TABLE II

Molality of HCl	Temperature, °C.	E, volts	E°(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 $E°(25°) = 0.386 ± 0.010$ 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 $E° = 0.118 ± 0.010$ 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.

(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.

BERKELEY 4, CALIF.

The Heat of Oxidation of Germanous Iodide to Germanic Acid

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

The $\Delta H°$ 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 GeI₂ and GeI₄.—A modification of the method of Powell and Brewer[2] was used for the preparation of GeI₂. 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 GeI₂ 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 GeI₄ 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 GeI₂ (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 KMnO₄ to the first appearance of iodine color (the titration being carried out under CO₂). 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 GeI₂, including one sample of sublimed GeI₂, were obtained.

(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).

The results were all in close agreement, and showed that GeI_2 has the CdI_2 type structure. The lattice constants $a = 4.249 \pm 0.004$ Å. and $c = 6.833 \pm 0.007$ Å. were measured. Powell and Brewer[2] have found much lower lattice constants for this compound, $a = 4.14$ and $c = 6.80$ (corrected figures); none of our samples were in agreement with their results. Our values for the lattice constants lead to a Ge–I distance of 2.99 Å., which is the same as the Cd–I distance in CdI_2. Credit is due Mrs. Carol H. Dauben for analyzing the diffraction patterns.

Calorimeter.—The calorimeter used in these measurements has been described previously.[4,5] All heats were measured at $25 \pm 1.0°$ and are expressed in terms of the defined calorie (1 cal. = 4.1833 int. joules).

The Direct Method.—In these experiments, the oxidizing solution used in the calorimeter was prepared by mixing measured amounts of a standard triiodide solution with 0.200 M $HClO_4$. An excess of 0.1009 N triiodide solution was pipetted into a one-liter volumetric flask and diluted to volume with 0.200 M $HClO_4$. This solution was then poured into the calorimetric dewar while flushing with carbon dioxide. After assembling the calorimeter and immediately before proceeding with the run, carbon dioxide was bubbled through the solution. The bulb containing the germanous iodide was attached to the end of a rod which had special stirring blades on it. The sample was introduced by plunging the rod down and breaking the bulb on the bottom of the dewar. After completion of the run, the calorimeter was immediately opened and 100-ml. aliquots of the residual solution were titrated with standard thiosulfate solution.

The germanous iodide used in these runs was about 96% pure. Approximately one hour was allowed for the samples to react, but in both runs a few grains of undissolved material remained. For these reasons, the moles of reacted GeI_2 calculated on the basis of the final titrations were lower than those calculated on the basis of the sample weighings.

THE DETAILS FOR THE RUNS

	Run 1	Run 2
Ml. 0.1009 N I_3^-	200	150
Moles GeI_2 weighed out, assuming 100% purity	0.00826	0.00721
Moles GeI_2 reacted, on basis of titration	0.00780	0.00671
Heat evolved, cal.	201.98	174.64
ΔH, kcal./mole	−25.9	−26.0

From considerations of temperature drift uncertainties and analytical inaccuracies, we judge the probable error of each of these measurements to be $\pm 4\%$ and therefore give
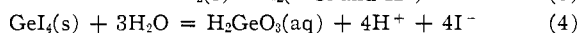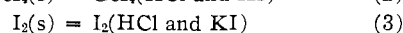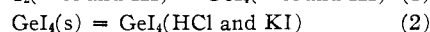
$$\Delta H° = -26.0 \pm 1.0 \text{ kcal./mole for}$$
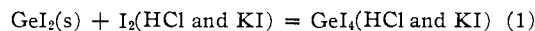$$GeI_2(s) + I_3^- + 3H_2O = H_2GeO_3(aq) + 4H^+ + 5I^-$$
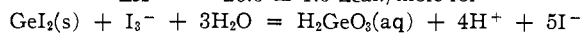
The Indirect Method.—The most convenient way of calorimetrically oxidizing GeI_2 rapidly and completely to a +4 germanium species was found to be the oxidation in approximately 4 molar hydrochloric acid. GeI_2 is quite soluble in 4 M HCl and may be oxidized in this medium to form a soluble +4 germanium species.
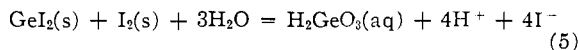
(4) B. J. Fontana, "National Nuclear Energy Series," IV-**19B**, McGraw-Hill Book Co., Inc., New York. N. Y., 1950, p. 321.
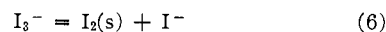(5) H. W. Zimmermann and W. M. Latimer, THIS JOURNAL, **61**, 1550 (1939).

Iodine was used as the oxidizing agent, germanic iodide was used as the reference +4 compound, and a 6% solution of potassium iodide in 3.88 M HCl was used as the solvent. The following is an outline of the various reactions whose heats were measured in order to obtain the heat desired.
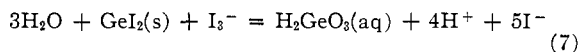
$$GeI_2(s) + I_2(\text{HCl and KI}) = GeI_4(\text{HCl and KI}) \quad (1)$$
$$GeI_4(s) = GeI_4(\text{HCl and KI}) \quad (2)$$
$$I_2(s) = I_2(\text{HCl and KI}) \quad (3)$$
$$GeI_4(s) + 3H_2O = H_2GeO_3(aq) + 4H^+ + 4I^- \quad (4)$$

The sum of equations (1), (3) and (4) minus (2) gives equation (5).

$$GeI_2(s) + I_2(s) + 3H_2O = H_2GeO_3(aq) + 4H^+ + 4I^- \quad (5)$$

By adding the following to (5)

$$I_3^- = I_2(s) + I^- \quad (6)$$

we obtain

$$3H_2O + GeI_2(s) + I_3^- = H_2GeO_3(aq) + 4H^+ + 5I^- \quad (7)$$

Reaction (1).—Four runs were carried out: two using one preparation of GeI_2 and 3.88 M HCl, and two using entirely different preparations. In each run, a bulb containing the germanous iodide was broken into a solution of 3.88 M HCl containing about 60 g. of potassium iodide per liter and an excess of iodine. In two runs the GeI_2 used analyzed 99% pure and in the other two the GeI_2 analyzed 96% pure. The values of ΔH obtained were −18.98, −19.30, −19.04 and −18.92 kcal./mole. Instead of trying to guess the impurities present in the GeI_2 samples and to estimate the corrections necessary to bring the heat up to that for 100% GeI_2, we shall merely assume a possible error of as much as 0.4 kcal./mole and take $\Delta H° = -19.06 \pm 0.4$ kcal./mole for reaction (1).

Reaction (2).—Reaction (2) involves the dissolution of solid germanic iodide in 3.88 M HCl containing 6% potassium iodide. Mistakenly, three runs were carried out without the potassium iodide; that is, GeI_4 was dissolved in 3.88 M HCl alone. The rate of solution was quite slow, but complete solution generally occurred after stirring for 30 minutes. The values of ΔH from these runs were −2.02, −1.52 and −1.70 kcal./mole (average −1.75). When runs were attempted using HCl containing potassium iodide, the rate of solution was found to be prohibitively slow. In the best of three attempts, a very high stirring speed was used in conjunction with extra stirring blades. Even then, only about 90% of the GeI_4 dissolved after 45 minutes. The result of this run with very low precision was −4.7 kcal./mole. Assuming that the inclusion of KI does not change the heat very much from that measured in the first three runs, we shall take $\Delta H = -3.0 \pm 2.0$ kcal./mole for reaction (2).

Reaction (3).—Baker and Adamson resublimed analytical reagent iodine was used. Two runs gave 0.65 and 0.63 kcal./mole. We shall take $\Delta H° = +0.64 \pm 0.05$ kcal./mole for reaction (3).

Reaction (4).—The bulb containing the GeI_4 was attached to a hollow shaft which not only had extra

stirring blades on the end, but also had a hole near the bottom which permitted bubbling inert gas through the solution in the calorimeter. The water in the calorimeter was deaerated before each run. Three runs gave for ΔH, -9.37, -9.46 and -9.34 kcal./mole. With the aid of the Debye–Hückel equation, these heats were extrapolated to infinite dilution to give -9.63, -9.72 and -9.57 kcal./mole. We shall take $\Delta H^\circ = -9.64 \pm 0.10$ kcal./mole for reaction (4).

By adding together the heats for reactions (1), (-2), (3) and (4), we obtain for (5), $\Delta H^\circ = -25.1 \pm 2.0$ kcal./mole. By adding $\Delta H^\circ = -1.0$ kcal./mole[6] for reaction (6), we obtain $\Delta H^\circ = -26.1 \pm 2.0$ kcal./mole for reaction (7).

The two experimentally independent methods have given essentially the same value for the heat of reaction (7), and we shall take $\Delta H^\circ = -26.0 \pm 1.0$ kcal./mole.

Pugh,[7] Laubengayer and Morton,[8] Schwarz

(6) National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Washington, D. C., 1947, et seq.

(7) W. Pugh, J. Chem. Soc., 1537 (1929).

(8) A. W. Laubengayer and D. S. Morton, THIS JOURNAL, 54, 2318 (1932).

and Huf[9] and Winkler[10] measured the solubility of GeO_2 at various temperatures. From the temperature coefficient of the solubility, we can obtain an approximate value for the heat of solution of the soluble form of GeO_2. It appears that the two low temperature measurements of Schwarz and Huf give solubilities which are too high. For the process $H_2O + GeO_2(ppt.) = H_2GeO_3(aq)$ we calculate $\Delta H^\circ = +3.3 \pm 1.0$ kcal./mole. Pugh gave the solubility of GeO_2 in water as 4.47 g. per liter at 25°, while Laubengayer and Morton reported 4.53 g. Taking an average of 4.50 g. per liter, we find $\Delta F^\circ = +1.86$ kcal./mole for the solution of GeO_2. Combining this with the above heat yields $\Delta S^\circ = +4.7 \pm 3.4$ e.u. By estimating $S^\circ = 13$ e.u. for GeO_2 (using Latimer's tables[11]) we calculate the entropy of $H_2GeO_3(aq)$ to be 34.5 $\pm$ 4.0 e.u.

For the oxidation of GeI_2 to GeO_2 by triiodide

$$2H_2O + GeI_2(s) + I_3^- = GeO_2(s) + 4H^+ + 5I^-$$
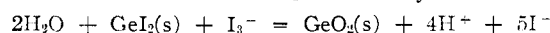
we calculate $\Delta H^\circ = -29.3 \pm 1.4$ kcal./mole.

(9) R. Schwarz and E. Huf, Z. anorg. Chem., 203, 195 (1931).

(10) C. Winkler, J. prakt. Chem., [2] 34, 213 (1886).

(11) W. M. Latimer, THIS JOURNAL, 73, 1480 (1951).

BERKELEY 4, CALIF.

The Vapor Pressure of Germanic Iodide. The Entropies of Germanic Halides. The Disproportionation of Germanous Iodide

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

Germanic iodide sublimes readily at temperatures in the neighborhood of 100°, and in this research the vapor pressure has been measured over a range of 55°. These data have been employed to calculate ΔF° and ΔH° for the sublimation. Since there are no values for the entropy of $GeI_4(g)$, the method of Hildebrand has been employed to estimate the vibrational frequencies and hence calculate the entropy. The vapor pressure of $GeI_4(g)$ over mixtures of Ge and GeI_2 has been measured over a range of 100°. These data have been employed to calculate ΔF° and ΔH° for the disproportionation of GeI_2.

The Vapor Pressure of $GeI_4(s)$.—A saturated vapor flow-method was employed. Germanic iodide crystals were placed in a horizontal glass tube which was heated to a constant temperature while a steady stream of argon was passed through the tube. By assuming that the gas was saturated with GeI_4 vapor in passing through the tube, the amount of GeI_4 which condensed out on the cooler portions of the tubing was taken as a measure of the vapor pressure.

Experimental Procedure.—Germanic iodide was prepared by the method of Foster and Williston.[2] The product was purified by recrystallization from chloroform followed by air drying at 80°.

Two methods for heating the tube containing the GeI_4 were used. In two low temperature experiments the tubing was heated by a vapor-jacket similar to that used in Abderhalden driers. The vapors of boiling benzene and of boiling water were used to maintain the temperatures 79.8 and 99.8°, respectively. Higher temperatures were maintained by heating the tubing in a horizontal tube furnace. A "Celectray" electronic controller (C. J. Tagliabue Mfg.

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

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

Co.) was used in conjunction with a chromel-alumel thermocouple to keep the temperature of the furnace constant to ±3°. The thermocouple was calibrated at the boiling point of water and the melting points of ice, tin and cadmium. A sheath of nickel foil was wrapped around the tubing where the GeI_4 was contained.

Linde argon was freed of oxygen and water by passing the gas consecutively through hot copper turnings and magnesium perchlorate. The total volume of gas passed in a run was determined by collecting the gas over water at the end of the flow system. (It was necessary to correct for the vapor pressure of water.) The runs were timed with an

TABLE I

THE VAPOR PRESSURE OF $GeI_4(s)$

Run	T, °K.	Time, min.	Flow rate, mole A/min.	Total pressure in tube, atm.	Calcd. vapor pressure of GeI_4, atm.
A	393	106	0.746×10^{-3}	0.999	8.2×10^{-4}
B	393	206	0.387×10^{-3}	1.007	8.4×10^{-4}
C	393	47	1.69×10^{-3}	1.008	7.1×10^{-4}
	393		0 (extrap.)		8.7×10^{-4}
D	408	75	0.527×10^{-3}	1.010	1.79×10^{-3}
E	379	203	$.774 \times 10^{-3}$	1.000	2.9×10^{-4}
F	373.0	215	$.735 \times 10^{-3}$	1.002	2.20×10^{-4}
G	353.0	380	$.634 \times 10^{-3}$	0.999	4.7×10^{-5}