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The Heat of Oxidation of Germanous Iodide and the Germanium Oxidation Potentials

W. L. Jolly and W. M. Latimer

March 1951

Berkeley, California

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I. Introduction

Germanium is one of the least studied of the stable elements, its inorganic chemistry being especially sketchy. The heat of formation of GeO_2 has been determined[1,4], and this permits an estimate of the oxidation potential for the couple Ge - H_2GeO_3. But no thermodynamic properties have been determined for any +2 germanium species. Unfortunately, the germanous ion cannot be studied directly because no germanium (II) species exists in any appreciable concentration in noncomplexing aqueous solutions. Germanous iodide, GeI_2, was chosen as a reference +2 compound because it is easily prepared and stable in dry air.

This report deals only with the experimentation designed to measure the heat of oxidation of $GeI_2(s)$ to germanic acid in aqueous solution. By estimating entropies it is then possible to obtain the oxidation potential for the couple:

$$GeI_2\ (s) + 3H_2O = H_2GeO_3 + 4H^+ + 2I^- + 2e^-.$$

Germanous iodide is slightly soluble in both water and perchloric acid solutions, and until further work is done on the measurement of the solubility product, it will be impossible to evaluate the corresponding potential involving germanous ion.

Several attempts were made to oxidize solid GeI_2 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 low solubility of GeI_2. 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 GeI_2 in 3.88 molar hydrochloric acid. In order to get the desired heat, it was necessary to add four different experimental heats. These two experimental approaches are presented separately in this report, even though they both lead to the same final result.

II. Experimental Procedures

Preparation of Germanous Iodide

A modification of the method of Powell and Brewer[9] was used. In a typical preparation, 6.0 g. of germanic oxide was dissolved in about 30 ml. conc. sodium hydroxide solution. Then 6 M HCl was added until the initial precipitate of GeO_2 just redissolved. With cooling, 60 ml. conc. HCl and 45 ml. 50% H_3PO_2 were added and the solution heated under carbon dioxide for 5-6 hours at 100°C. The resulting solution was cooled, and germanous hydroxide precipitated by addition of aqueous ammonia. The hydroxide was filtered off under nitrogen and the moist material added to about 45 ml. 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 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 $Mg(ClO_4)_2$.

Chemical Analysis of Germanous Iodide

An appropriate sample of GeI_2 (ca 0.3 g.) was weighed out and dissolved in 20 ml. 6 M HCl in an atmosphere of carbon dioxide. Then 30 ml. water were added and the solution titrated with 0.1 N $KMnO_4$ to the first appearance of iodine color (the titration being carried out under CO_2). This endpoint permitted a calculation of the germanium (II) content. Seventy ml. conc. HCl along with 5 ml. 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:

Ge (II); found: 21.77%, 21.65%; theory: 22.24%

I^- ; found: 77.22%, 77.84%; theory: 77.76%

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. The results were all in close agreement, and showed that GeI_2 has the CdI_2 type structure. The lattice constants a = 4.249 ± .004 Å and c = 6.833 ± .007 Å were measured. Now Powell and Brewer[9] have found much lower lattice constants for this compound, viz., a = 4.14 and c = 6.80 (corrected figures); but none of our samples gave results anywhere near 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.

Preparation of Germanic Iodide

The method of Foster and Williston[3] was used for preparing GeI_4. The product was purified by recrystallization from chloroform followed by air drying at 80°C. One preparation was analyzed by titrating the iodide with standard permanganate.

Iodide found: 87.9%, 86.8%

Theoretical iodide: 87.55%

Probably the purified material was better than 99% pure.

Preparation of Standard Solutions

The potassium permanganate solutions and the triiodide solutions were both standardized against standard arsenite solutions. The standard arsenite solutions were prepared from analytical reagent arsenious oxide. All standard acid solutions were standardized against solutions of sodium hydroxide which were in turn standardized against potassium acid phthalate.

Calorimeter

The calorimeter used in these measurements has been described previously.[2, 6] All heats were measured at 25.0 ± 1.0 °C. and are expressed in terms of the defined calorie.[8]

Whenever a calorimetric run was carried out using a solution containing some easily oxidized species, the solution was well saturated with some inert gas before proceeding with the run. In some cases, very slowly soluble materials were dissolved, and in such cases extra stirring blades were attached near the bottom of the central stirring shaft.

III. Results

A. 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 indissolved material remained. For these reasons, the moles of reacted GeI_2 calculated on the basis of the final titrations were lower than that calculated on the basis of the sample weighings. The details for the runs are given below:

	Run 49	Run 50
Ml. 0.1009 N I_3^-	200	150
Moles GeI_2 weighed out, assuming 100% purity	.00826	.00721
Moles GeI_2 reacted, on basis of titration	.00780	.00671

	Run 49	Run 50
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 ±4% and therefore give

$$\Delta H = -26.0 \pm 1.0 \text{ kcal for}$$

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

B. 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 4M HCl (perhaps germano-chloroform, $GeHCl_3$, forms) and may be oxidized in this medium to form a soluble +4 germanium species.

Iodine was chosen as the best oxidizing agent for two reasons. First, iodine was a convenient oxidizing agent to have in excess because it cannot oxidize iodide. (It was necessary to employ an excess of oxidizing agent because of the ease of oxidation of germanium (II) solutions by traces of air). Second, since germanic iodide was used as a reference +4 germanium compound, the use of iodine as an oxidizing agent avoids the necessity of measuring the heats of solution of several extra compounds in 3.88 M HCl.

The main disadvantage of using a complexing solution such as 3.88 M HCl as a reaction medium is that the heats of formation of all the dissolved species are unknown and extra calorimetric experiments

are required to relate the heats to infinite dilution in water.

The formula for the +4 germanium compound which exists in 3.88 M HCl is unknown; perhaps it is H_2GeO_3 or $GeCl_6^{=}$. Fortunately, it makes no difference what arbitrary formula we use in our equations. In order to relate the heat of formation of this +4 species to that for $H_2GeO_3(aq)$, it is necessary to know the heats of solution of some reference +4 compound in both water and 3.88 M HCl. First of all $GeCl_4$ was tried. The heat of solution of $GeCl_4$ in water was measured by Roth and Schwartz[11] (one successful experiment) who recorded that the reaction is poor for calorimetry because the GeO_2 formed in the initial hydrolysis is very slowly soluble. In our attempts to measure this heat the same difficulty was encountered. Oddly enough, this difficulty is even more important when $GeCl_4$ is dissolved in 3.88 M HCl. A very slowly soluble white product (an oxide or oxychloride) forms when liquid $GeCl_4$ is added to 3.88 M HCl.

Germanium tetra-iodide was finally decided upon as a reference +4 compound. Again, very slow solution was found in 3.88 M HCl, but not nearly as slow as was the case with $GeCl_4$.

The following is an outline of the various reactions whose heats were measured in order to finally obtain the heat desired.

(1) $GeI_2(s) + I_2(HCl \text{ and } KI) = GeI_4\ (HCl \text{ and } KI)$

(2) $GeI_4(s) = GeI_4\ (HCl \text{ and } KI)$

(3) $I_2(s) = I_2\ (HCl \text{ and } KI)$

(4) $GeI_4(s) + 3H_2O = H_2GeO_3(aq) + 4H^+ + 4I^-$

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

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

By adding the following to (5)

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

we obtain

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

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 runs 7 and 8 the GeI_2 used analyzed 99% pure and in runs 35 and 36 the GeI_2 analyzed 96% pure.

Run	Grams 3.88 M HCl	Grams KI	Grams I_2	Moles GeI_2	Heat Evolved(cal.)	ΔH (kcal/mole)
7	1008	60.0	0.97	.002778	52.74	-18.98
8	1003	57.0	0.48	.001268	24.47	-19.30
35	1070	80.4	1.24	.003252	61.91	-19.04
36	1019	60.0	0.74	.002406	45.53	-18.92

Average ΔH = -19.06 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

$$\Delta H = -19.06 \pm 0.4 \text{ kcal/mole for}$$

(1) $GeI_2(s) + I_2(HCl \text{ and } KI) = GeI_4(HCl \text{ and } KI)$

Reaction (2)

Reaction (2) involves the dissolution of solid germanic iodide in 3.88 M HCl containing about 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 results of these runs are shown below.

Run	Grams 3.88 M HCl	Moles GeI_4	Heat evolved (cal.)	ΔH (kcal/mole)
31	1004	.003796	7.66	-2.02
32	1007	.002657	4.03	-1.52
33	1004	.003473	5.905	-1.70
			Average ΔH =	-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 is very low in precision, but the details are nevertheless given.

Run 48

Moles GeI_4	.001806
Grams 3.88 M HCl	1008
Grams KI	60.0
Heat evolved (cal.)	8.4
ΔH (kcal/mole)	-4.7

The value -4.7 kcal/mole probably only gives the order of magnitude. Assuming that the inclusion of KI does not change the heat very much from that measured in runs 31, 32, and 33, we shall take

$\Delta H = -3.0 \pm 2.0$ kcal/mole for

(2) $GeI_4(s) = GeI_4$ (HCl and KI)

Reaction (3)

In a rough preliminary run it was found that the heat of this reaction is very small, and hence the iodine was not weighed out into the bulb with great precision. (A semi-analytical balance rather than an analytical balance was used.) The potassium iodide was dissolved in 3.88 M HCl and diluted with the same acid to one liter. This solution was then used in the calorimeter. The iodine used was Baker and Adamson Resublimed Analytical Reagent Iodine.

Run	Grams KI	Moles I_2	Heat evolved (cal.)	ΔH (kcal/mole)
44	60.0	.0116	-7.58	+0.65
45	60.0	.0220	-13.82	+0.63

We shall take $\Delta H = +0.64 \pm 0.05$ kcal/mole for

(3) $I_2(s) = I_2$ (HCl and KI)

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. In runs 28 and 29 the water in the calorimeter was degassed with CO_2; in run 30, with argon.

Run	Grams water	Moles GeI_4	Heat evolved (cal.)	ΔH (kcal/mole)
28	980	.004459	41.78	-9.37
29	1016	.004480	42.39	-9.46
30	1016	.003788	35.38	-9.34

With the aid of the Debye-Hückel equation, these heats were extrapolated to infinite dilution:

Run	ΔH°
28	-9.63
29	-9.72
30	-9.57

We shall take $\Delta H^\circ = -9.64 \pm 0.10$ kcal/mole for

(4) $GeI_4(s) + 3H_2O = H_2GeO_3 + 4H^+ + 4I^-$.

By adding together the heats for reactions

(1)	-19.06 ± 0.4	kcal/mole
-(2)	$+3.0 \pm 2.0$	
(3)	$+0.64 \pm 0.05$	
(4)	-9.64 ± 0.1	

We obtain for (5): -25.1 ± 2.0 kcal/mole

By adding $\Delta H = -1.0$ kcal/mole[8] for

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

we obtain $\Delta H = -26.1 \pm 2.0$ kcal/mole for reaction (7).

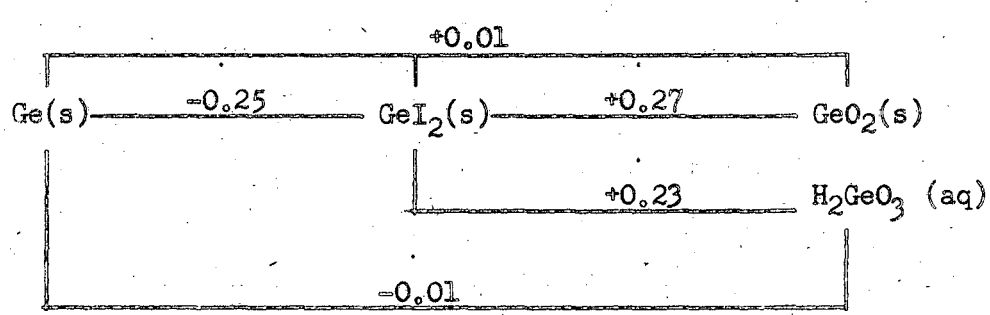
(7) $3H_2O + GeI_2(s) + I_3^- = H_2GeO_3 + 4H^+ + 5I^-$.

Conclusions

Two independent experimental methods have given essentially the same value for the heat of reaction (7), and we shall take $\Delta H = -26.0 \pm 1.0$ kcal/mole. Estimating entropies of 43 and 36 for H_2GeO_3 (aq) and $GeI_2(s)$, respectively, we find $\Delta S = +30.4 \pm 2.0$ e.u. for reaction (7).[8] These values yield $\Delta F = -35.1$ kcal/mole, and by employing the value $E^\circ = -0.534$ v. for the $I^- - I_3^-$ couple[5] we calculate $E^\circ = +0.23 \pm .04$ v. for the couple

$$3H_2O + GeI_2(s) = H_2GeO_3 + 4H^+ + 2I^- + 2e^-$$

Using the known heat of formation of GeO_2, -128.4 kcal/mole, and estimated its entropy at 12 e.u., we obtain -114.4 kcal/mole for the free energy of formation of GeO_2. ($S^\circ_{298} = 10.1$ for germanium metal). Pugh[10] has given the solubility of GeO_2 in water as 4.47 g. per liter at 25°, while Laubengayer and Morton[7] reported 4.53 g. Taking an average of 4.50 g./liter, we find $\Delta F = +1.86$ kcal/mole for the solution of GeO_2. Hence we obtain the following potential diagram for germanium in acid solution.



According to this diagram, GeI_2 is very unstable with respect to disproportionation in 1 M acid. The chemical behavior of GeI_2 is to the contrary. Perhaps it is not wise to employ the heat of oxidation of

GeO_2 as measured by Hahn and Juza[4] and Becker and Roth[1], for they undoubtedly formed the glassy oxide in their bomb calorimeters. It is well known that the solubility and other properties of GeO_2 depend markedly on the crystal form. One would expect a more negative heat of formation for the soluble crystalline modification, and consequently greater stability for the +2 state of germanium. The disproportionation of germanous iodide to the metal and germanic iodide is being studied in an effort to clarify the situation.

Acknowledgments

This work was sponsored by the Atomic Energy Commission.

References

1. Becker, G. and Roth, W. A., Z. physik. Chem. A 161, 69 (1932).
2. Fontana, B. J., Nat. Nuclear Energy Series, IV-19B, McGraw Hill, N. Y., 1950, p. 321.
3. Foster, L. S. and Williston, A. F., Inorganic Syntheses 2, 112 (1946).
4. Hahn, H. and Juza, R., Z. anorg. allgem. Chem. 244, 120 (1940).
5. Latimer, W. M., "Oxidation Potentials", Prentice Hall, N. Y., 1938, p. 57.
6. Latimer, W. M., and Zimmerman, H. W., J. Am. Chem. Soc. 61, 1550 (1939).
7. Laubengayer, A. W. and Morton, D. S., J. Am. Chem. Soc. 54, 2318 (1932).
8. National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Washington, D. C.
9. Powell, H. M. and Brewer, F. M., J. Chem. Soc. 1938, 197.
10. Pugh, W., J. Chem. Soc. 1929, 1537.
11. Roth, W. A. and Schwartz, O., Z. physik. Chem. 134, 466 (1927).