[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XI. The Heat Capacity of β-Gallium Oxide from 15 to 300°K.[1]

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The heat capacities of a sample of 98.67% β-Ga_2O_3 have been measured from 15 to 300°K., and have been accurately corrected for the heat capacities of the impurities present. Graphical integration of the heat capacity curve yields a molal entropy of 20.23 ± 0.1 e.u. at 298.16°K. A table of thermodynamic functions has been prepared for β-gallium oxide at smoothed values of the temperature.

Introduction

No low temperature heat capacity measurements have been reported previously for a gallium compound. In the present investigation, the heat capacities of crystalline β-gallium sesquioxide have been measured in the range 15 to 300°K.

Two forms of the sesquioxide exist, designated α and β by Goldschmidt, Barth and Lunde.[2] The α-form cannot be prepared completely water-free, and inverts exothermally and irreversibly to the β-form when heated in air to 625°. The β-form is stable up to its melting point, and is apparently monotropic.[3]

Experimental Method

Sample.—In order to prepare crystalline gallium oxide it is necessary to dehydrate the hydrated oxide, since the ignited oxalate, acetate or camphorate all yield a product which is non-crystalline.[3] Approximately two-thirds of a mole of the oxide was prepared in two separate lots, using two gallium samples of 99.1 and 99.7% purity as starting material. Hoffman's procedure was used, with minor modification, to prepare an aqueous solution of the pure gallate, from which the hydrated oxide was obtained.[4]

This involved a single ether extraction of the chloride from concentrated hydrochloric acid, a precipitation of residual heavy metals from this extract with hydrogen sulfide, formation of the gallate with an aqueous solution of sodium hydroxide, and removal of residual iron as the hydrated oxide by filtration from this solution. The strongly alkaline gallate solution was then acidified with hydrochloric acid, and gallium hydroxide precipitated with ammonium hydroxide. The gelatinous precipitate was washed free of the last traces of chloride ion by repeated centrifuging from hot distilled water.

This hydrated oxide was then partially dehydrated by heating over the bunsen flame in a porcelain evaporating dish. The β-form of the oxide was obtained by heating this partially dehydrated product at 1300° in a covered platinum crucible for four hours, following the procedure of Lundell and Hoffman.[5]

The two lots of oxide were pulverized to a fine powder in a porcelain mortar, passed through a 100-mesh copper wire gauze, and then mixed together very thoroughly. The sample of oxide, prepared in this manner, was found to be non-hygroscopic, which confirmed the findings of Lundell and Hoffman.[5] Prior to filling the calorimeter, however, the sample was stored in a desiccator over phosphorus pentoxide. An X-ray diffraction powder pattern obtained for the sample showed quite sharp lines, and was essentially the same as that reported for β-gallium oxide by Laubengayer and Engle,[3a] and by Foster and Stumpf.[3b]

A qualitative spectroscopic analysis of the sample, made at the time of its preparation, indicated small quantities of Mg, Al, B, Si, Sn and Ca as impurities. The sample was roughly estimated to be better than 99.5% Ga_2O_3.

The heat capacity measurements were then taken, using this sample, prior to obtaining the results of a subsequent quantitative spectroscopic analysis. This analysis[6] showed: V_2O_5, MoO_3, PbO, MnO, all 0.001%; CuO, 0.008%; MgO, 0.01%; SnO_2, 0.02%; Fe_2O_3 and Al_2O_3 each 0.05%; ZnO, 0.1%; and SiO_2, 0.21%, or an over-all purity of 99.62% Ga_2O_3. However, two independent chemical analyses for SiO_2 gave identical results of 1.16% SiO_2. Evidently the spectroscopic value for SiO_2 was invalid. This reduced the purity to 98.67% Ga_2O_3. The silica impurity was probably introduced by the action of the alkaline gallate solution of the glassware in which it was prepared.

A correction was applied to all of the heat capacity points for those impurities present in amounts exceeding 0.001%, as listed in the above analysis. The heat capacity values used for this correction are those listed by Kelley,[7] except those for SiO_2, for which Simon's[8] data for cristobolite were used below 50°K.

Experimental Results

The calorimetric data were obtained with calorim-

TABLE I

HEAT CAPACITY OF GALLIUM OXIDE

(β-Ga_2O_3) mol. wt. 187.44, 0.5024 mole (β-Ga_2O_3)

Mean temp., °K.	C_p, cal./deg./mole	Mean temp., °K.	C_p, cal./deg./mole
15.82	0.101	88.46	6.561
18.89	.146	89.07	6.630
21.22	.207	95.37	7.312
23.43	.265	103.09	8.136
25.64	.344	110.41	8.906
27.94	.438	118.32	9.732
30.60	.578	127.15	10.62
33.56	.762	136.41	11.47
36.91	1.042	146.70	12.43
40.54	1.353	156.80	13.35
44.29	1.683	165.76	14.09
48.61	2.157	173.88	14.73
53.02	2.656	182.01	15.34
54.23	2.784	189.83	15.92
58.08	3.226	198.92	16.52
58.60	3.303	207.91	17.07
61.78	3.603	217.62	17.74
64.15	3.863	226.86	18.26
66.61	4.123	235.78	18.77
69.27	4.370	247.01	19.40
69.65	4.392	254.44	19.80
70.54	4.524	264.03	20.33
70.59	4.492	272.90	20.83
75.54	5.101	273.47	20.83
76.45	5.199	283.04	21.27
82.03	5.862	292.26	21.72
83.34	6.010	300.79	22.00

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(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) V. M. Goldschmidt, T. Barth and G. Lunde, *Skrifter Norske Videnskaps-Akad., Oslo, Mat. Naturv. Klasse*, No. 7, 24 (1925).

(3) (a) A. W. Laubengayer and H. R. Engle, THIS JOURNAL, **61**, 1210 (1939); (b) L. M. Foster and H. C. Stumpf, *ibid.*, **73**, 1590 (1951).

(4) J. I. Hoffman, *J. Research Natl. Bur. Standards*, **13**, 665 (1934).

(5) G. E. F. Lundell and J. I. Hoffman, *ibid.*, **15**, 409 (1935).

(6) All figures are in weight per cent.

(7) K. K. Kelley, *Bur. of Mines Bull.*, 477 (1948).

(8) F. Simon, *Ann. Physik*, [4] **66**, 404 (1922).

eter number 3, the construction and operation of which have been described.[9]

For the heat capacity measurements the calorimeter was filled with 94.163 g. (0.5024 mole) of β-Ga_2O_3. The heat capacities obtained, after correction for the effects of the impurities present, are tabulated in Table I. The heat capacities follow the law $C_p = aT^3$ up to 38°K., with a equal to 2.02×10^{-5} cal. deg.$^{-4}$ mole^{-1}. These data are expressed in terms of the defined thermochemical calorie equal to 4.1833 international joules.

TABLE II

THERMODYNAMIC FUNCTIONS FOR GALLIUM OXIDE (β-Ga_2O_3)

Temp., °C.	C_p, cal./deg./mole	S^0 cal./deg./mole	$H^0 - H_0^0$	$-(F^0 - H_0^0)/T$
16	0.083	0.028	0.331	0.007
25	0.317	.105	1.975	.026
50	2.311	.826	30.829	.209
75	5.049	2.279	122.72	.643
100	7.812	4.117	284.06	1.276
125	10.40	6.142	512.16	2.044
150	12.74	8.248	801.86	2.902
175	14.84	10.37	1147.2	3.818
200	16.60	12.47	1540.9	4.770
225	18.14	14.52	1975.5	5.740
250	19.58	16.51	2447.3	6.718
275	20.88	18.44	2953.4	7.696
298.16	21.95	20.23	3468.1	8.597
300	22.03	20.30	3490.1	8.669

Thermodynamic functions derived from the smooth heat capacity curve by graphical integration, are listed in Table II at convenient temperatures.

The molal entropy at 298.16°K. is 20.23 ± 0.1 e.u., of which only 0.03 e.u. was obtained by extrapolation below 16°K.

Discussion

No irregularity was observed in the heat capacity curve for β-Ga_2O_3. The correction for impurities was applied in the form of a multiplying factor, with the assumption that the impurities existed in the oxide in a state such that their heat capacities were those of the pure compounds in their standard states. This correction made the largest contribution at the lowest temperatures, (0.5% from 40–300°K., and 0.5 to 7.5% from 40–15°K.).

It was noted that prior to the application of the correction, the data did not follow an aT^3 law below 25°K.

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[9] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

[CONTRIBUTION FROM THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Vapor Pressure of Germanium[1]

BY ALAN W. SEARCY[2]

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The vapor pressure of liquid germanium has been determined over a 370° range by the Knudsen effusion method. The data lead to the equation $\Delta F = 87{,}490 + 2.00\, T \ln T - 45.5T$ for vaporization of liquid germanium. The vapor pressure results combined with estimated heat capacity and heat content data yield 84.0 ± 1.5 kcal. for the heat of sublimation of germanium at 298.15°K. Germanium vapor is demonstrated to react with a heated platinum collector plate.

Recently germanium has been shown to form compounds with many of the transition metals.[3,4] The author and co-workers plan to measure germanium partial pressures over some of these compounds. The present paper reports a determination of the vapor pressure of germanium itself.

Experimental

The vapor pressure of a substance inside a container whose temperature is known can be determined from the weight of the material passing through a small knife-edged orifice in the container into a vacuum in a measured time interval. The pressure is calculated from the Knudsen effusion equation

$$P = W(T/M)^{1/2}/44.38\ at.$$

Where P is the pressure in atmospheres, W is the weight of material of molecular weight M effusing in time t through the orifice of area a square centimeters at a temperature T°K. In the present research, germanium was effused from either a 0.336- or a 0.175-cm. diameter hole in the lid of a small graphite crucible. Spectrographic analysis of the germanium showed no evidence of significant impurity. Nevertheless, a preliminary degassing run was made to drive off any impurities sufficiently volatile to affect the pressure measurements. X-Ray diffraction analysis of germanium heated to 2125°K. in a graphite container showed no evidence of carbon contamination.

For a vapor pressure determination the germanium was heated in a graphite crucible which was nested inside tantalum and molybdenum radiation shields. Concentric holes through a set of tantalum plates above the hole in the graphite crucible collimated the beam of germanium atoms effused from the crucible.

The weight of germanium effused in each experiment was determined from the gain in weight of a platinum collector plate suspended on a water-cooled stand approximately 6 cm. above the effusion hole. About 10% of the effusing germanium was collected on this plate. The sticking coefficient on the collector (fraction of the molecules striking the collector which collided inelastically) was determined to be 1.01 ± 0.10 by comparing the approximate weight loss of the crucible with the weight gain of the collector during three of the determinations. A number of blank runs made with the same shields and temperatures used for germanium pressure determinations established that about 9% of the weight gain of the collector during a determination resulted from a collection of germanium which had struck hot radia-

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[1] Presented at the Meeting of the American Chemical Society in Cleveland, April, 1951. Work supported by the Atomic Energy Commission.

[2] Department of Chemistry, Purdue University, Lafayette, Indiana.

[3] H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

[4] A. W. Searcy, R. J. Peavler and H. J. Yearian, THIS JOURNAL, **74**, 566 (1952).