H^+ + 4E^-$ and $4H^+ + 4E^- = 2H_2(g)$.

The molal reduction-potential E_0 of tellurium corresponding to this reaction may, therefore, be calculated by substituting the mean value of the electromotive force E of the cell at 25° given in Table I and the mean of the values given in the last column of Table II, in the equation:

$$E_0 = E + \frac{RT}{4F} ln \frac{(\Sigma\ Te)}{(H^+)}$$

The value thus calculated was found to be —**0.5590** volt.

This value does not differ very greatly from the value —0.549 found by Kasarnowsky for total tellurium equal to 1 formal in 2.5 *N* hydrochloric acid.

Summary

The electromotive forces of the cells of the type, $Te(s) + TeO_2(s)$, $HClO_4$ (0.10 − 0.74 *N*), H_2 (1 atm.), were measured at 25° and 45° and the respective values were found to be —0.5286 and —0.5213. The free energy at 25° of tellurium dioxide was computed from the first of these values and found to be —64,320 cal., and its heat content, as derived from the cell measurements at the two temperatures, was found to be —77,700 cal.

From measurements of the cell at both temperatures with both "amorphous" and "metallic" tellurium it was shown that the two forms of tellurium are identical in free energy and heat content.

Solubility determinations of tellurium dioxide in 0.103, 0.292 and 0.737 *N* perchloric acid were made. The results showed that the dissolved tellurium is proportional to the hydrogen-ion activity and therefore that it exists in the form of a univalent ion such as $Te(OH)_3^+$ or $TeO(OH)^+$ at these concentrations of perchloric acid. From the mean electrode-potential of the cell at 25°, the molal reduction potential of tellurium

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[16] Ref. 1, p. 58.

[17] Ref. 7, p. 336.

corresponding to the electronic reaction, $Te(s) + H_2O = TeO(OH)^+ + 3H^+ + 4E^-$, was found to be —0.5590 volt.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XVI. THE PURIFICATION AND ATOMIC WEIGHT OF HOLMIUM[1]

BY FRANK H. DRIGGS WITH B. S. HOPKINS

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Introduction

The object of the work described in this paper was (1) to continue the purification of holmium material and (2) to determine the atomic weight of holmium using the chloride-to-silver ratio.

Only one determination of the atomic weight of holmium has previously been made. This work was carried out by Holmberg[2] in 1911 who purified the holmium obtained from 29 kg. of euxenite and determined its atomic weight using the oxide-to-sulfate ratio. Two analyses gave the values 163.57 and 163.40.

Sources of Material

The material used in the study of this element was obtained from three different sources.

1. **Texas Gadolinite.**—The rare earths were extracted from this ore in 1917 by L. F. Yntema. The finely powdered mineral was extracted with hot hydrochloric acid and the rare earths were precipitated with oxalic acid. The cerium group earths were separated as the double alkali sulfates and any cerium remaining in the yttrium group was removed by the bromate method of James.[3] The yttrium group earths were then converted to the bromates by the usual method.

2. **Norway Fergusonite.**—Forty-five kg. of Norway fergusonite was treated in 1.5kg. lots with hydrochloric and nitric acid and the rare earths were precipitated with oxalic acid. Since the percentage of cerium in this ore was exceedingly small there was no necessity for the removal of this element. The oxalates were converted to the bromates by the usual method.

3. **Series M (Bromates).**—This was an yttrium group bromate series, the previous history of which is a little uncertain. It was derived from double alkali sulfate residues furnished by the Welsbach Company,

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[1] This communication is an abstract of a thesis submitted by Frank H. Driggs, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Holmberg, *Z. anorg. Chem.*, **71,** 226 (1911).

[3] James, THIS JOURNAL, **34,** 757 (1912).