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

and ΔH°_{298} = 30,100 cal./mole, ΔF°_{298} = 17,900 cal./mole, ΔS°_{298} = 41.0 cal./deg.-mole.

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

The Equilibrium $Ge(s) + GeO_2(s) = 2GeO(g)$. 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 GeO_2(s) has been determined calorimetrically to be $\Delta H_f^\circ = -129.2 \pm 2.0$ kcal./mole.

The Equilibrium $Ge(s) + GeO_2(s) = 2GeO(g)$.—Bues and v. Wartenberg[2] have reported vapor pressures of GeO(g) over both Ge + 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 GeO(s) = GeO(g), Bues and v. Wartenberg give the equation

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

and for the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$, they give the equation

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

These data give for the reaction $^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(s)$ 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 $\Delta C^\circ_p = -3$ cal./deg. mole and ΔS°_{298} = 42 e.u. for both sublimations. From the equation $\Delta H^\circ_0 = \Delta F^\circ - 6.9T \log T + 62T$, we have calculated values of ΔH° for the two sets of data of Bues and v. Wartenberg. For the reaction $^1/_2$ Ge(s) + $^1/_2GeO_2$(s) = GeO(g), the average ΔH°_0 = 54.1 kcal./mole. For the reaction GeO(s) = 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 $^1/_2$Ge(s) + $^1/_2GeO_2$(s) = 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

TABLE I

OBSERVED VAPOR PRESSURES AND CALCULATED VALUES OF ΔH°_0[3]

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

$$\Delta F^\circ = 54{,}600 + 6.9T \log T - 62T \text{ (cal./mole)}$$
$$\Delta H^\circ = 54{,}600 - 3T \text{ (cal./mole)}$$
$$\Delta S^\circ = 59 - 6.9 \log T \text{ (cal./deg. mole)}$$

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 Mastick[4] 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 Herzberg[5] 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 oxygen[7] and the heat of formation of GeO_2(s).[8] From these data we calculate ΔH°_{298} = 50 kcal./mole for $^1/_2$

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(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).

(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., 1950.

(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.

$Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$, 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)
$Ge(g) + O(g) = GeO(g)$	−159
$Ge(s) = Ge(g)$	85.2
${}^1/_2O_2(g) = O(g)$	59.2
${}^1/_2GeO_2(s) = {}^1/_2Ge(s) + {}^1/_2O_2(g)$	64.2
${}^1/_2Ge(s) + {}^1/_2GeO_2(s) = GeO(g)$	50

Bues and v. Wartenberg have calorimetrically determined $\Delta H^\circ = -26.3$ kcal./mole for the reaction $Ge(s) + GeO_2(s) = 2GeO(s)$ 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 Roth[10] and Hahn and Juza.[11] These investigators found the heat of formation of $GeO_2(s)$ 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 thiosulfate 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

ΔH_1: $Ge(s) + 2ClO^-(soln.) = GeO_2(soln.) + 2Cl^-(soln.)$

ΔH_2: $GeO_2(s) = GeO_2(soln.)$

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

ΔH_3: $Ge(s) + 2ClO^-(soln.) = GeO_2(s) + 2Cl^-(soln.)$

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

The germanic oxide used was obtained from the Fairmount 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 ± 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 ± 1° 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 Standards[7] gives −27.83 kcal./mole for the heat of formation of HClO (1000 H_2O). Pitzer[13] 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./mole[7] for Cl^-, we calculate $\Delta H_f^\circ = -129.2 \pm 2.0$ kcal./mole for the heat of formation of $GeO_2(s)$. Within experimental error, this value agrees with the values obtained by Becker and Roth[10] 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	ΔH_3
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 $GeO_2(s)$ 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 formation[7] for H^+, I^-, H_2O and I_3^- to yield $\Delta H_f^\circ = -136.9$ kcal./mole for the heat of formation of $GeO_2(s)$. 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
$2GeI_2(s) = Ge(s) + GeI_4(g)$	30.1
$GeI_4(g) = GeI_4(s)$	−20.1
$GeI_4(s) + 3H_2O = H_2GeO_3 + 4H^+ + 4I^-$	− 9.6
$H_2GeO_3 = H_2O + GeO_2$	− 3.3
$2GeO_2(s) + 10I^- + 8H^+ = 2GeI_2(s) + 2I_3^- + 4H_2O$	58.6
$GeO_2(s) + 4H^+ + 6I^- = Ge + 2H_2O + 2I_3^-$	55.7

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