[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY][1]

The Heat Capacity of Gallium from 15 to 320°K. The Heat of Fusion at the Melting Point

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A gram atom of gallium (99.99% purity) was prepared, and measurements were taken with this sample and with four other gallium samples, over the range 15 to 300°K., to obtain the heat capacity of the solid. The heat capacity of liquid gallium was measured from 303 to 322°K., and was found to decrease with increasing temperature over this range. The heat of fusion of a sample of pure gallium was measured in a calorimeter designed specifically for the purpose and was found to be 1335 ± 1.0 cal./g. atom. The entropy of fusion is 4.407 ± 0.004 e.u. at the melting point. A lambda point in the heat capacity curve for the solid observed at 292.4°K., was shown to have been caused by eutectic melting of tin, present as an impurity in those gallium samples for which the anomaly was observed. A table of thermodynamic functions has been prepared for gallium at smoothed values of the temperatures. The entropies at 298.16°K., and at the melting point, 302.94°K., are 9.82 ± 0.05 e.u. and 9.92 ± 0.05 e.u. (entropy of fusion not included), respectively, of which 0.15 e.u. was contributed by extrapolation below 16°K.

Introduction

Clusius and Harteck[2] measured the heat capacity of solid gallium between 15 and 200°K. and Roth, Meyer and Zeumer,[3] reported empirical equations for the heat capacities of the solid and liquid, as a function of temperature, near the melting point. These data were obtained as a part of their work on the calorimetric determination of the heat of fusion. The work done by Clusius and Harteck is incomplete and admittedly inaccurate because of the large heat transfer corrections required, and because less than a tenth of a gram atom of gallium was available.

The heat of fusion of gallium has been measured calorimetrically by Berthelot,[4] and by Roth, Meyer and Zeumer,[3] and piezometrically by Richards and Boyer.[5]

It appeared desirable to redetermine the low temperature heat capacities and heat of fusion of pure gallium with the accuracy obtainable with modern calorimetric methods, in order to properly evaluate the entropy through the melting point.

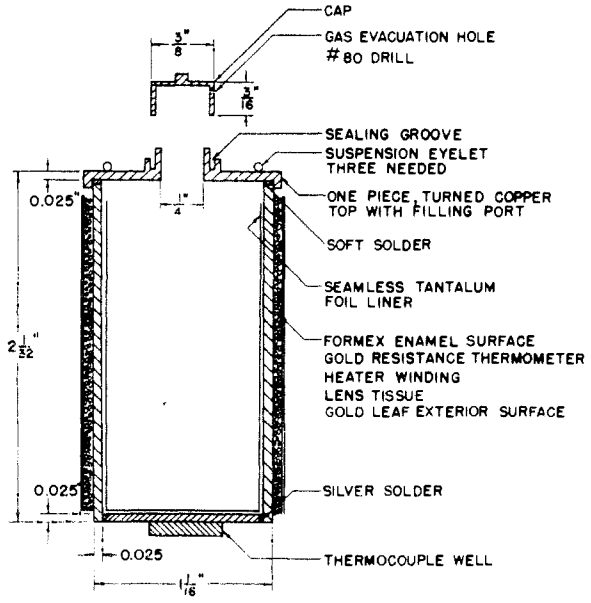

Fig. 1.—Calorimeter (HF) and cap.

Apparatus.—In the course of this research, three different calorimeters were employed. The bulk of the heat capacity data for the solid was obtained with calorimeters No. 2 and 4. These calorimeters have been previously described.[6]

The heat capacity measurements for the liquid and the heat of fusion measurements were taken with a small calorimeter designed especially for this purpose (calorimeter (HF)).

Since liquid gallium rapidly dissolves soft solder at 30°, and expands upon solidification, it was necessary to modify the standard calorimeter design in order to work with this liquid metal in the calorimeter.

Calorimeter (HF) was made of copper, and designed to hold 100 g. of liquid gallium.

A diagram of this calorimeter is shown in Fig. 1.

The principal modifications of the standard design were the omission of internal heat transfer vanes, the use of a seamless tantalum foil liner, the change in the type of closing cap, and the use of enameled alloyed gold resistance thermometer wire.

The seamless tantalum liner was constructed from 0.001 inch annealed tantalum foil, by folding a hexagon, cut from a four inch square of foil, into a seamless cylindrical cup. The folds along the sides of this cup provided the necessary free space to accommodate the volume increase which occurs upon solidification of liquid gallium. Tantalum was selected as a liner material because of its high thermal conductivity as compared with a non-metal and because it is not appreciably attacked by liquid gallium at 30°.

The change in the design of closing cap eliminated the possibility of Cerrobend solder dropping into the calorimeter during the sealing process. In sealing the calorimeter the groove circumscribing the filling port is filled with molten Cerrobend solder, the cap slipped into place, and the solder allowed to solidify.

By winding the resistance thermometer-heater with enameled alloyed gold wire instead of double nylon wrapped wire, about 1.5 times more resistance can be wrapped on. The calorimeter wall surface was given two coats of General Electric Formex enamel, each coat being air-dried and then baked for one-half hour at 120°. A 187-ohm resistance thermometer-heater winding of No. 40 B and S gage Formex enameled alloyed gold wire (0.15% Ag) was wrapped over this insulating surface. The winding was covered with a single layer of lens tissue paper, cemented to the winding with General Electric adhesive No. 7031, and then air-dried. Finally, a layer of gold leaf was cemented over the lens tissue with the same adhesive, and the calorimeter baked at 50° for four hours.

Preparation and Analysis of Samples.—In this research gallium samples of the following purities were used:[7] 99.80% (A), 99.75% (B), 99.99% (C), and 99.98% (D).

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

(2) K. Clusius and P. Harteck, *Z. physik. Chem.*, **134**, 243 (1928).

(3) W. A. Roth, I. Meyer and H. Zeumer, *Z. anorg. allgem. Chem.*, **214**, 309 (1933).

(4) M. Berthelot, *Ann. chim. phys.*, **5**, 242 (1878).

(5) T. W. Richards and S. Boyer, THIS JOURNAL, **43**, 274 (1921).

(6) H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).

(7) All analyses are given in weight per cent.

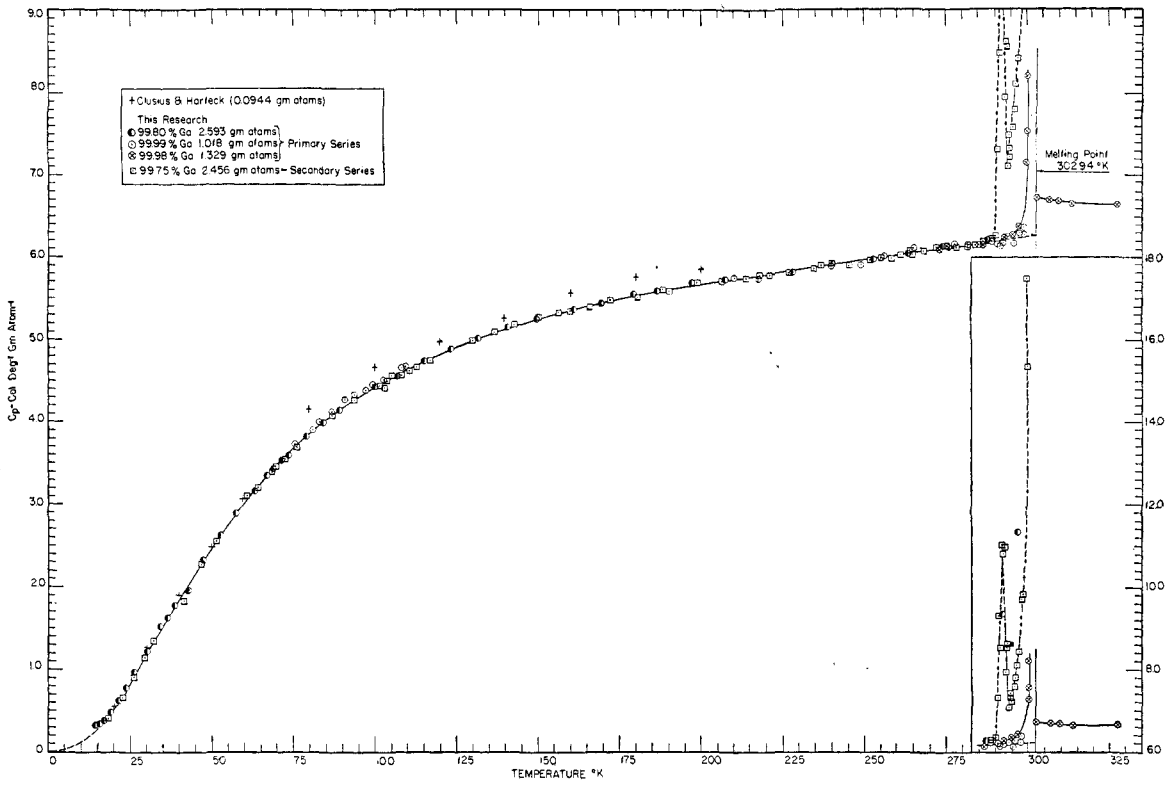

Fig. 2.—Heat capacity of gallium.

Sample (A) was part of a lot of gallium supplied as 99.99% purity by the manufacturer.[8]

The sample was contaminated by partial melting in the calorimeter prior to the initial series of heat capacity runs. The figure 99.80% for (A) was obtained from premelting data and from a quantitative spectroscopic analysis of the contaminated gallium after removal from the calorimeter upon completion of the heat capacity runs. The principal impurities were Sn (0.07%), Cu (0.06%), and Fe (0.06%).

Sample (B) was derived from (A) after further contamination by melting in the calorimeter subsequent to the initial series of heat capacity runs. The value 99.75% for this sample is an estimate based upon premelting data and spectrographic analysis of the contaminated sample.

Sample (C) was obtained by purifying a gram atom of (B), using the procedure of Hoffman,[9] with minor modifications. Essentially, the purification consisted of a separation of the gallium from the bulk of the impurities by an ether extraction of the chloride from concentrated hydrochloric acid, followed by a precipitation of heavy metals with hydrogen sulfide. The gallate was then formed in concentrated alkali, and iron removed as the hydrated oxide. The metal was obtained from this aqueous gallate solution by electrolysis, using a platinum spiral as cathode, and a platinum foil anode. The metal so obtained was finally recrystallized seven times by cooling the melt and picking out single crystals as they formed, the last drop of liquid from each crystallization being rejected.

An analysis was not procured for the highly purified material subsequently used, but a spectrographic analysis of the tailings from the recrystallization gave:

Zn <	0.001%	Al	0.001	Pb <	0.001
Cu	.004	Fe <	.010	Mn <	.001
V	.004	Mg	.004		
Mo <	.001	Sn <	.005		

This would indicate that the purity of sample (C), as run, was 99.99%, and premelting data taken from the series of heat capacity runs on this sample confirm this figure.

Sample (D) was a part of lot No. 1525-D, obtained from the Aluminum Corporation of America, Pittsburgh, Pa., and the spectrographic analysis given by the manufacturer for this lot was Cu, V, Mo, Al, Mg—all < 0.001%, with no other impurities present in amounts exceeding 0.001%. Premelting data, however, indicated that the sample, as employed in calorimeter (HF), was 99.98%.

(8) Obtained on loan through the courtesy of the Eagle-Picher Co., Joplin, Missouri. Analysis was spectroscopic.

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

Experimental Results

Heat Capacity Measurements.—The initial series of heat capacity measurements was made in calorimeter No. 2, over a range from 14 to 297°K.

The calorimeter was filled with Sample (A) consisting of 180.791 g. (2.593 gram atoms) of gallium in the form of small pieces which had been broken from a large crystalline mass. Upon completion of this series, it was apparent that at 292°K., one point on the heat capacity curve was anomalously high.

In order to investigate this region more thoroughly, a second series of measurements was undertaken, using the same gallium sample, which established two facts: (1) a definite lambda point in the heat capacity curve at 292.4°K., and (2) all points lower by about 0.2 cal./deg./g. atom than corresponding points in the first series.

Points were then taken to trace out a new heat capacity curve over the range 17 to 300°K. Later it was found that the lower values for the second series were due to loss of an undetermined amount of gallium from the calorimeter by leakage of liquid metal through the soldered bottom seam. The weight of sample actually used during the heat capacity run was estimated to within 0.2% from the ratio of values taken from the two heat capacity curves. The sample, as run in this series, was sample (B).

A third series of points was taken with 71.289 g.

(1.018 gram atoms) of sample (C), using calorimeter No. 4. The purpose of the series was to determine whether an impurity in the gallium was the cause of the lambda point observed in the heat capacity curve at 292°K. No lambda point was observed with this sample of pure gallium. However, it was noticed that after taking premelting points, subsequent runs at 292°K. gave anomalously high values.

Finally, this sample was melted in the calorimeter and points were taken at 292°K. A large lambda curve was traced out, the heat under the lambda being proportional to the tin content of the gallium sample, as was shown by a spectroscopic analysis of the contaminated sample. This tin had been dissolved from the soldered joints in the calorimeter by the liquid gallium.

Additional heat capacity points for the solid and points for the liquid were obtained with sample (D) in calorimeter (HF) in conjunction with the heat of fusion determinations.

All of the points are shown in Fig. 2. The term "primary series" has been used for that series for which the sample weight was determined directly.

TABLE I

HEAT CAPACITY OF GALLIUM (PRIMARY SERIES) ATOMIC WT. 69.72

$T_{av.}$, °K.	C_p, cal./deg./g. atom
Sample A	
99.80% Ga,	
2.593 g. atom	
14.42	0.300
15.56	0.320
17.17	0.374
19.05	0.469
21.30	0.607
23.97	0.770
26.88	0.969
30.36	1.216
34.44	1.506
38.87	1.775
43.10	1.945
47.59	2.308
52.85	2.607
57.74	2.882
63.35	3.137
68.71	3.406
73.71	3.580
78.93	3.809
84.17	3.980
89.22	4.136
94.40	4.291
100.06	4.419
107.02	4.559
115.12	4.732
123.44	4.866
131.66	5.007
140.64	5.142
149.72	5.258
160.85	5.361
169.20	5.447
179.36	5.544
186.31	5.598
197.16	5.701
207.17	5.729
217.59	5.748
228.02	5.816
239.90	5.897
252.57	5.961
263.26	6.048
273.97	6.108
281.69	6.160
287.88	6.206
292.01	9.349
296.94	11.33
Sample C	
99.99% Ga,	
1.018 g. atoms	
67.14	3.340
71.66	3.537
75.79	3.708
78.44	3.821
80.98	3.890
83.09	3.987
86.81	4.112
90.95	4.268
93.95	4.327
99.48	4.442
102.70	4.510
108.24	4.658
109.40	4.665
210.15	5.753
249.13	5.907
256.17	6.023
273.19	6.083
277.58	6.161
282.16	6.172
284.88	6.150
288.51	6.203
290.44	6.181
291.57	6.157
292.53	6.177
293.91	6.249
296.01	6.175
297.74	6.287
298.13	6.289
298.84	6.370
Sample D	
99.98% Ga,	
1.329 g. atoms	
274.00	6.110
275.61	6.130
281.69	6.160
282.84	6.140
283.17	6.133
286.52	6.140
293.42	6.238
293.94	6.300
295.73	6.281
297.48	6.377
299.71	7.247
299.89	7.545
300.19	8.201
Liquid	
302.92[a]	6.736
306.86	6.700
309.65	6.681
313.52	6.657
322.75	6.641

[a] Subcooled liquid.

The weight of sample for the series termed "secondary" was obtained indirectly, as previously mentioned.

Tables I and II list the experimental values of the molal heat capacities in defined thermochemical calories for the primary and secondary series.

TABLE II

HEAT CAPACITY OF GALLIUM (SECONDARY SERIES) 99.75% Ga, ATOMIC WEIGHT 69.72, 2.456[a] G. ATOMS (SAMPLE B)

$T_{av.}$, °K.	C_p, cal./deg./g. atom	$T_{av.}$, °K.	C_p, cal./deg./g. atom	ΔT, °K.
17.69	0.406	217.71	5.778	
22.13	0.660	220.62	5.799	
26.23	0.910	227.45	5.821	
29.52	1.145	234.73	5.872	
32.16	1.338	236.69	5.898	
34.36	1.486	240.09	5.905	
36.62	1.610	245.35	5.919	
41.37	1.931	251.82	5.973	
46.92	2.278	254.88	5.990	
51.59	2.549	258.27	5.979	
61.70	3.084	261.11	6.021	
64.18	3.186	263.70	6.069	
67.39	3.337	264.83	6.052	
68.74	3.388	268.19	6.091	
69.70	3.413	272.18	6.133	6.983
72.27	3.534	275.12	6.129	6.734
75.98	3.688	278.28	6.132	6.854
76.79	3.692	281.55	6.154	6.570
81.25	3.892	283.64	6.163	1.058
86.87	4.081	286.17	6.179	3.001
93.80	4.277	286.36	6.181	1.049
97.27	4.383	289.08	6.218	2.973
100.59	4.431	290.00	6.244	1.770
102.88	4.409	290.83	7.32	2.233
103.73	4.481	291.23	8.58	0.829
105.05	4.558	291.63	9.36	2.215
107.97	4.563	291.97	10.84	0.742
110.51	4.625	292.06	11.00	0.706
112.92	4.676	292.11	10.92	0.443
116.99	4.738	292.77	7.95	0.937
130.19	4.976	292.94	8.61	1.441
136.85	5.086	293.38	8.55	0.868
143.11	5.180	293.71	7.11	1.010
149.82	5.245	294.06	7.50	2.581
156.56	5.336	294.37	7.33	1.585
160.13	5.361	294.46	7.21	0.998
166.09	5.412	295.51	7.59	1.529
172.29	5.483	295.68	7.80	1.519
180.13	5.515	296.22	8.11	2.425
187.75	5.594	297.05	8.41	1.430
189.88	5.581	298.24	9.72	2.110
198.62	5.690	298.44	9.79	1.240
206.28	5.721	299.73	17.69	1.305
213.86	5.754	299.86	15.36	0.853

[a] Computed to within 0.2% from the mean ratio of the smoothed values of points taken with a known weight of gallium (primary series) to the smoothed values of points taken with an unknown weight of gallium (secondary series).

Smoothed values of the thermodynamic functions, obtained graphically from the heat capacity curve, are given in Table III.

The molal entropy at 298.16°K. is 9.82 + 0.05 e.u., of which 0.23 e.u. was obtained by extrapolation below 15°K.

TABLE III

THERMODYNAMIC FUNCTIONS FOR GALLIUM

Temp., °K.	C_p, cal./deg. g. atom	S^0, cal./deg. g. atom	$H^0 - H_0^0$, cal./g. atom	$-(F^0 - H_0^0)/T$, cal./deg./g. atom
16	0.321	0.152[a]	1.496[a]	0.058[a]
25	0.841	0.395	6.574	0.132
50	2.452	1.492	47.128	0.549
75	3.668	2.732	124.61	1.070
100	4.425	3.902	226.72	1.635
125	4.907	4.941	343.44	2.194
150	5.255	5.869	470.76	2.731
175	5.502	6.698	6.0537	3.239
200	5.692	7.446	745.48	3.719
225	5.815	8.124	889.32	4.172
250	5.953	8.744	1036.4	4.598
275	6.127	9.320	1187.5	5.002
298.16	6.230[b]	9.820	1330.6	5.357
300	6.236[b]	9.858	1342.1	5.384
302.94	6.246[b]	9.919[c]	1360.4[c]	5.428[c]
320	6.645	14.68	2809.4	5.900

[a] Extrapolated from 0°K. [b] Extrapolated from 296°K. [c] Thermal function values for fusion not included.

Heat of Fusion Measurements

Three determinations were made of the heat of fusion of gallium. For these determinations 92.644 g. of pure gallium (Sample (D)) was weighed into calorimeter (HF). The measurements were carried out in the usual manner, and heat capacity points were obtained for the solid from 290°K., into the premelting range, as well as five points in the liquid range, up to 322°K.

The mean value of the three determinations was 1335 ± 1.0 cal./g. atom. The melting point was taken as 29.78°.[10]

The entropy of fusion is 4.407 ± 0.004 e.u., at the melting point.

The experimental fusion heats are listed in Table IV.

TABLE IV

HEAT OF FUSION OF GALLIUM, AT. WT. 69.72, 1.329 G. ATOMS

Run No.	Temp. interval, °K.	Total heat input (cor.), cal.	$\int C_p dT$, cal.	ΔH, cal./g. atom
1	301.56–307.12	1845.25 ± 1.0	70.95 ± 0.2	1335.3 ± 0.9
2	301.97–307.36	1843.97 ± 1.8	69.28 ± .2	1335.6 ± 1.5
3	300.45–308.09	1871.18 ± 0.9	97.33 ± .2	1334.9 ± 0.8
			Mean value	1335.2 ± 1.0

(10) W. Roeser and J. Hoffman, *J. Research Natl. Bur. Standards*, **13**, 673 (1934).

Discussion

The lambda point in the heat capacity curve for the solid at 292.4°K. was caused by eutectic melting. The eutectic composition is 90% gallium and 10% tin, by weight, and the eutectic temperature is between 19 and 20°.[11] Because the eutectic is so gallium-rich, considerable heat effect is produced by eutectic melting for a comparatively small amount of tin, present as an impurity.

No corrections were applied to the heat capacity data for impurities present in the 99.80 and 99.75% gallium samples.

In drawing the final heat capacity curve, the points for the initial series were given principal weight because of the sizable sample used (2.593 g. atoms).

The heat capacity of the solid does not follow the Debye T^3 law below 20°K. The curve was extrapolated by using extrapolated Θ_D values.

The heat capacity of the liquid was found to decrease with increasing temperature over the temperature range for which it was determined (303 to 322°K.). This result is similar to that obtained by Ginnings, Douglas and Ball,[12] with liquid sodium, with liquid potassium and with mercury.

The value of 1335 ± 1.0 cal./g. atom for the heat of fusion of gallium obtained in this research is comparable with 1336 ± 7 cal./g. atom obtained by Roth, Meyer and Zeumer,[3] and 1330 cal./g. atom obtained by Berthelot,[13] both values being obtained calorimetrically. Richards and Boyer[5] reported a value of 1327 cal./g. atom at 173 megabars, by a piezometric method.

In Fig. 2 the data of Clusius and Harteck[2] on the heat capacity of the solid are plotted for comparison. The entropy of 9.82 ± 0.05 e.u. at 298.16°K. may be compared with the value 10.2 ± 0.05 e.u. derived by Kelley[14] from the data of Clusius and Harteck,[2] and of Roth, Meyer and Zeumer.[3]

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(11) N. A. Pushkin, S. Stepanovic and V. Stajic, *Z. anorg. allgem. Chem.*, **209**, 329 (1932).

(12) (a) D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950), RP 2110; (b) T. B. Douglas, A. F. Ball and D. C. Ginnings, *ibid.*, **46**, 334 (1951), RP 2204.

(13) M. Berthelot, *Compt. rend.*, **86**, 786 (1878).

(14) K. K. Kelley, Bureau of Mines, Bull. 477 (1948).