High-Temperature Thermal Properties of Germanium

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High-temperature heat contents of germanium were measured over the temperature range of 298° to 1514° K., using a diphenyl ether drop calorimeter. Smoothed values of the thermal properties of germanium, $H^\circ_T - H^\circ_{298}$, Cp, $S^\circ_T - S^\circ_{298}$, and $(G^\circ_T - H^\circ_{298})/T$, have been derived and are tabulated at even 100° intervals. The heat of fusion is 8830 cal. per gram atom at the melting point, 1210.4° K., yielding an entropy of fusion of 7.30 cal. per deg. per gram atom.

THE high-temperature thermal properties of germanium have not heretofore been well established. Reported heat content data (*12, 13*) are incomplete and inconclusive, and reported high-temperature heat capacity measurements (*3, 4*) do not agree with each other or with the heat content values. Reported values for the heat of fusion (*4, 13, 14, 15*) vary from 7130(±350) cal. per gram atom (*15*) to 8930 cal. per gram atom (*13*).

Because accurate high-temperature thermal data are needed for many types of thermodynamic calculations involving germanium systems, it was decided to measure high-temperature heat contents of high-purity germanium. This paper reports the results of such measurements in the temperature range of 298° to 1514° K.

EXPERIMENTAL

Heat content measurements were made using a diphenyl ether Bunsen-type drop calorimeter, similar in principle to one described previously (*7*). The present apparatus is considerably larger than the earlier model and is designed to drop samples enclosed in sealed capsules, thus permitting measurements on liquids and on substances with appreciable vapor pressures.

The experimental procedure will be described only briefly here. The encapsulated sample is suspended by a wire in a platinum-wound vertical tube furnace and heated to a given temperature, which is measured by a Pt−Pt+10% Rh thermocouple, then dropped into the calorimeter. Heat from the specimen enters a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0° K., melting some of the solid isothermally. The resulting increase in volume is measured by displacement of mercury from the bottom of the diphenyl ether chamber into a horizontal calibrated capillary tube or into a weighed beaker, depending on the amount of heat involved. The heat effect is obtained from the measured volume change using the calibration factor determined by Jessup (*9*) and confirmed by separate calibrating runs using platinum as a secondary standard.

Germanium having a purity stated by the supplier to be 99.99+% was used in the study. The samples were sealed under vacuum in silica capsules which showed no evidence of reaction with the germanium within the temperature range studied. Four samples were required because the capsules ultimately failed from the 5% expansion in volume of germanium on freezing (*11*). The sample and capsule weights are recorded in Table I. Corrections for the heat contents of the silica capsules

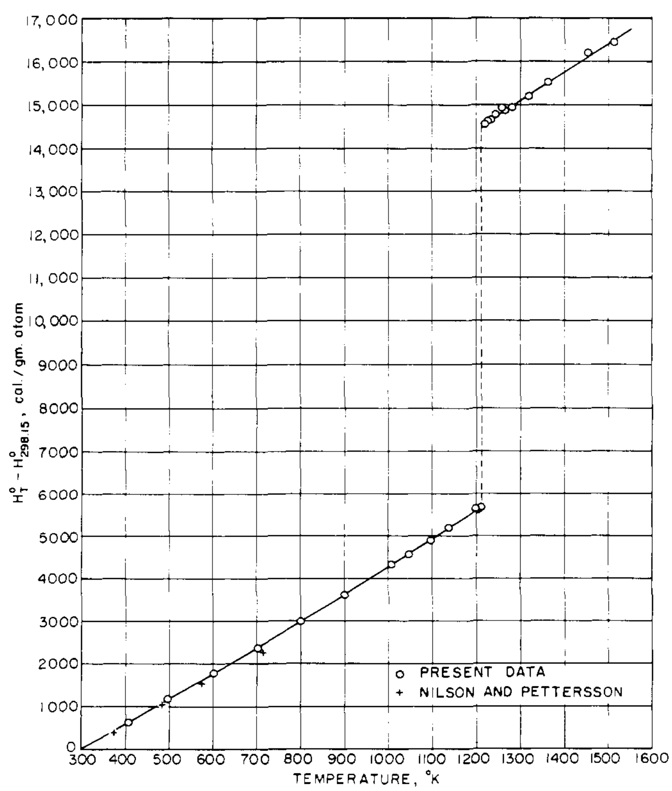

Figure 1. High-temperature heat content of germanium

Table I. Sample Weights in Grams

	Sample No. 1	2	3	4
Ge	10.9690	10.2540	8.8084	4.8276
Capsule	1.3945	1.8127	3.2434	3.3655

Table II. Experimental Results

(GERMANIUM AT. WT. = 72.59)

T, °K.	$H^\circ_T - H^\circ_{298.15}$ Cal./Gram Atom	T, °K.	$H^\circ_T - H^\circ_{298.15}$ Cal./Gram Atom
Sample No. 1		Sample No. 3	
406.4	622	1200.2	5627
497.1	1163	1227.1	14619
600.4	1782	1281.4	14944
700.9	2374	1264.9	14863
798.6	2997	1047.1	4564
900.0	3610	1363.6	15523
1007.2	4311	1319.8	15203
1095.8	4891		
1136.2	5173	Sample No. 4	
1206.9	5618	1258.1	14922
1209.4	5663	1454.3	16220
		1243.2	14764
Sample No. 2		1513.8	16471
1218.0	14528	1233.2	14656

Table III. Thermal Properties of Germanium

T, °K.	$H°_T - H°_{298.15}$ Cal./Gram Atom	Cal./Deg./Gram Atom Cp	$S°_T - S°_{298.15}$	$\frac{G°_T - H°_{298.15}}{T}$
298.15	0	5.58	0.00	−7.43
400	585	5.85	1.68	−7.65
500	1175	5.95	3.00	−8.08
600	1775	6.03	4.10	−8.57
700	2382	6.10	5.03	−9.06
800	2996	6.19	5.85	−9.54
900	3622	6.33	6.59	−10.00
1000	4264	6.50	7.26	−10.43
1100	4923	6.68	7.89	−10.84
1200	5599	6.86	8.48	−11.24
1210.4(s)	5670	6.87	8.54	−11.29
1210.4(ℓ)	14500	6.60	15.84	−11.29
1300	15090	6.60	16.31	−12.13
1400	15750	6.60	16.80	−12.98
1500	16410	6.60	17.26	−13.75

T_m = 1210.4°K. ΔH_m = 8830 cal. per gram atom. ΔS_m = 7.30 cal. per deg. per gram atom.

and the heat loss accompanying the drops were determined by dropping a capsule filled with platinum throughout the measured temperature range, using tabulated heat content data for platinum (*8*). The measured heat contents of germanium were corrected for the small difference between the calorimeter temperature, 300° K., and the standard reference temperature 298.15° K., using $Cp_{298.15}$ = 5.58 cal. per deg. per gram atom, obtained from the low-temperature Cp data of Flubacher, Leadbetter, and Morrison (*2*). Calculations were made using the 1961 International Atomic Weights (*1*). The accuracy of the measured values is estimated to be of the order of ±0.3%.

RESULTS

The experimental results are listed in Table II in the order that the runs were made and are shown plotted in Figure 1. Table III lists smoothed values of the thermal properties of germanium corresponding to the selected curves which fit the data within an average precision of ±10 and ±35 cal. per gram atom in the solid and liquid ranges, respectively. The selected values join smoothly with the low-temperature Cp data of Flubacher, Leadbetter, and Morrison (*2*), whose reported value of $S°_{298.15}$ = 7.43 cal. per deg. per gram atom was also used in calculation of the values of the Gibbs energy function, $(G°_T - H°_{298.15})/T$. The heat of fusion, 8830 cal. per gram atom, was obtained by extrapolating the solid and liquid data to the melting temperature, 1210.4° K., determined by Greiner and Breidt (*5*) and Hassion, Thurmond, and Trumbore (*6*). Since only small extrapolations were required, the uncertainty in this value should be no greater than ±40 cal. per gram atom. No premelting of the solid was detectable even in the run at 1209.4° K., only 1° K. below the melting temperature. The entropy of fusion, 7.30 cal. per deg. per gram atom, is very similar to the correspondingly large value for that of silicon, 7.18 cal. per deg. per gram atom (*10*).

The very early heat content measurements of Nilson and Pettersson (*12*), shown plotted in Figure 1, are 6% to 10% low. The heat content data of Shchipanova and Gel'd (*13*) from 600° to 1523° K. are ambiguously and inconclusively reported, which precludes exact comparisons; the best conclusion appears to be that their values are about 2 to 4% lower than those presently obtained. The Cp data obtained using a temperature modulation technique by Gerlich, Abeles, and Miller (*3*) from 300° to 900° K. agree at 300° K. but rapidly become too high with increasing temperature, becoming 11% high for T> 600° K. The Cp data of Greiner (*4*) at 873° and 1173° K. are about 9% low. Values of the heat of fusion reported by Shchipanova and Gel'd, 8930 cal. per gram atom, and Tarwater (*14*), 8920 (±200) cal. per gram atom, are only slightly higher than the value found here; however, those reported by Greiner, 8100 (±800) cal. per gram atom, and Wittig (*15*), 7130 (±350) cal. per gram atom, are much too low.

NOMENCLATURE

T = temperature, °K.
Cp = heat capacity at constant pressure
$S°_{298.15}$ = standard entropy at 298.15° K.
$H°_T - H°_{298.15}$ = heat content (enthalpy) increment between 298.15° K. and temperature T
$S°_T - S°_{298.15}$ = entropy increment between 298.15° K. and temperature T
$(G°_T - H°_{298.15})/T$ = Gibbs energy function with respect to 298.15° K.
$T_m, \Delta H_m, \Delta S_m$ = temperature, heat, and entropy of melting

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