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Enthalpy and Heat-Capacity Standard Reference Material: Synthetic Sapphire (α-Al_2O_3) from 10 to 2250 K

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Heretofore unpublished enthalpy data which were used in the derivation of smooth enthalpy and heat-capacity data for NBS SRM 720 (α-Al_2O_3, heat capacity and enthalpy standard) are presented along with some details of the high-temperature experiments. Recent NBS low-temperature measurements on SRM 720 are smoothed by a least-squares spline technique and a revised table of certified values for enthalpy and heat capacity of α-Al_2O_3 from 10 K to near the melting point (2250 K) is presented.

Key words: Aluminum oxide; corundum; drop calorimetry; enthalpy; heat capacity; high temperature; Standard Reference Material; synthetic sapphire.

1. Introduction

Standard Reference Material 720 (α-Al_2O_3) has been offered by the NBS Office of Standard Reference Materials since 1970 [1][1] as a heat-capacity and enthalpy standard certified in the temperature range 273.15 K to 2250 K. The relative enthalpy data, whose smoothed representation appears in [1], were obtained in two different types of drop calorimeter: a Bunsen ice calorimeter was used from 273.15 K to 1173.15 K [2] and an adiabatic receiving calorimeter from 1173.15 K to 2250 K. The smoothed relative enthalpy values of [1] rely as well for the absolute ice-point enthalpy ($H_{273.15\ K} - H_{0\ K}$) upon a much earlier low-temperature heat-capacity study [3] on the "Calorimetry Conference Sample" of pure α-Al_2O_3.

A detailed presentation of the original ice-calorimeter enthalpy data along with a description of the smoothing procedure used to obtain the enthalpy and heat-capacity values appearing in [1] has been given in [2]. Unfortunately, the original receiving-calorimeter enthalpy data were never published due to the death of one of the principal experimenters and subsequent personnel changes.

The present work presents this enthalpy data and describes certain aspects of the experiments in the receiving calorimeter. In addition, it documents a re-smoothing of the NBS low-temperature heat-capacity data [4] on SRM 720 obtained since 1970. New smooth heat-capacity data for SRM 720 in the temperature interval 10 K to 2250 K are presented. The present smooth enthalpy data above 273.15 K differ by less than 0.01% from the corresponding valnes given in [1].

2. High-Temperature Enthalpy Data, 1173 K to 2250 K

Enthalpy data above 1173.15 K were obtained by S. Ishihara in a high-temperature adiabatic receiving calorimeter. Some physical and operational details of this apparatus have been given in [5] and [6]. These experiments were carried out with the calorimeter and furnace containing purified argon gas at about 0.1 atm. pressure. The single-crystal segments of α-Al_2O_3 were contained in a molybdenum capsule (mass: 9.26727 g) with a close-fitting, though not hermetically-sealed, lid. The capsule was suspended from a doubled and twisted loop of 8-mil tungsten wire by a small tantalum hook (hook mass: 0.56097 g). Thirteen evenly-spaced temperatures from 1173 K to 2250 K were chosen, and one day's experiments

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[1] Figures in brackets indicate literature references at the end of this paper.

TABLE 1. *Heat-Content Data for α-$Al_2O_3(s)$, SRM 720.*

Furnace Temperature T_{68}	Date (1969)	Heat to Calorimeter at 298.15 K	Specimen Mass	$H_T - H_{298.15}$	Deviation from eq. (3) of [2]	
K		J	mol[b]	J mol^{-1}	J mol^{-1}	%
		F 5386.39[a]	0.0295095	99871.6	+ 24.06	+0.024
1173.18	24 Mar.	C 2439.23				
		C 2439.35				
		F 5384.10	0.0295094	99794.3	− 53.24	−0.053
		F 5681.19	0.0303910	103184.8	− 0.57	−0.001
1199.25	7 Apr.	C 2545.30				
		C 2545.25				
		F 5680.87	0.0303914	103174.6	− 10.77	−0.010
		C 2855.86				
1299.16	4 Apr.	F 6474.38	0.0311633	116114.8	+ 41.71	+0.036
		F 6474.87	0.0311633	116156.8	+ 83.71	+0.072
		C 2855.04				
		C 3060.22				
1401.65	10 Mar.	F 6474.38	0.0317601	129563.7	+123.18	+0.095
		F 7175.51	0.0317601	129553.7	+113.38	+0.088
		C 3060.87				
		C 3467.73				
1501.15	19 Mar.	F 7914.37	0.0311937	142549.3	+ 3.60	+0.003
		F 7913.75	0.0311937	142612.1	+ 66.40	+0.047
		C 3565.15				
		F 8441.51	0.0303913	156264.1	− 66.65	−0.043
1604.90	6 Mar.	C 3692.44				
		C 3691.51				
		F 8353.12	0.0298344	156254.7	− 76.05	−0.049
		C 4002.05				
1702.22	4 Mar.	F 9003.15	0.0295487	169249.4	−110.34	−0.065
		F 9003.65	0.0295487	169251.4	−108.34	−0.064
		C 4002.49				
		C 4461.57				
1799.86	27 Mar.	F10147.78	0.0311923	182307.8	−210.67	−0.115
		F10147.78	0.0311923	182307.8	−207.47	−0.114
		F 4461.18				
		F10946.89	0.0311712	196456.3	+ 12.42	+0.006
1902.65	17 Mar.	C 4823.11				
		C 4823.88				
		F10947.56	0.0311671	196479.3	+ 35.42	+0.018
		F11264.44	0.0295326	210507.7	+242.33	+0.115
2004.13	12 Mar.	C 5047.60				
		C 5047.53				
		F11264.44	0.0295218	210509.9	+244.53	+0.116
		C 5125.11				
2101.61	21 Apr.	F11697.26	0.0293640	223816.6	+214.15	+0.096
		F11692.47	0.0293223	223971.5	+369.05	+0.165
		C 5125.11				

TABLE 1. *Continued.*

Furnace Temperature T_{68}	Date (1969)	Heat to Calorimeter at 298.15 K	Specimen Mass	$H_T - H_{298.15}$	Deviation from eq. (3) of [2]	
K		J	mol[b]	J mol^{-1}	J mol^{-1}	%
		C				
2203.28	16 Apr.	F[c]		237748.5	+173.77	+0.073
		F		237625.0	+ 50.27	+0.021
		C				
		F13886.37	0.0315029	244676.5	−322.90	−0.132
2257.11	14 Mar.	C 6178.35				
		C 6177.04				
		F13855.68	0.0313787	244708.7	−290.70	−0.119

[a] "C" prefixes data for empty capsule.
"F" prefixes data for capsule and sample.
[b] Molecular Weight = 101.9613.
[c] Original heat and mass data are available but it was not possible to trace the corrections applied to yield the molar values (col. 5), which were used in evaluation of the smoothing function (eq. (3) of [2]).

consisted of four enthalpy measurements at a single one of these temperatures. The temperature for any particular day was chosen randomly with the aid of a table of random numbers. The first and last enthalpy measurements of a day were made on the same system (either the empty capsule or the same capsule filled with α-Al_2O_3). Experienee has shown that this method of scheduling one day's experiments makes it possible to take into account small changes in the pyrometer characteristics or sample capsule mass changes due either to interaction with the sample or with the carbon atmosphere created by the induction furnace susceptor.

Results of the high-temperature measurements are given in table 1. The initial sample capsule temperatures are given in column 1. These were measured with an automatic optical pyrometer which was focused on the bottom of the sample capsule through a small aperture in the furnace susceptor. A separate output signal from the pyrometer was used to control the furnace temperature. Column 3 gives the measured heat to the calorimeter at 298.15 K. The aetual terminal temperature of the ealorimeter and capsule in the equilibrating period after an experiment was usually less than 320 K. In order to reference all heat data to 298.15 K, it was necessary to add to each measured heat a correction equal to the enthalpy of the capsule (plus sample and carbon contamination, if present) at the terminal temperature of the calorimeter relative to 298.15 K. These corrections ranged from onc to two percent of the measured heat. The enthalpy data necessary to calculate the corrections for carbon, tantalum, aluminum oxide, and molybdenum, were taken from references [7], [8], [9] and [2], respectively. The heat content of the aluminum oxide constituted about 55 percent of the total measured heat at all temperatures. The differing values for specimen mass (column 4) indicate that in some experiments different amounts of α-Al_2O_3 were used, though the difference can correspond to at most one or two small pieces of specimen. In the correction of specimen mass data for atmospheric buoyancy, a density of 3.97 g em^{-3} for α-Al_2O_3 was used. The molar enthalpy values in eolumn 5 were obtained from net heat values (F-C differences from column 3) by division by the applieable specimen mass (eolumn 4).

The present, high-temperature enthalpy results (table 1) and those from [2] in the range 273.15 K to 1173.15 K were represented by a single smoothing funetion derived by the method of least squares (eq. (3) of [2]). The last two columns of table 1 give the absolute and percent deviation of the present high-temperature data from this equation.

3. Low-Temperature Heat Capacity Data, 8.6 K to 273.15 K

Chang [4] has measured in an automated adiabatic calorimeter [10] the low-temperature heat capacity of α-Al_2O_3 chosen from the same NBS SRM 720 lot as was the material for the high-temperature measurements presented above. A piecewise representation of this low-temperature heat-capacity data, smooth in derivatives to order two, has been obtained using a least-squares spline-fitting technique. The value of this function, as well as its first and second derivatives, match precisely at 273.15 K corresponding values derived from the function [2] representing the enthalpy above 273.15 K.

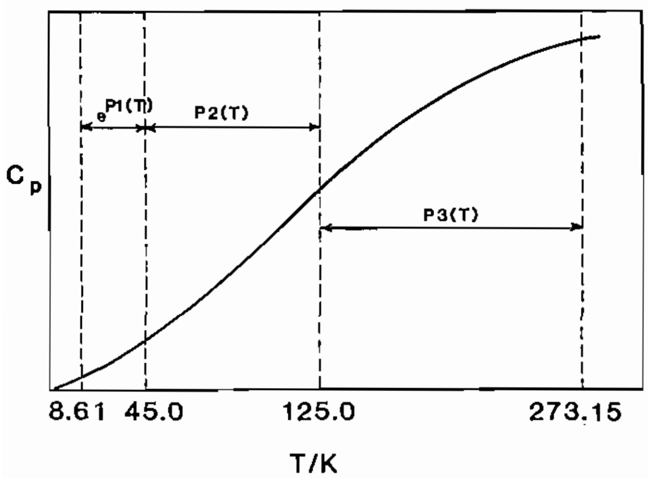

FIGURE 1. Temperature ranges for spline fit of low-temperature heat-capacity data for Al_2O_3.

The piecewise representation is illustrated in figure 1., where P1, P2, and P3 are polynomials of the form

$$\sum_{i=0}^{6} \frac{A_i}{i!} (T - T_0)^i \qquad (1)$$

T_0 is a reference temperature, different for each temperature interval.

45.0 K $> T \geq 8.61$ K; C_p = exp(P1) J mol^{-1} K^{-1}; T_0 = 8.61 K

$$\begin{aligned} A_0 &= -0.5147E+01 \\ A_1 &= +0.34127E+00 \\ A_2 &= -0.333446E-01 \\ A_3 &= +0.450764E-02 \\ A_4 &= -0.51464E-03 \\ A_5 &= +0.397864E-04 \\ A_6 &= -0.152136E-05 \end{aligned} \qquad (1a)$$

125 K $> T \geq 45.0$ K; C_p = P2 J mol^{-1} K^{-1}; T_0 = 40.0 K

$$\begin{aligned} A_0 &= +0.6966E+00 \\ A_1 &= +0.59387E-01 \\ A_2 &= +0.40357E-02 \\ A_3 &= +0.95173E-04 \\ A_4 &= -0.35910E-05 \\ A_5 &= -0.6498E-07 \\ A_6 &= +0.4089E-08 \end{aligned} \qquad (1b)$$

273.15 K $> T \geq 125$ K; C_p = P3 J mol^{-1} K^{-1}; T_0 = 125 K

$$\begin{aligned} A_0 &= +0.21993E+02 \\ A_1 &= +0.38853E+00 \\ A_2 &= +0.13955E-02 \\ A_3 &= -0.83967E-04 \\ A_4 &= +0.19133E-05 \\ A_5 &= -0.31778E-07 \\ A_6 &= +0.29562E-09 \end{aligned} \qquad (1c)$$

The low-temperature heat-capacity data [4] are represented by these smoothing functions with computed percent standard deviations (S_c) for each of the three fitting intervals as follows:

45.0 K $> T \geq 8.61$ K ; S_c = 0.97

125.0 K $> T \geq 45.0$ K ; S_c = 0.13

273.15 K $> T \geq 125.0$ K ; S_c = 0.05

According to Chang [4], "It is estimated that the accuracy of the smoothed (low-temperature) values are better than 0.1% at temperatures between 100 and 350 K . . . Below 100 K, the inaccuracy is estimated to become progressively larger, reaching perhaps 1% around 50 K and 10% around 10 K."

4. Enthalpy of SRM 720 (α-Al_2O_3), 10 K to 2250 K

Smooth heat-capacity values were computed from eqs (1), above. Below 8.6 K, a T^3 dependence of heat capacity was assumed. Using these values, the heat-capacity functions were integrated to obtain the absolute enthalpy of α-Al_2O_3 in the temperature range 10 K to 273.15 K. Above 273.15 K, enthalpy and heat-capacity values were derived from the following equation (reproduced for convenience from [2]):

$$H_T - H_{273.15} = AT^{-2} + BT^{-1} + C\ln T + K + DT + ET^2 + FT^3 + GT^4 + HT^5 \text{ J mol}^{-1} \qquad (2)$$

$A = +6.6253E+07$	$E = -8.57516E-02$
$B = -4.54238E+06$	$F = +4.299063E-05$
$C = -5.475599E+04$	$G = -1.15192E-08$
$K = +2.5819702E+05$	$H = +1.26351E-12$
$D = +2.574076E+02$	

Table 2 presents these smooth heat-capacity and enthalpy data for α-Al_2O_3.

TABLE 2. *Enthalpy and heat capacity of standard reference material 720.*

Temp	H_T-H_{0K}	C_p	Temp.	H_T-H_{0K}	C_p
K	J mol^{-1b}	J mol^{-1} K^{-1}	K	J mol^{-1}	J mol^{-1} K^{-1}
			440	2295_3	100.6_9
10	0.02_3	0.009_1	450	2396_5	101.7_1
15	0.11_5	0.030_7	460	2498_7	102.6_8
20	0.36_4	0.073_2	470	2601_8	103.6_0
25	0.89_8	0.14_6	480	2705_9	104.4_8
30	1.90_5	0.26_5	490	2810_8	105.3_3
35	3.64_6	0.44_3	500	2916_5	106.1_3
40	6.46_0	0.69_7	510	3023_0	106.9_0
45	10.7_7	1.04_6	520	3130_3	107.6_4
50	17.1_1	1.50_6	530	3238_3	108.3_5
60	38.1_8	2.79_3	540	3347_0	109.0_2
70	74.6_8	4.59_2	550	3456_3	109.6_7
80	$131._7$	6.90_1	560	3566_3	110.2_9
90	$214._2$	9.67_8	570	3676_9	110.8_9
100	$326._6$	12.85_5	580	3788_1	111.4_6
110	$472._4$	16.34_7	590	3899_8	112.0_2
120	$654._3$	20.0_7	600	4012_1	112.5_5
130	$874._3$	23.9_5	610	4124_9	113.0_6
140	$1133._7$	27.9_3	620	4238_2	113.5_5
150	$1433._1$	31.9_5	630	4352_0	114.0_2
160	$1772._7$	35.9_5	640	4466_3	114.4_8
170	$2152._0$	39.9_0	650	4581_0	114.9_2
180	$2570._3$	43.7_5	660	4696_1	115.3_5
190	$3026._7$	47.5_0	670	4811_7	115.7_6
200	$3519._9$	51.1_2	680	4927_6	116.1_6
210	$4048._7$	54.6_1	690	5044_0	116.5_5
220	$4611._6$	57.9_5	700	5160_7	116.9_2
230	$5207._1$	61.1_4	720	5395_3	117.6_4
240	$5833._9$	64.1_8	740	5631_3	118.3_2
250	$6490._3$	67.0_0	760	5868_5	118.9_6
260	$7175._0$	69.8_2	780	6107_1	119.5_6
270	$7886._3$	72.4_2	800	6346_8	120.1_4
273.15	$8115._6$	73.2_1	820	6587_6	120.6_9
280	$8622._8$	74.8_7	840	6829_5	121.2_1
290	$9383._2$	77.2_0	860	7072_4	121.7_1
298.15	1002_0	79.0_1	880	7316_3	122.2_0
300	1016_6	79.4_1	900	7561_2	122.6_6
310	1097_1	81.5_1	920	7807_0	123.1_1
320	1179_6	83.4_9	940	8053_6	123.5_5
330	1264_1	85.3_7	960	8301_1	123.9_7
340	1350_3	87.1_6	980	8549_5	124.3_7
350	1438_3	88.8_4	1000	8798_6	124.7_7
360	1528_0	90.4_5	1020	9048_6	125.1_6
370	1619_2	91.9_7	1040	9299_2	125.5_3
380	1711_9	93.4_1	1060	9550_7	125.9_0
390	1806_0	94.7_8	1080	9802_8	126.2_6
400	1901_4	96.0_8	1100	1005_{60}	126.6_1
410	1998_2	97.3_2	1120	1030_{90}	126.9_5
420	2096_1	98.5_0	1140	1056_{40}	127.2_9
430	2195_1	99.6_2	1160	1081_{80}	127.6_1

TABLE 2. *Continued*

Temp	H_T-H_{0K}	C_p	Temp	H_T-H_{0K}	C_p
K	J mol^{-1}	J mol^{-1} K^{-1}	K	J mol^{-1}	J mol^{-1} K^{-1}
1180	1107_{40}	127.9_4	1700	1790_{80}	$134._{31}$
1200	1133_{00}	$128._{25}$	1750	1858_{10}	$134._{73}$
1250	1197_{30}	$129._{01}$	1800	1925_{50}	$135._{13}$
1300	1262_{00}	$129._{74}$	1850	1993_{20}	$135._{50}$
1350	1327_{10}	$130._{43}$	1900	2061_{00}	$135._{85}$
1400	1392_{40}	$131._{08}$	1950	2129_{00}	$136._{18}$
1450	1458_{10}	$131._{70}$	2000	2197_{20}	$136._{50}$
1500	1524_{10}	$132._{29}$	2050	2265_{50}	$136._{80}$
1550	1590_{40}	$132._{84}$	2100	2334_{00}	$137._{10}$
1600	1657_{00}	$133._{36}$	2150	2402_{60}	$137._{41}$
1650	1723_{80}	$133._{85}$	2200	2471_{40}	$137._{73}$
			2250	2540_{30}	$138._{06}$

[a] Temperatures expressed on IPTS-68 scale.
[b] Molecular Weight = 101.9613.

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