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Enthalpy, Heat Capacity, and Heat of Fusion of Aluminum from 366° to 1647° K.

R. A. McDONALD
Thermal Research Laboratory, The Dow Chemical Company, Midland, Mich.

The enthalpy, $H_T - H_{298.15^\circ K.}$, of aluminum has been determined primarily to establish the heat capacity of liquid aluminum, which was essentially constant at 7.59 cal. per (mole deg.) from 933° to 1650° K. The heat of fusion was 2560 ± 50 cal. per mole. Smoothed values of enthalpy and heat capacity from 298° to 1700° K. are given.

THE LITERATURE on the enthalpy and heat capacity of aluminum has been well documented by Kelley (*8*), Stull and Sinke (*23*), and most recently by Hultgren and coworkers (*7*). While solid aluminum would not appear to need reinvestigating, the experimental data for liquid aluminum are not in good agreement and, for the most part, just begin to cover the liquid range.

The development of refractory materials more resistant to attack by molten aluminum has made the measurement of liquid aluminum enthalpy more practical and the work reported here was undertaken to obtain more definitive data in the liquid range. Observations were made also in the solid range as an internal check on the applied corrections.

EXPERIMENTAL

The aluminum was contained in a covered refractory crucible which was sealed in a platinum-10% rhodium alloy capsule by arc welding under a helium pressure of about 8 cm. mercury. High purity aluminum was purchased from the United Mineral and Chemical Corporation and was machined into cylinders to fit the crucibles. Spectrographic analysis detected 2.7 p.p.m. of Cu, 1.8 p.p.m. of Fe, and 2.0 p.p.m. of Si.

Crucibles of titanium diboride—National Carbon Co. Division of Union Carbide Corp.—and of boron nitride—Cerac, Inc.—were used. The reason for using two different crucibles will soon become evident. Titanium diboride was the only crystalline phase detected by x-ray diffraction in a sample of the titanium diboride. However, 0.02% Al, 3% Cr, 1.2% Fe, 0.07% Mo, and 0.04% V were found by spectrographic analysis.

Enthalpy, $H_T - H_{298.15^\circ K.}$, was measured in a copper block drop calorimeter already described (*12*), correcting for the heat content of the platinum-10% rhodium alloy capsule from previous empty capsule measurements.

A titanium diboride crucible with cover—8.736 grams—was sealed in a platinum-10% rhodium alloy capsule—15.029 grams—by arc welding under helium at about 8 cm. of mercury pressure. The enthalpy of the empty crucible was determined, but the top and bottom of the crucible stuck to the metal capsule and, therefore, was not used again. An aluminum cylinder—6.072 grams—was contained in a second titanium diboride crucible—12.554 grams—sealed in a platinum-10% rhodium capsule—14.406 grams—for the first series of measurements on aluminum. This series ended when the crucible cracked, apparently from the stress brought about by the rapid heating of the aluminum, allowing molten aluminum to attack the capsule, which then fell apart.

Additional titanium diboride crucibles could not be purchased, and boron nitride was selected as the crucible material for further experiments. Two crucibles were purchased.

A glaze was found on the first crucible after measuring its enthalpy. The glaze contained boric acid, identified by x-ray diffraction, and was soluble in methanol. Consultation with the manufacturer confirmed the presence of boron oxide as a constituent of a proprietary oxide binder.

Extraction of the boron nitride crucibles and covers with A.C.S. grade methanol in a Soxhlet extractor for 22 hours resulted in a weight loss of 11 to 12%. This eliminated the glazing and lowered the enthalpy of the crucible, but the treatment was not sufficient to remove all of the boron oxide as shown by subsequent reaction with the aluminum sample.

One of the methanol extracted boron nitride crucibles with cover, weighing 5.344 grams, was sealed in a 14.728-gram platinum–10% rhodium alloy capsule for the empty crucible runs. For the second series of aluminum enthalpy measurements, 5.869 grams of Al, a 5.336-gram BN crucible, and a 14.962-gram capsule were used. The second series of measurements was terminated when corrosion of the capsule became evident. The capsule was opened after making one more drop at 727° K. The area of attack of the capsule was located at the juncture of the crucible and its cover. There was also a blackening of the inner wall of the boron nitride crucible and some coating of parts of the aluminum slug. X-ray diffraction analysis has identified $9Al_2O_3 \cdot 2B_2O_3$, AlN, α-Al_2O_3, and H_2BO_3 in the reaction products.

After the aluminum sample slug was cleaned mechanically, a hydrogen gas evolution analysis indicated that at least 98.5% of the original aluminum sample still was present as aluminum metal after the final measurement.

RESULTS

Even though the titanium diboride crucible was not pure titanium boride, the observed enthalpy is in agreement with the data of Walker, Ewing, and Miller (*25*), who indicated a sample purity of 99.7%, and with values given by Mezaki, Tilleux, and Barns (*14*). There is also reasonable agreement with the work of Osment (*17*) up to about 1650° K. The observed enthalpies of titanium diboride Table I, were smoothed as suggested by Shomate (*20*) to obtain the values in Table II. Table I also shows the per cent deviation of the observed values from the smoothed data.

The enthalpy of the extracted boron nitride crucibles was somewhat higher—2.5% maximum—than published values (*13*) up to about 1500° K. This is attributed to the presence of impurities in the boron nitride crucible.

The observed enthalpy data for aluminum are listed in Table III. The heat content of the solid aluminum was about 32% of the total heat measured in the titanium diboride crucible series and about 40% of the total in the boron nitride crucible series. With liquid aluminum, the proportion is somewhat more favorable at about 40 and 46%, respectively.

Table I. Observed Enthalpy of Titanium Diboride[a, b]

T, ° K.	$H_T - H_{298.15}$, Cal./Mole	Deviation from Smooth Curve Cal./mole	 %
326.7	326.1	+16	+5.16
441.8	1,769	-1	-0.06
445.3	1,822	+4	+0.22
558.0	3,483	-11	-0.31
667.8	5,266	+10	+0.19
757.1	6,742	-10	-0.14
890.0	9,082	+26	+0.29
954.7	10,155	-37	-0.36
970.4	10,478	+2	+0.02
1072.1	12,373	+77	+0.63
1155.5	13,821	+21	+0.15
1246.7	15,419	-33	-0.21
1305.7	16,453	-87	-0.52
1320.5	16,770	-40	-0.24
1385.1	17,991	-7	-0.04
1457.2	19.346	+8	+0.04
1544.0	20,944	-8	-0.04
1642.3	22,926	+126	+0.55
1765.6	25,176	+32	+0.13

[a] Not greater than 95.7% pure. [b] Gram molecular wt. = 69.54.

Table II. Smoothed Enthalpy of Titanium Diboride[a, b]

T, ° K.	$H_T - H_{298.15}$, Cal./Mole	T, ° K.	$H_T - H_{298.15}$, Cal./Mole
298.15	0	1100	12,800
300	19.47	1200	14,610
400	1,210	1300	16,431
500	2,608	1400	18,272
600	4,152	1500	20,126
700	5,791	1600	22,005
800	7,492	1700	23,894
900	9,233	1800	25,808
1000	11,005		

[a] Not greater than 95.7% pure. [b] Gram molecular wt. = 69.54.

Table III. Observed Enthalpy of Aluminum[a]

T, ° K.	$H_T - H_{298.15}$, Cal./Mole	Deviation from Smooth Curve Cal./mole	 %
365.8	380.9	-19	-4.75
426.0[b]	762.4	-9	-1.17
431.1[b]	821.6	+20	+2.49
486.7	1,137	-17	-1.47
528.9[b]	1,459	+30	+2.10
595.6	1,852	-18	-0.96
656.8[b]	2,301	+18	+0.79
727.5[c]	2,776	-4	-0.01
762.1[b]	2,990	-36	-1.19
775.6[b]	3,137	+15	+0.48
777.1	3,111	-22	-0.70
805.5[b]	3,351	+10	+0.30
870.7[b]	3,867	+36	+0.94
895.4[b]	3,966	-60	-1.49
909.1	4,114	-21	-0.51
920.8	4,265	+36	+0.85
(933.0)	(M.P.)		
941.4	6,974	+22	+0.32
998.6[b]	7,342	-43	-0.58
1011.5[b]	7,500	+17	+0.22
1081.0[b]	7,980	-30	-0.38
1097.8	8,152	+14	+0.17
1208.4[b]	9,027	+50	+0.55
1244.9	9,247	-8	-0.08
1384.2	10,298	-14	-0.13
1512.1	11,254	-28	-0.25
1647.2	12,328	+21	+0.17

[a] Gram atomic wt. = 26.98. [b] Aluminum contained in TiB_2 crucible. Others (without superscript) in BN crucible. [c] Last "drop" in BN crucible.

Rough average heat capacities of solid aluminum were obtained at 50° intervals from the best curve, drawn by eye, of a large scale enthalpy *vs.* temperature plot. The rough heat capacities then were smoothed graphically, taking into account the low temperature heat capacity studies of Giauque and Meads (*4*) and Griffiths and Griffiths (*6*). The single crystal heat capacities reported by Giauque and Meads were lowered slightly to apply to the multicrystalline state as indicated by the work of Maier and Anderson (*11*). The smoothed heat capacities, at 20° intervals, then were integrated by a computer to obtain the smoothed enthalpies given in Table IV. Deviations of the observed from the smoothed data are shown in Table III.

The evaluations of Hultgren, *et al.* (*7*), are only slightly lower than the smoothed enthalpies presented here, except near the melting point, where the deviation increases to about 1%.

There is a corresponding increase in the slope of the heat capacity *vs.* temperature curve as shown in Figure 1. This has been reported by Awbery and Griffiths (*2*),

Table IV. Smoothed Enthalpy and Heat Capacity of Aluminum[a]

T, °K.	$H_T - H_{298.15}$, Cal./Mole	C_p, Cal./(Mole °K.)	T, °K.	$H_T - H_{298.15}$, Cal./Mole	C_p, Cal./(Mole °K.)
298.15	0	5.81	933(*l*)	6,888	7.59
300	11	5.81	1000	7,396	7.59
400	611	6.16	1100	8,155	7.59
500	1,242	6.45	1200	8,914	7.59
600	1,900	6.72	1300	9,673	7.59
700	2,586	7.00	1400	10,431	7.59
800	3,303	7.37	1500	11,190	7.59
900	4,065	7.90	1600	11,949	7.59
933(c)	4,328	8.12	1700	12,708	7.59

[a] Gram atomic wt. = 26.98.

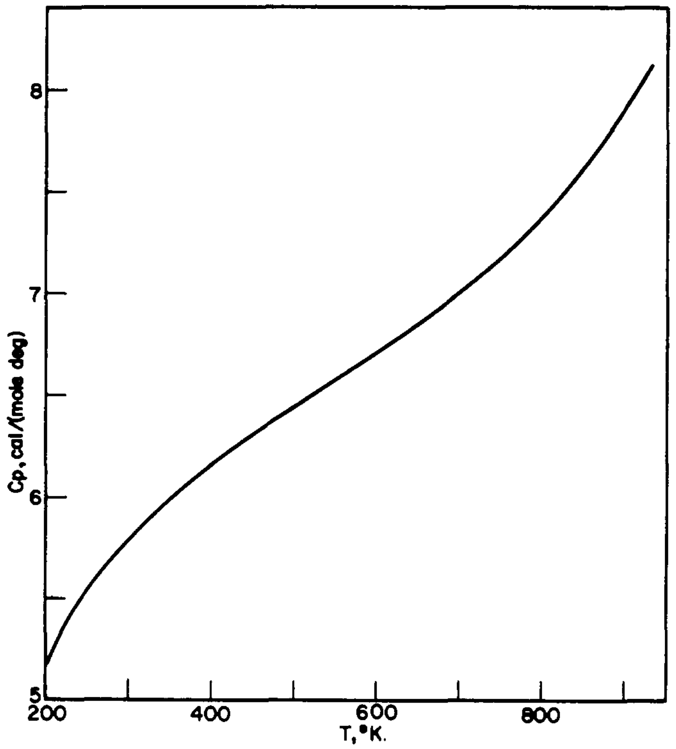

Figure 1. Heat capacity of aluminum

Seekamp (*19*), Laemmel (*10*), and Pochapsky (*18*), also. The ogee-shaped heat capacity curve is similar to those of the solid alkali metals (*3*).

The observed liquid aluminum enthalpies were smoothed using a least squares straight line fit:

$$H_T - H_{298.15}, \text{ cal./mole} = 7.588T - 191.2 \ (933^\circ \text{ to } 1650^\circ \text{ K.})$$

from which

$$C_p(l), \text{ cal./(mole deg.)} = 7.59 \ (933^\circ \text{ to } 1650^\circ \text{ K.}).$$

Deviations of experimental enthalpies from the straight line are given in Table III. The data of Awbery and Griffiths (*2*) are in good agreement, those of Wust, Meuthen, and Durrer (*27*) and of Glaser (*5*) are about 1.5 to 3% lower, and the values reported by Umino (*14*) are 11 to 12% lower.

The paper by Awbery and Griffiths (*2*) gives 0.66 cal. per (gram deg.) for the mean specific heat of liquid aluminum between 933° and 1033° K. which must be an error; it could have been 0.33 cal. per (gram deg.) which corresponds to about 8.9 cal. per (mole deg.). Umino (*24*) found 6.23 cal. per (mole deg.) in the 933° to 1273° K. range. Wust, Meuthen, and Durrer (*27*) reported 6.8 to 6.2 cal. per (mole deg.) from the melting point to 1273° K. The two enthalpy values by Glasser (*5*) lead to specific heat of 7.58 cal. per (mole deg.) between 933° and 963° K.

Table V. Heat of Fusion of Aluminum

ΔH_m, Cal./Mole	Observer or Evaluator
2149	Umino (*24*)
2493	Awbery and Griffiths (*2*)
2455	Awbery (*1*)
2500 ± 30	Kubaschewski, *et al.* (*9*)
2470 ± 40	Wittig (*26*)
2660 ± 50	Oelsen, Rieskamp, and Oelsen (*16*)
2630 ± 50	Oelsen, Oelsen, and Thiel (*15*)
2550	Stull and Sinke (*23*)
2570	Kelley (*8*)
2570	Hultgren, *et al.* (*7*)
2577	Speros and Woodhouse (*21*)
2560 ± 50	This work

Extrapolation of the solid and liquid aluminum enthalpy curves to 933° K. yields 2560 cal. per mole for the heat of fusion. [The melting point of 933° K. is a secondary reference point on the International Practical Temperature Scale of 1948 (*22*).] If one were to consider the extra increase in enthalpy below the melting point as premelting and ignored it in smoothing the data, then the heat of fusion would be about 2590 cal. per mole. Because of the scatter of the observed enthalpy data, an error of ±50 cal. per mole in the heat of fusion is quite possible. Values found in the literature are listed in Table V.

The probable error in the enthalpy measurements caused by the reaction of the aluminum sample with the boron nitride crucible has been considered. Assuming Kopp's additivity rule, comparative summations for the two main reaction products, AlN and $9Al_2O_3 \cdot 2B_2O_3$, indicated a maximum error of minus 10% in the experimental temperature range and is usually much less than this. Since only 2.5% or less of the aluminum reacted, the error thus introduced should not exceed 0.25%. However, all of the error ends up in the aluminum enthalpy. With the quantities of materials used, the heat from the aluminum sample nearly equaled the heat from the boron nitride crucible, so one might expect the enthalpy of aluminum to be low by about 0.5%.

The fact that the last measurement, at 727.5° K., falls well in line with earlier measurements—made before any reaction is presumed to have occurred—also indicates that no large error has been introduced.

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Equilibrium Distributions of the Dimethylethylbenzene and Methyldiethylbenzene Isomers

SIGMUND M. CSICSERY
Chevron Research Company, Richmond, Calif.

Data on the equilibrium distribution of the dimethylethylbenzene and methyldiethylbenzene isomers are not available. Based on known equilibrium distributions of other polyalkylbenzenes, these equilibrium distributions may be predicted. Disproportionation of methylethylbenzene can produce these isomers. Disproportionation runs were made at different temperatures at varying space velocities to various degrees of equilibration. Under conditions where the methylethylbenzenes approach equilibrium, the trialkylbenzenes are at equilibrium, also. Thermodynamic equilibria were calculated from these data at two different temperatures. The experimental equilibrium data were in good agreement with the theoretical estimates.

DATA on the equilibrium distributions of the dimethylethylbenzene and methyldiethylbenzene isomers are not available. They were estimated from the equilibrium distributions (Table I) of similar compounds.

However, the ethyl group creates some steric hindrance. The effect of the steric hindrance on the equilibrium distribution can be approximated if one compares the ortho/para ratios of xylenes and methylethylbenzenes. At 327° C. these ratios are 0.96 and 0.49. The author applied this factor (0.5) for the corresponding dimethylethylbenzenes and methyldiethylbenzenes. Estimated equilibrium distributions are shown in Table II.

These distributions may be established experimentally by isomerization of the dimethylethylbenzene and methyldiethylbenzene isomers. However, these trialkylbenzenes are not readily available in pure form. In this paper, the author shows a new and simple method to obtain the equilibrium distribution of the dimethylethylbenzene and methyldiethylbenzene isomers using methylethylbenzenes which are readily available in pure form.

Disproportionation of the methylethylbenzenes gives

Table I. Equilibrium Concentrations[a] of C_8 and C_9 Alkylbenzenes in the Ideal Gas State at 327° C.

Xylenes, Mole %	
Ortho	22.9
Meta	53.3
Para	23.8
Ortho/Para	0.96
Methylethylbenzenes, Mole %	
Ortho	16.3
Meta	50.3
Para	33.4
Ortho/Para	0.49
Trimethylbenzenes, Mole %	
1,2,3-(Hemimellitene)	13.7
1,2,4-(Pseudocumene)	62.2
1,3,5-(Mesitylene)	24.1

[a] Calculated from data taken from reference (7).