

$$\begin{aligned}\Delta H^\circ &= 32,500 - 8T \\ \Delta F^\circ &= 32,500 + 8T \ln T - 94.6T \\ \Delta S^\circ &= 86.6 - 8 \ln T\end{aligned}$$

$$\begin{aligned}\text{and } \Delta H_{298}^\circ &= 30,100 \text{ cal./mole, } \Delta F_{298}^\circ = 17,900 \text{ cal./} \\ \text{mole, } \Delta S_{298}^\circ &= 41.0 \text{ cal./deg. mole.}\end{aligned}$$

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The Equilibrium $\text{Ge(s)} + \text{GeO}_2(\text{s}) = 2\text{GeO(g)}$. The Heat of Formation of Germanic Oxide

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The vapor pressure of GeO(g) over germanium and germanic oxide has been measured over the range 758–859°K. and the results have been compared with similar data obtained by Bues and v. Wartenberg. Vapor pressure data for GeO(s) obtained by the latter investigators have been discussed. The heat of formation of $\text{GeO}_2(\text{s})$ has been determined calorimetrically to be $\Delta H_f^\circ = -129.2 \pm 2.0$ kcal./mole.

The Equilibrium $\text{Ge(s)} + \text{GeO}_2(\text{s}) = 2\text{GeO(g)}$.—Bues and v. Wartenberg² have reported vapor pressures of GeO(g) over both $\text{Ge} + \text{GeO}_2$ and GeO in the neighborhood of 1000°K. Some inconsistencies in their data have been noticed and will be discussed here. For the reaction $\text{GeO(s)} = \text{GeO(g)}$, Bues and v. Wartenberg give the equation

$$4.57 \log P_{\text{atm}} = -63,000/T + 57.9$$

and for the reaction $\frac{1}{2}\text{Ge(s)} + \frac{1}{2}\text{GeO}_2(\text{s}) = \text{GeO(g)}$, they give the equation

$$4.57 \log P_{\text{atm}} = -54,800/T + 42.0$$

These data give for the reaction $\frac{1}{2}\text{Ge(s)} + \frac{1}{2}\text{GeO}_2(\text{s}) = \text{GeO(s)}$ at 1000°K., $\Delta H^\circ = -8.2$ kcal./mole, $\Delta F^\circ = +7.7$ kcal./mole and $\Delta S^\circ = -15.9$ e.u. Such a large entropy change is difficult to imagine for such a proportionation; one would expect the entropy change to be very close to zero or slightly positive.

If we admit the existence of solid GeO , then it appears that Bues and v. Wartenberg have erred in drawing a straight line through their $\log P$ vs. $1/T$ plot for GeO . In general, it is more satisfactory to estimate entropies and heat capacities when interpreting vapor pressure data. We have estimated $\Delta C_p^\circ = -3$ cal./deg. mole and $\Delta S_{298}^\circ = 42$ e.u. for both sublimations. From the equation $\Delta H_0^\circ = \Delta F^\circ - 6.9T \log T + 62T$, we have calculated values of ΔH° for the two sets of data of Bues and v. Wartenberg. For the reaction $\frac{1}{2}\text{Ge(s)} + \frac{1}{2}\text{GeO}_2(\text{s}) = \text{GeO(g)}$, the average $\Delta H_0^\circ = 54.1$ kcal./mole. For the reaction $\text{GeO(s)} = \text{GeO(g)}$, the calculated values of ΔH_0° ranged from 46.8 to 49.0 kcal./mole.

Using a Knudsen effusion cell, we have measured the vapor pressure of what we thought to be GeO(s) over the temperature range 758–859°K. In Table I we have listed our experimental results and the calculated values of ΔH_0° .

The average ΔH_0° , 55.1 kcal./mole, is in fair agreement with the value calculated from Bues and v. Wartenberg's data for the reaction $\frac{1}{2}\text{Ge(s)}$

(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) W. Bues and H. v. Wartenberg, *Z. anorg. allgem. Chem.*, **266**, 281 (1951).

TABLE I

OBSERVED VAPOR PRESSURES AND CALCULATED VALUES OF ΔH_0°

T , °K.	Pressure, atm.	ΔH_0° , cal./mole
770	1.3×10^{-6}	53,160
788	1.8×10^{-6}	53,790
816	2.6×10^{-6}	55,030
835	1.06×10^{-5}	53,940
758	6.7×10^{-8}	56,790
816	1.5×10^{-6}	55,930
790	3.7×10^{-7}	56,440
859	7.7×10^{-6}	55,960

$+ \frac{1}{2}\text{GeO}_2(\text{s}) = \text{GeO(g)}$. We therefore feel that our solid phase was a mixture of germanium and germanium dioxide. By averaging the two values of ΔH_0° , we calculate the equations for the sublimation of GeO from a mixture of Ge and GeO_2

$$\Delta F^\circ = 54,600 + 6.9T \log T - 62T \text{ (cal./mole)}$$

$$\Delta H^\circ = 54,600 - 3T \text{ (cal./mole)}$$

$$\Delta S^\circ = 59 - 6.9 \log T \text{ (cal./deg. mole)}$$

At 298°K., $\Delta H^\circ = 53.7 \pm 1.0$ kcal./mole. It is possible to calculate the heat of this reaction from independent data. Brewer and Mastick⁴ have shown that linear Birge-Sponer extrapolations of vibrational levels give the correct dissociation energies for CO , SiO , SnO and PbO . Hence we feel confident in using the value $\Delta H^\circ = 159$ kcal./mole for the dissociation of GeO(g) (calculated by Herzberg⁵ using a linear Birge-Sponer extrapolation). In Table II we have presented the latter heat, the heat of sublimation of germanium,⁶ the dissociation energy of oxygen⁷ and the heat of formation of $\text{GeO}_2(\text{s})$.⁸ From these data we calculate $\Delta H_{298}^\circ = 50$ kcal./mole for $\frac{1}{2}$

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

(4) L. Brewer and D. Mastick, *J. Chem. Phys.*, **19**, 834 (1951).

(5) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1930.

(6) A. W. Searcy, University of California Radiation Laboratory Report 1403 (1951).

(7) National Bureau of Standards Selected Values of Chemical Thermodynamic Constants, Washington, D. C., 1947, *et seq.*

(8) Cf. the second part of this paper.

$\text{Ge(s)} + \frac{1}{2}\text{GeO}_2\text{(s)} = \text{GeO(g)}$, as compared with 53.7 kcal./mole determined experimentally. The agreement is excellent, in view of the uncertainty in the dissociation energy of GeO(g) .

TABLE II

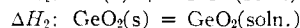
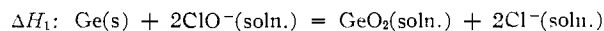
HEATS OF REACTION	
Reaction	ΔH_{298}° (kcal./mole)
$\text{Ge(g)} + \text{O(g)} = \text{GeO(g)}$	-159
$\text{Ge(s)} = \text{Ge(g)}$	85.2
$\frac{1}{2}\text{O}_2\text{(g)} = \text{O(g)}$	59.2
$\frac{1}{2}\text{GeO}_2\text{(s)} = \frac{1}{2}\text{Ge(s)} + \frac{1}{2}\text{O}_2\text{(g)}$	64.2
$\frac{1}{2}\text{Ge(s)} + \frac{1}{2}\text{GeO}_2\text{(s)} = \text{GeO(g)}$	50

Bues and v. Wartenberg have calorimetrically determined $\Delta H^\circ = -26.3$ kcal./mole for the reaction $\text{Ge(s)} + \text{GeO}_2\text{(s)} = 2\text{GeO(s)}$ at 298°K. This result cannot be reconciled with their vapor pressure data without assuming an unusually large entropy for the reaction. From their observation that GeO(s) disproportionates to Ge and GeO_2 at temperatures around 600°, we conclude that their calorimetric data are spurious and that GeO(s) is thermodynamically unstable at all temperatures below 600°. This instability of germanous oxide is analogous to the instability of SiO^9 and SnO^7 . From the values of ΔH_0° which we have calculated from Bues and v. Wartenberg's and our vapor pressure data, we calculate that GeO(s) is unstable by about 7 kcal./mole.

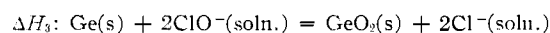
The Heat of Formation of Germanic Oxide.—

The heat of oxidation of germanium to germanic oxide by oxygen has been measured by Becker and Roth¹⁰ and Hahn and Juza.¹¹ These investigators found the heat of formation of $\text{GeO}_2\text{(s)}$ to be -128.1 and -128.6 kcal./mole, respectively. It was considered desirable to check these values by measuring the heat of oxidation of the metal by some aqueous oxidizing agent. It was found that when germanium metal is very finely pulverized, an alkaline solution of hypochlorite effects complete solution in a relatively short time. High alkalinity is probably necessary in order to dissolve any oxide which forms on the surface of the metal.

Experimental Procedures.—The hypochlorite solution was prepared by passing chlorine into approximately 0.8 molar potassium hydroxide. The hypochlorite content was then determined volumetrically using a standard thio-sulfate solution. Two such batches of hypochlorite solution were prepared; each batch was used for a separate series of runs. In each of these series, two measurements were made of the heat of solution of metallic germanium and one measurement was made of the heat of solution of germanic oxide. These heats refer to the reactions



The first heat minus the second gives ΔH_3 , the heat of the reaction



In subsequent calculations, the heats of formation of $\text{ClO}^-(\text{soln.})$ and $\text{Cl}^-(\text{soln.})$ are taken to be the same as those in infinitely dilute aqueous solution.

The germanic oxide used was obtained from the Fair-

mount Chemical Co. (purest As free). It was dried before use by heating at 900° for several hours.

Some spectroscopically pure germanium powder was obtained from the Belmont Chemical Co. That which passed through a 400-mesh sieve was used in the calorimetric experiments. The metal completely dissolved in the calorimeter in about 20 minutes; this rather long time is responsible for most of the uncertainties in heats.

The sieved metal was analyzed by oxidizing with hydrogen peroxide and then igniting to the oxide. The entire impurity is assumed to be GeO_2 . The results of four separate analyses gave for % Ge: 89.7, 89.7, 89.1 and 90.1. We shall use $89.65 \pm 0.25\%$. The heats were therefore corrected assuming 10.35% of the material to be GeO_2 .

The calorimetric experiments were carried out at $25 \pm 1^\circ$ and are reported in terms of the defined calorie (1 cal. = 4.1833 int. joules). The same calorimeter was used as in previously reported studies.¹²

Calculations.—From the experimental data in Table III, we calculate the average $\Delta H_3 = -160.2 \pm 1.8$ kcal./mole. The National Bureau of Standards⁷ gives -27.83 kcal./mole for the heat of formation of HClO (1000 H_2O). Pitzer¹³ tabulated 3.32 kcal./mole as the heat of ionization of HClO ; hence $\Delta H_f^\circ = -24.5$ kcal./mole for ClO^- . Using $\Delta H_f^\circ = -40.02$ kcal./mole⁷ for Cl^- , we calculate $\Delta H_f^\circ = -129.2 \pm 2.0$ kcal./mole for the heat of formation of $\text{GeO}_2\text{(s)}$. Within experimental error, this value agrees with the values obtained by Becker and Roth¹⁰ and Hahn and Juza.¹¹ We calculate as a weighted average of all three values, $\Delta H_f^\circ = -128.5 \pm 0.5$ kcal./mole.

TABLE III
CALORIMETRIC DATA

Material dissolved	Hypochlorite solution		Corrected heats, kcal./mole	
	Molarity of KOH	Molarity of ClO^-	ΔH_1	ΔH_2
Ge	0.8	0.039	-170.0	-161.0
Ge	.8	.039	-170.5	-161.5
GeO_2	.8	.039		-9.0
Ge	.8	.081	-165.5	-156.5
Ge	.8	.081	-170.7	-161.7
GeO_2	.8	.081		-9.0

By appropriate combination of heats determined by Jolly and Latimer^{12,14} it is possible to evaluate the heat of formation of $\text{GeO}_2\text{(s)}$ indirectly. In Table IV are listed five independent reactions and their corresponding heats at 298°K. The heat corresponding to the sum of these reactions may be combined with known heats of formation⁷ for H^+ , I^- , H_2O and I_2^- to yield $\Delta H_f^\circ = -136.9$ kcal./mole for the heat of formation of $\text{GeO}_2\text{(s)}$. The experimental uncertainties in the heats listed in Table IV are sufficient to explain the discrepancy between this value and that determined more directly.

TABLE IV
HEATS OF REACTION^{12,14}

Reaction	ΔH_{298}° , kcal./mole
$2\text{GeI}_2\text{(s)} = \text{Ge(s)} + \text{GeI}_4\text{(g)}$	30.1
$\text{GeI}_4\text{(g)} = \text{GeI}_4\text{(s)}$	-20.1
$\text{GeI}_4\text{(s)} + 3\text{H}_2\text{O} = \text{H}_2\text{GeO}_3 + 4\text{H}^+ + 4\text{I}^-$	-9.6
$\text{H}_2\text{GeO}_3 = \text{H}_2\text{O} + \text{GeO}_2$	-3.3
$2\text{GeO}_2\text{(s)} + 10\text{I}^- + 8\text{H}^+ = 2\text{GeI}_2\text{(s)} + 2\text{I}_3^- + 4\text{H}_2\text{O}$	58.6
$\text{GeO}_2\text{(s)} + 4\text{H}^+ + 6\text{I}^- = \text{Ge} + 2\text{H}_2\text{O} + 2\text{I}_3^-$	55.7

The authors wish to thank Prof. Leo Brewer for his helpful suggestions with regard to the problem of the stability of GeO .

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(9) Russell K. Edwards, University of California Radiation Laboratory Report 1639 (1952).

(10) G. Becker and W. A. Roth, *Z. physik. Chem.*, **A161**, 89 (1932).

(11) H. Hahn and R. Juza, *Z. anorg. allgem. Chem.*, **244**, 120 (1940).

(12) W. L. Jolly and W. M. Latimer, *THIS JOURNAL*, **74**, 5752 (1952).

(13) K. S. Pitzer, *ibid.*, **59**, 2368 (1937).

(14) W. L. Jolly and W. M. Latimer, *ibid.*, **74**, 5754 (1952).