$$\Delta H_s = 3174.3 \times 2.303 \times 1.987 = 14{,}525 \text{ cal. mole}^{-1} \quad (9)$$

$$\Delta H_f = \Delta H_s - \Delta H_v = 14{,}525 - 8174 = 6351 \text{ cal. mole}^{-1} \quad (10)$$

$$\Delta S_f = \Delta H_f/T = 6351/402.8 = 15.77 \text{ e.u.} \quad (11)$$

Chemical Behavior.—Tellurium tetrafluoride is unstable in the presence of traces of water.[5]

$$TeF_4 + 2H_2O \longrightarrow TeO_2 + 4HF \quad (12)$$

and is completely consumed by glass or silica[5] containers at 200°.

$$TeF_4 + SiO_2 \longrightarrow TeO_2 + SiF_4 \quad (13)$$

It also reacts with copper at the same temperature. The products of this reaction were identified by chemical analyses and X-ray diffraction patterns.

$$TeF_4 + 4Cu \longrightarrow Cu_2Te + 2CuF_2 \quad (14)$$

Silver is attacked similarly, but the reactions with gold and nickel are very slow. Platinum appears to be inert at temperatures below 300°.

OAK RIDGE, TENNESSEE

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

The Solubility of Hydrous Germanous Oxide and the Potential of the Germanous Oxide–Germanic Oxide Couple

BY WILLIAM L. JOLLY[1] AND WENDELL M. LATIMER

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The solubility of the brown form of hydrous GeO has been determined as $2 \pm 1 \times 10^{-4}$ mole per liter. From potential measurements, GeO(yellow) = GeO(brown), $\Delta F° = -7.2$ kcal./mole and GeO(brown) + H_2O = $GeO_2 + 2H^+ + 2e^-$, $E° = 0.118 \pm 0.010$ volt at 25°.

Freshly prepared hydrous germanous oxide (precipitated with alkali in the cold) is yellow, and it stays this color if stored under water at room temperature. But if an aqueous suspension of the yellow oxide is boiled, or if it is treated with aqueous hydrochloric acid, the color changes to dark brown.

Solubility of Germanous Oxide. Preparation of Brown GeO.—Germanous hydroxide was precipitated by adding aqueous ammonia to a hydrochloric acid solution of +2 germanium. The precipitate was washed thoroughly with water by repeated centrifugation and decantation and then an aqueous suspension of the material was boiled for about 45 minutes in an inert atmosphere. A final centrifugation yielded a brown paste of hydrous GeO.

Solubility Measurements.[2]—The hydroxide was equilibrated with the solvent (water or aqueous hydrochloric acid) at 25°. A filtered sample of the supernatant solution was titrated with standard permanganate, using iodide as an indicator.

An average of $2 \pm 1 \times 10^{-4}$ molar was obtained for the solubility of brown germanous hydroxide in water. The solubility in aqueous hydrochloric acid is less than 0.01 molar for hydrochloric acid concentrations less than 4 *M* HCl, and increases rapidly for concentrations beyond 4 *M* HCl.

Everest and Terrey[3] found germanous hydroxide to be insoluble in alkaline solutions and hence discredited the report of Hantzsch,[4] who postulated "germano-formic acid." They measured the solubility of the hydroxide in water and found a solubility of 5.0×10^{-3} molar. Their method of analysis consisted of oxidizing the +2 germanium in solution to germanic acid and then titrating this acid after addition of glycerol. (Any germanic acid already present or formed by air oxidation of the germanous hydroxide would have led to high results.) Everest and Terrey apparently used the yellow form of GeO in their investigation.

The GeO, GeO_2 Electrode.—From the spontaneous conversion of yellow GeO to brown GeO, the yellow form is obviously thermodynamically unstable with respect to the brown form. The following cell was studied for the purpose of obtaining a quantitative measure of the instability: GeO(yellow), GeO_2, 0.0025 *M* HCl, GeO(brown), GeO_2. The hydrochloric acid concentration in this cell was low enough so that the yellow GeO changed very slowly to the brown form. The two electrodes consisted of noble metal wire spirals packed with pastes of GeO and GeO_2. In Table I, the observed e.m.f. of the cell is given as a function of time from preparation of the cell. From the initial cell potential, *ca.* 0.155 volt, we calculate $\Delta F° = -7200$ cal./mole for the following two-electron reaction: GeO(yellow) = GeO(brown). As was expected, the cell potential dropped gradually with time, because of spontaneous conversion of the yellow GeO to brown GeO.

Two more cells were prepared and observations made concurrently. Both were of the type—GeO, GeO_2, *x M* HCl, Hg_2Cl_2, Hg, but one contained yellow GeO initially and the other contained brown GeO.

TABLE I

CELL VOLTAGES

Time, hours	*E*, volts	Time, hours	*E*, volts
1.0	0.155	43.5	0.098
3.0	.156	47.5	.090
6.8	.129	117	.064
21.5	.122		

Cell Materials and Experimental Procedure.—Double distilled mercury was washed with nitric acid and rinsed well with water. U. S. P. mercurous chloride was washed by decantation with water. The hydrochloric acid solutions were prepared by appropriate dilution of stock solutions, which had been standardized by titration of weighed amounts of mercuric oxide by the iodo-mercurate method. In one case, the hydrochloric acid was prepared by diluting some constant boiling acid. The molalities and activity coefficients were calculated from the data of Harned and Owen.[5] Whenever the electrolyte was changed, the cell was rinsed very thoroughly by draining and adding the fresh electrolyte. This rinsing was repeated at hourly intervals until the cell potential changed less than a millivolt. The most dilute solution of HCl was used first, and the most concentrated last. Therefore one would expect the first run with the cell containing the yellow GeO to be in disagreement with the later runs, where the HCl concentration was sufficient to rapidly convert the GeO to the stable form.

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[1] Taken from a thesis presented by William L. Jolly for partial satisfaction of the requirements for the Ph.D. degree, University of California, 1952.

[2] For experimental details, the reader is referred to University of California Radiation Laboratory Report 1638, "Some Problems in the Chemistry of Germanium," January, 1952.

[3] D. A. Everest and H. Terrey, *J. Chem. Soc.*, 2282 (1950).

[4] A. Hantzsch, *Z. anorg. Chem.*, **30**, 316 (1902).

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

TABLE II

Molality of HCl	Temperature, °C.	E, volts	$E^\circ(25°)$, volts
	Brown GeO		
0.00260	25.0	0.690	0.381
	19.0	.675	
	31.0	.707	
0.1042	25.0	.519	.391
	19.6	.514	
	33.3	.526	
1.06	25.0	.400	.393
	21.5	.4007	
	33.2	.4017	
	Yellow GeO (Initially)		
0.00260	25.0	0.850	0.541
	19.0	.834	
	31.0	.865	
0.1042	25.0	.505	.377
	19.6	.499	
	33.3	.514	
1.043	25.0	.395	.387
	21.5	.394	
	33.2	.396	

The cells were immersed in a thermostated bath whose temperature was held constant to ±0.1°. Potentials were measured at 25.0° and at temperatures about 6° above and below this temperature. The details are given in Table II.

Discussion.—We see that the first run using the yellow GeO gave a standard potential 0.155 volt higher than the average of all the other standard potentials, in agreement with the preceding experiment. We shall take $E^\circ(25°) = 0.386 \pm 0.010$ volt for GeO(brown) + $Hg_2Cl_2 + H_2O = GeO_2$ (ppt.) + $2Hg + 2H^+ + 2Cl^-$. Since the standard potential of the calomel electrode is −0.268 volt,[6] we calculate $E^\circ = 0.118 \pm 0.010$ volt for the GeO (brown)-GeO_2 couple.

An attempt to calculate the entropy of the cell reaction from the temperature coefficients of the potential at various concentrations gave discordant results.

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(6) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Second Edition, Prentice Hall, Inc., New York, N. Y., 1952.

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

The Heat of Oxidation of Germanous Iodide to Germanic Acid

BY WILLIAM L. JOLLY[1] AND WENDELL M. LATIMER

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The ΔH° at 25° for the reaction $GeI_2(s) + I_3^- + 3H_2O = H_2GeO_3(aq) + 4H^+ + 5I^-$ has been determined as -26.0 ± 1.0 kcal./mole by two experimental procedures. The heat of oxidation to give GeO_2 has been calculated from solubility data.

Several attempts were made to measure the heat of oxidation of solid germanous iodide to germanic acid both in aqueous solution and in perchloric acid solutions, but even with use of very high stirring speeds in the calorimeter, it was found impossible to obtain complete reaction in a reasonable time. The reason for this lies in the fact that germanous iodide hydrolyzes to the hydrous oxide, which is relatively insoluble in non-complexing aqueous solutions. However, in two runs practically complete solution and reaction of the GeI_2 was effected, and the residual solutions were analyzed in order to determine the extent of reaction. These two runs constitute one set of data toward the evaluation of the desired heat. A second set of data resulted from a more roundabout approach, namely, one involving the oxidation of germanous iodide in 3.88 molar hydrochloric acid. In order to get the desired heat, it was necessary to add four different experimental heats.

Preparation of GeI_2 and GeI_4.—A modification of the method of Powell and Brewer[2] was used for the preparation of GeI_2. In a typical preparation, 6.0 g. of germanic oxide was dissolved in about 30 ml. of concd. sodium hydroxide solution. Then 6 molar HCl was added until the initial precipitate of GeO_2 just redissolved. With cooling, 60 ml. of concd. HCl and 45 ml. of 50% H_3PO_2 were added and the solution heated under carbon dioxide for 5–6 hours at 100°. The resulting solution was cooled and germanous hydroxide was precipitated by addition of aqueous ammonia. The hydroxide was filtered off under nitrogen and the moist material added to about 45 ml. of iodine-free hydriodic acid (constant boiling). The suspension was heated with stirring at 80° for half an hour, cooled and the resulting crystals of GeI_2 were filtered off and washed with 50 ml. of a 30% aqueous solution of constant boiling hydriodic acid. The germanous iodide was dried and freed of GeI_4 by heating at 100° in vacuum overnight. The dry material was stored in a vacuum desiccator over magnesium perchlorate.

Germanic iodide was prepared by the method of Foster and Williston.[3] The product was purified by recrystallization from chloroform followed by drying at 80°.

Chemical Analysis of Germanous Iodide.—An appropriate sample of GeI_2 (*ca.* 0.3 g.) was weighed out and dissolved in 20 ml. of 6 M HCl in an atmosphere of carbon dioxide. Then 30 ml. of water was added and the solution was titrated with 0.1 N $KMnO_4$ to the first appearance of iodine color (the titration being carried out under CO_2). This end-point permitted a calculation of the germanium(II) content. Seventy ml. of concd. HCl along with 5 ml. of chloroform were then added and the titration continued. (Vigorous stirring was necessary.) The disappearance of the iodine color from the chloroform layer indicated the completion of the oxidation of iodide to ICl_2^-. From this one titration, it was thus possible to determine both germanium and iodide. Typical results follow. *Anal.* Calcd.: Ge(II), 22.24; I^-, 77.76. Found: Ge(II), 21.77, 21.65; I^-, 77.22, 77.84.

X-Ray Analysis of Germanous Iodide.—The X-ray diffraction patterns of several samples of freshly prepared GeI_2, including one sample of sublimed GeI_2, were obtained.

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[1] Taken from a thesis presented by William L. Jolly for partial satisfaction of the requirements for the Ph.D. degree, University of California, 1952.

[2] H. M. Powell and F. M. Brewer, *J. Chem. Soc.*, 197 (1938).

[3] L. S. Foster and A. F. Williston, *Inorg. Syntheses*, **2**, 112 (1946).