Thermal Properties of Aluminum Oxide From 0° to 1,200° K

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Accurate measurements of the heat capacity of α-aluminum oxide (corundum) from 13° to 1,170° K are described. An adiabatic calorimeter was used from 13° to 380° K and a drop method was used with a Bunsen ice calorimeter from 273° to 1,170° K. The results are compared in the range 273° to 380° K, where the two methods overlap. From the data, smoothed values of the heat capacity, enthalpy, entropy, and Gibbs free energy from 0° to 1,200° K are derived and tabulated.

1. Introduction

One of the fundamental functions of the National Bureau of Standards is to develop new standards as the need arises. As the science of thermodynamics assumes new import in modern technology, the need for calorimetric standards becomes urgent. At the meeting on April 21, 1948, the Fourth Conference on Low Temperature Calorimetry [1] considered this problem of calorimetric standards and recommended three materials to serve as heat-capacity standards over a wide temperature range. These materials were benzoic acid (10° to 350° K), n-heptane (10° to 300° K), and α-aluminum oxide (10° to 1,800° K). The Bureau was asked to prepare very pure samples of these materials which would be available to those laboratories interested in very precise measurements of heat capacity. By having samples of any one substance taken from one source of very high purity, it was hoped to have a means of comparing measurements made in different laboratories under different experimental conditions. The Bureau has prepared samples of these three materials that are not regarded as part of the Standard Sample series of the Bureau, but will be designated here as Calorimetry Conference samples, and has made these available without charge to a limited number of laboratories. Measurements have already been made at the Bureau on the Calorimetry Conference sample of benzoic acid [1],[2] normal heptane [2], and aluminum oxide. A brief summary [3] of the results of these measurements and details of the measurements on benzoic acid [1] and normal heptane [2] have been published in other reports. It is the purpose of the present report to give the complete results of heat capacity measurements on the Calorimetry Conference sample of aluminum oxide, which up to the present have covered the range from 13° to 1,173° K.

Aluminum oxide in the form of corundum (α-Al_2O_3)[3] has a number of properties that make it ideal for a heat-capacity standard over a wide temperature range. It is commercially available in the form of synthetic sapphire with impurities present in such small quantities that the heat capacity of the sample should be the same as that of a pure sample within the accuracy of present calorimetric measurements. The sapphire is a crystalline solid without known transitions or changes of state up to its melting point (near 2,000° C [4]). It is nonvolatile, nonhygroscopic, and chemically stable in air, and does not absorb carbon dioxide. Except at the lowest temperatures, it has a high heat capacity per unit volume. It is extremely hard and should be free from mechanical effects such as strains due to cold-working, which cause small but significant changes in the thermal properties of metals. In summary, it appears that the synthetic sapphire should be an excellent standard for heat-capacity measurements over most of the temperature range up to its melting point.

The Bureau has previously made measurements [5] over the range 0° to 900° C on a sapphire sample (not Calorimetry Conference sample) in order to determine the suitability of the material as a standard. The measurements described in the present report are on the Calorimetry Conference sample and consist of two independent calorimetric investigations using entirely different methods and apparatus for the low- and high-temperature ranges. In the range 13° to 380° K, an adiabatic calorimeter was used. In the range 273° to 1,170° K, a "drop" calorimeter was used, similar to the earlier high-temperature experiments [5, 6] except that an entirely new and improved apparatus was used.

2. Sample

The aluminum oxide sample investigated was colorless synthetic sapphire (corundum) and was a portion of the material prepared for the Calorimetry Conference by F. W. Schwab [4] of the Chemistry Division at the Bureau. This material, originally purchased from the Linde Air Products Company in the form of split boules, was coated with a hard opaque form of aluminum oxide which was removed by immersing in fused potassium pyrosulfate. Fol-

[1] The Conference on Low Temperature Calorimetry was renamed the Calorimetry Conference at the meeting held on September 6, 1950, in order to include other fields of calorimetry.

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

[3] The β-Al_2O_3 is an impure alumina which can be formed when the molten aluminum oxide is slowly cooled in the presence of certain impurities. The γ-Al_2O_3, which can be prepared by heating $Al(OH)_3$, is metastable, transforming to α-Al_2O_3 at about 1,000° C. The α-Al_2O_3, known as corundum, containing traces of chromium, is red and called ruby, while that containing traces of iron and titanium is blue and called blue sapphire. The synthetic corundum or synthetic sapphire used in the preparation of the Calorimetry Conference sample was highly pure and contained no coloration.

[4] Deceased.

lowing this cleaning process, a portion (about one-fifth of the boules was examined by C. P. Saylor of the Bureau for inclusions, and the total volume of the inclusions was estimated to be less than 1 part per million of the volume of the aluminum oxide crystals.

The cleaned boules were crushed, and about 85 percent of the material was collected in particle sizes between 0.02 and 0.08 in. The impurities from the crushing and sieving processes were removed by digesting in hot hydrochloric acid. The material was then thoroughly washed and dried at about 300° C. This product showed no loss in weight on subsequent drying at 110° C or heating for 2 hours at 1,200° C. To obtain the highest degree of uniformity in all samples, all the material was thoroughly mixed in a large bottle and packaged in 70-g units of about 30 ml volume. Later some of these 70-g units were divided into smaller units.

Spectrographic analyses made by B. F. Scribner, of the Bureau, of a sample from one of the packaged 70-g units indicated the purity to be between 99.98 and 99.99 percent by weight. The only impurities present in quantities greater than trace amounts were silicon, 0.005 percent; iron, 0.005 percent; and chromium, 0.002 percent. It seems likely that the impurities present would not affect the heat capacity of the sample by more than 0.02 percent in the temperature range covered by the measurements described in this paper.

3. Low-Temperature Calorimetry

3.1. Method and Apparatus

The heat-capacity measurements in the low-temperature range, from about 13° to 380° K, were made by means of an adiabatic calorimeter of a design similar to that described by Southard and Brickwedde [7]. Details of the design and operation have been previously described [8]. Briefly, the aluminum-oxide sample was sealed in a copper sample container of about 125-cm^3 capacity. In order to attain a rapid thermal equilibrium, tinned copper vanes were arranged radially from a central well to the outer wall of the container and held in place by a thin coating of pure tin applied to the inner surfaces. A small quantity of helium gas was also sealed with the sample to increase the rate of thermal equilibrium. The central well contained a heater-platinum resistance thermometer assembly. The outer surface of the container and the adjacent inner surface of the adiabatic shield, within which the container was placed, were gold plated and polished to minimize radiative heat transfer. The space surrounding the container and shield was evacuated to a pressure of 10^{-6} mm Hg or less to make negligible the heat transfer by conduction and convection. During the heat-capacity experiments the temperature of the shield was kept the same as that of the container surface by means of shield heaters, manually controlled, and constantan-chromel-P differential thermocouples. Two sets of thermocouples, one of three junctions and the other of two, and three individual heaters were used in the control of the shield temperature.

The electrical power input was measured by means of a Wenner potentiometer in conjunction with a standard cell, volt box, and standard resistor. The time interval of heating was measured by means of a precision interval timer operated on a standard frequency of 60 cps furnished by the Time Section of the Bureau. The timer was compared periodically with standard second signals and found to vary not more than 0.02 sec per heating period, which was never less than 2 min. Temperatures were measured by means of a platinum-resistance thermometer and a high-precision Mueller bridge. The platinum-resistance thermometer was calibrated above 90°K in accordance with the 1948 International Temperature Scale [9], and between 10° and 90°K with a provisional scale [10], which is maintained by a set of platinum-resistance thermometers which had been compared with a helium-gas thermometer. The provisional scale as used in the calibration of the thermometer when the measurements reported in this paper were made was based upon the value 273.16°K for the ice point and 90.19°K for the temperature of the oxygen point. Above 90°K, the temperatures in degrees Kelvin were obtained by adding 273.16 deg to the temperatures in degrees Celsius (International Temperature Scale of 1948 [9]).[5] All electric instruments and accessory apparatus were calibrated at the Bureau.

3.2. Heat-Capacity Measurements

The heat-capacity measurements on aluminum oxide were made from about 13° to 380°K in sample container A and calorimeter G. The container and calorimeter were previously used in the heat-capacity investigation of benzoic acid [1]. Two sets of measurements were made, one on the container filled with sample and the other on the empty container. To minimize the correction for curvature, the heat-capacity measurements were closely spaced wherever the curvature was large. Generally, the temperature change per heating interval was about 1 to 3 deg below 30°K, 3 to 5 deg from 30° to 80°K, and 5 to 10 deg above 80°K. Wherever significant, the curvature correction was applied according to the relation [12]:

$$Z_{T_m}=Q/\Delta T-\left(\frac{\partial^2 Z}{\partial T^2}\right)_{T_m}\frac{(\Delta T)^2}{24}-\left(\frac{\partial^4 Z}{\partial T^4}\right)_{T_m}\frac{(\Delta T)^4}{1920}\cdots, \quad (1)$$

where Z_{T_m} is the corrected heat capacity of the container plus sample or of the empty container at the mean temperature T_m of the heating interval ΔT, and Q is the electric energy added. In evaluating this equation, the derivatives of Z with respect

[5] At the Tenth General Conference held in 1954, the General Conference on Weights and Measures adopted a new definition of the thermodynamic temperature scale by assigning the temperature 273.16°K to the triple-point temperature of water. For details regarding the adoption of this new scale, see reference [11].

The provisional temperature scale as it is presently maintained at the National Bureau of Standards, and referred to as degrees K (NBS–1955), is numerically 0.01 deg lower than the former NBS scale [10].

to T were replaced by the derivatives of $Q/\Delta T$ obtained from numerical differentiation of the table of $Q/\Delta T$ given at equally spaced integral temperatures. The last term involving the fourth derivative of Z was found to have negligible effect upon the observed heat-capacity values of the present measurements.

In both sets of measurements the observed heat capacities, corrected for curvature, were plotted on a large scale as deviations from approximate empirical equations. The smoothed heat capacities at equally spaced integral temperatures were then obtained by combining smooth deviation curves and empirical equations. Net heat capacities (heat capacities of sample alone) were obtained by subtracting the tabulated heat capacities of the empty container from those of the container plus sample at the corresponding even temperatures. As the mass of the sample container was slightly different for the two sets of experiments, because of the differences in the masses of solder and of copper, a correction was applied from known heat capacities of copper, tin, and lead. The heat-capacity correction for the tin-lead solder used in the experiments was based on the assumption of additivity of the heat capacities of lead and tin. A small correction was applied also for the heat capacity of the helium gas used in the container-plus-sample experiments.

Below 90° K, as in previous heat-capacity investigations, irregularities were observed in the deviation curves which were attributed to a possible nonlinearity in the temperature scale. No attempt was made to smooth out these irregularities, consequently the heat-capacity values given in table 5 below 90° K are not smooth.

TABLE 1. *Principal data for the low-temperature heat-capacity experiments*

Heat capacity of the empty container.

°K=°C+273.16°

T_m [a]	Z [b]	ΔT [c]
Run 1		
°K	abs j deg^{-1}	°K
89.0896 [d]	28.430	7.1869
95.9914	30.357	6.8585
102.4506	31.990	6.2619
109.1428	33.532	7.1227
116.0984	34.972	6.7905
122.6402	36.204	6.4304
130.9216	37.590	10.1327
140.3588	39.017	9.7413
150.4504	40.228	9.4420
159.7734	41.267	9.2040
168.3587	42.108	9.9666
178.2289	42.967	9.7738
188.9167	43.710	9.6018
198.9354	44.370	10.4355
209.2254	44.994	10.2848
219.5162	45.542	10.1671
229.7576	46.034	10.3250
Run 2		
209.9676	45.016	8.1647
218.0798	45.418	8.0260
226.3061	45.886	8.2294
234.6631	46.260	8.3165
242.9446	46.613	8.2454
251.1602	46.963	8.1802
259.3164	47.278	8.1298
267.6288	47.589	8.0173
275.9040	47.881	8.0137
283.8902	48.192	7.9667
291.8209	48.403	7.9228
299.7292	48.668	7.8738
307.5902	48.888	7.8282
Run 3		
302.8075	48.750	9.4616
312.0283	49.023	9.2020
321.3953	49.263	9.2297
331.2921	49.480	10.4543
341.7204	49.720	10.4034
352.1300	49.949	10.2967
362.4692	50.160	10.3018
371.9913	50.347	10.2502
382.1172	50.572	10.2016
392.3058	50.752	10.1736
Run 4		
°K	abs j deg^{-1}	°K
83.2986 [d]	28.527	11.0770
93.1512	29.539	8.6283
100.7570	31.574	6.6831
107.1874	33.096	6.2778
113.3456	34.420	6.0387
159.5566	41.216	9.3307
166.5164	41.918	4.5880
173.3924	42.512	9.1632
182.7866	43.257	9.6253
237.9008	46.358	9.2206
245.8150	46.738	8.2077
254.0879	47.075	8.1382
Run 5		
304.7873	48.805	9.1827
313.8714	49.068	9.0857
322.9346	49.290	9.0408
374.6302	50.418	11.9057
386.4098	50.668	11.6334
Run 6		
53.7250	14.383	4.8468
58.5081	16.619	4.7188
63.1913	18.749	4.6466
67.6234	20.644	4.2176
72.0621	22.412	4.6598
77.2272	24.383	5.0705
82.6014	26.329	5.0778
87.6256	27.969	4.7810
92.6416	29.469	5.4410
Run 7		
14.2602	0.5339	1.8420
16.0816	.7038	1.6006
17.7074	.9008	1.6212
19.0610	1.1642	1.6958
20.6604	1.4093	1.4011
23.4240	2.0294	4.2023
26.6294	2.8692	2.2066
28.7608	3.4909	2.0163
30.7806	4.1799	2.0254
32.6688	4.8770	1.7378
34.6603	5.6600	2.2432
Run 8		
°K	abs j deg^{-1}	°K
15.2068 [d]	0.6268	1.6041
16.7593	.8352	1.3612
18.2634	1.0475	1.6270
19.9670	1.2069	1.7401
21.6416	1.6121	1.4090
23.4686	2.0363	2.4852
25.2602	2.7490	3.0469
28.4700	3.4038	1.2777
31.1032	4.3110	2.8988
34.8307	5.6149	2.9642
39.0760	7.3408	6.0834
44.4174	9.8742	4.5990
49.2119	12.248	4.9900
54.0722	14.550	4.7297
59.1485	16.911	5.4216
63.4778	18.880	3.2369
Run 9		
68.9392	21.160	4.3727
74.2704	23.252	6.2897
80.2911	25.488	5.7316
86.3360	27.568	6.3621
92.5106	29.419	5.8815

[a] T_m is the mean temperature of the heating interval.
[b] Z is the observed mean heat capacity over the interval ΔT.
[c] ΔT is the temperature interval of heating.
[d] The temperatures given are believed to be accurate to ±0.01° K. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

The values of heat capacity obtained were at helium gas pressure varying from 5 cm Hg at room temperature to about one-twentieth of this pressure at the lowest temperature and to about 6 cm Hg at the highest temperature. In the case of aluminum oxide the conversion of the heat capacity to 1-atm pressure makes negligible change. Therefore all computation and analyses have been carried out as if the measurements were made at constant 1-atm pressure.

Two separate series of heat-capacity measurements, I and II, containing 225.6384 and 251.7915 g of sample, respectively, were made to check the reproducibility of the results obtained. After one series of measurements, the sample container was removed from the calorimeter and was emptied of the sample. The container was refilled, pumped, and resealed with helium gas and was replaced in the calorimeter for the second series of measurements. The container was installed in the calorimeter in as nearly identical conditions as possible for all the heat-capacity measurements, including those on the empty sample container.

The measurements of series I were made in the temperature intervals 13° to 120° and 280° to 380° K, and those of series II in the interval 80° to 380° K. The principal data (with no curvature corrections) from the heat-capacity measurements on the empty container and from those of series I and II are given in tables 1, 2, and 3, respectively. In each run, the data are given consecutively as obtained and no measurements are omitted. The data given for the

TABLE 2. *Principal data for the low-temperature heat-capacity experiments*

Heat capacity of the series I measurements: °K = °C + 273.16°. Mass of sample: 225.6384 g. Accessory data: 0.0200 g less copper; 0.1656 g less solder (Pb/Sn = 63/37); 0.00048 mole helium.

T_m[a]	Z[b]	ΔT[c]
Run 1		
°K	abs j deg⁻¹	°K
315.2861[d]	231.769	8.1976
322.5024	235.019	8.2351
330.6604	238.561	8.0809
Run 2		
59.5032	23.061	7.0414
64.7179	27.303	3.3880
68.3190	30.303	3.8141
72.2842	33.680	4.1103
76.2082	37.154	3.7319
80.1500	40.778	4.1617
84.1258	44.634	3.7994
Run 3		
55.7048	20.086	4.2270
59.6496	23.161	3.6636
63.6237	26.396	4.2856
67.6666	29.752	3.7966
71.2874	32.911	3.4446
74.6914	35.706	3.1632
77.9026	38.779	3.6392
81.8120	42.338	4.0007
85.7008	46.045	3.7778
89.3006	49.476	3.4198
Run 4		
63.0544	25.919	5.2995
68.1058	30.195	4.9827
73.0679	34.359	4.7620
77.6875	38.492	4.4772
82.1565	42.650	4.4606
Run 5		
13.8258	0.5526	1.1034
14.9963	.6841	1.2325
16.2778	.8415	1.3385
17.7382	1.0657	1.0803
19.1043	1.2913	1.1638
20.3928	1.5548	1.4211
22.4450	2.0317	2.6635
25.4314	2.8563	3.2891
28.7078	3.9557	3.2636
31.6039	5.1617	2.6244
Run 6		
°K	abs j deg⁻¹	°K
15.1330[d]	0.7008	1.0092
15.2916	.8084	0.7061
17.0526	.9637	1.4139
18.6076	1.2044	1.0960
20.0228	1.4600	1.1344
21.2429	1.7062	1.2996
23.0923	2.1713	2.3950
25.9987	3.0341	3.4276
29.6864	4.3670	3.9455
33.1906	5.8519	2.9460
36.6302	7.5040	3.8541
40.6728	9.3631	4.4307
46.5650	12.907	5.3350
50.0730	16.414	4.9001
55.0944	20.039	5.1408
60.7070	24.070	6.0060
Run 7		
30.7404	4.8022	4.4283
34.2881	6.4371	2.7672
37.6890	8.1747	3.9646
42.4029	10.907	5.4733
47.5484	14.233	4.8079
52.3739	17.633	4.8590
57.2966	21.391	5.0724
62.1372	25.179	4.5297
Run 8		
80.2273	40.846	2.6237
83.6336	44.274	4.7271
88.2694	48.794	4.3066
92.5147	52.617	3.9642
97.1220	56.956	5.2304
102.1428	61.879	4.8112
107.4316	67.213	4.4201
111.7449	71.874	4.1076
115.7892	76.721	3.9311
119.6214	79.670	3.7333
Run 9		
°K	abs j deg⁻¹	°K
280.3006[d]	213.764	10.8239
290.4555	219.387	10.0531
300.4250	224.562	9.8212
310.1439	229.327	9.6148
319.6856	233.772	9.4267
328.9603	237.886	9.2560
338.0361	241.739	9.1136
347.5210	245.519	9.8583
357.3062	249.287	9.7119
366.9429	252.770	9.5724
Run 10		
85.0368	46.411	4.7539
89.5836	49.733	4.3399
93.7634	53.719	4.0177
98.2665	58.167	5.1904
103.3427	63.097	4.7620
108.6620	68.457	5.8706
112.6708	72.538	4.1007
116.8162	75.827	3.1836
122.8816	82.030	4.9474
Run 11		
283.3723	215.464	11.3246
294.5308	221.524	11.0100
305.5440	227.122	10.9080
316.2990	232.280	10.4800
326.9900	237.062	10.2831
337.0008	241.376	10.0782
347.1885	245.454	10.0736
357.0773	249.254	9.7490
366.9514	251.790	9.8601
376.5920	254.197	9.5812
386.0893	257.423	9.4334

[a] T_m is the mean temperature of the heating interval.
[b] Z is the observed mean heat capacity over the interval ΔT.
[c] ΔT is the temperature interval of heating.
[d] The temperatures given are believed to be accurate to ±0.01° K. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

TABLE 3. *Principal data for the low-temperature heat-capacity experiments*

Heat capacity of the series II measurements: °K=°C+273.16°. Mass of sample: 251.7915 g. Accessory data: 0.0200 g less copper; 0.0801 g less solder (Pb/Sn=63/37); 0.00049 mole helium.

T_m [a]	Z [b]	ΔT [c]
Run 1		
°K	abs j deg⁻¹	°K
200.9238[d]	171.569	2.2296
202.1093	173.663	2.2011
208.0005	178.078	7.3614
215.4383	184.676	7.2942
222.8137	190.797	7.0665
229.0619	196.180	6.8663
235.9524	201.626	6.6700
242.6875	206.946	7.0342
249.6356	212.184	6.9619
256.4192	217.031	6.7064
264.1309	222.494	8.7190
272.7374	228.167	8.4040
281.1330	233.540	8.2052
Run 2		
276.6334	231.961	9.3525
286.8938	237.126	9.1682
294.9807	241.915	9.0056
303.8843	246.982	9.8016
313.5825	252.226	9.5049
321.7922	256.416	9.4319
331.1412	260.959	9.2661
340.3321	265.205	9.1168
349.3795	268.185	8.9790
358.2966	272.697	8.8663
367.0920	276.485	8.7363
375.7393	279.735	8.6314
Run 3		
°K	abs j deg⁻¹	°K
81.5532	43.994	5.3020
86.5929	49.168	4.7774
91.1444	53.888	4.3255
95.9096	59.144	4.0049
101.2260	64.434	7.8292
108.6192	72.513	6.9560
116.0441	80.730	7.6938
125.3199	91.281	10.7264
135.4438	102.793	9.6193
144.5309	113.046	8.8538
152.8638	122.318	7.0932
161.9874	131.760	9.2744
170.4326	141.306	8.6159
178.7976	149.968	8.1146
187.1146	158.324	8.5157
195.4246	166.404	8.1016
Run 4		
84.8279	47.356	5.2481
89.9190	52.478	4.7343
94.3592	57.150	4.3461
97.8929	60.855	2.7214
104.8445[d]	68.354	7.5252
111.9806	76.234	6.7444
119.1638	84.294	7.6225
128.4444	92.582	6.9369
134.7754	102.014	9.7289
144.0438	112.502	8.8129
152.5128	121.929	8.1249
159.7528	129.675	0.3549
166.3338	137.194	7.2172
174.4844	145.522	8.6745
184.2188	155.423	10.7948
Run 5		
°K	abs j deg⁻¹	°K
197.7738	166.606	7.4592
205.9064	174.122	8.8089
213.1362	182.610	6.0578
220.0717	188.605	8.2182
228.1400	195.354	7.9252
236.5203	204.466	7.5688
247.0176	210.157	7.4358
253.9024	215.208	6.2437
260.6347	219.678	6.1210
266.0071	223.736	6.0038
272.0474	227.738	5.8068
279.3828	232.447	8.7741
Run 6		
273.1030	228.438	6.6810
280.7973	233.398	8.7085
288.4109	238.565	8.5177
297.9028	243.530	8.3418
306.0650	248.130	8.1827
314.2167	252.457	8.1208
322.2305	256.587	7.9087
330.0795	260.378	7.7814
337.8150	263.989	7.6795
345.4454	267.478	7.5914
352.9806	270.676	7.4599
Run 7		
335.6755	262.989	9.6406
345.1906	267.296	9.4643
354.6007	271.343	9.3380
363.8720	275.100	9.2066
373.0174	278.669	9.0643

[a] T_m is the mean temperature of the heating interval.
[b] Z is the observed mean heat capacity over the interval ΔT.
[c] ΔT is the temperature interval of heating.
[d] The temperatures given are believed to be accurate to ±0.01° K. Figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

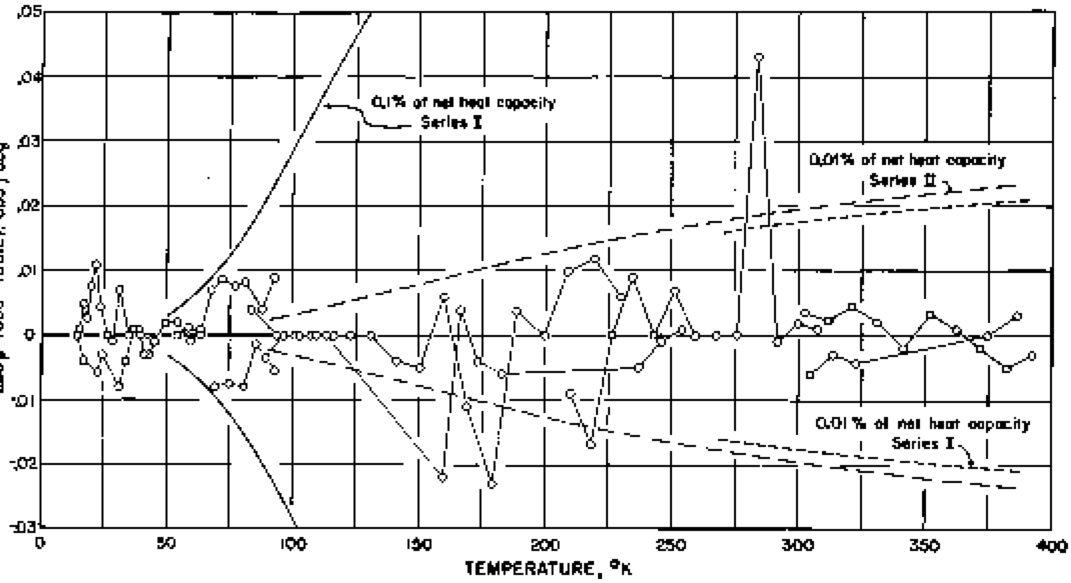

FIGURE 1. *Deviations of the experimental heat capacities (corrected for curvature) from smoothed tabular values obtained for the empty container.*

The results of the same run are connected by lines. The deviation boundaries are given in terms of the net heat capacity (heat capacity of sample).

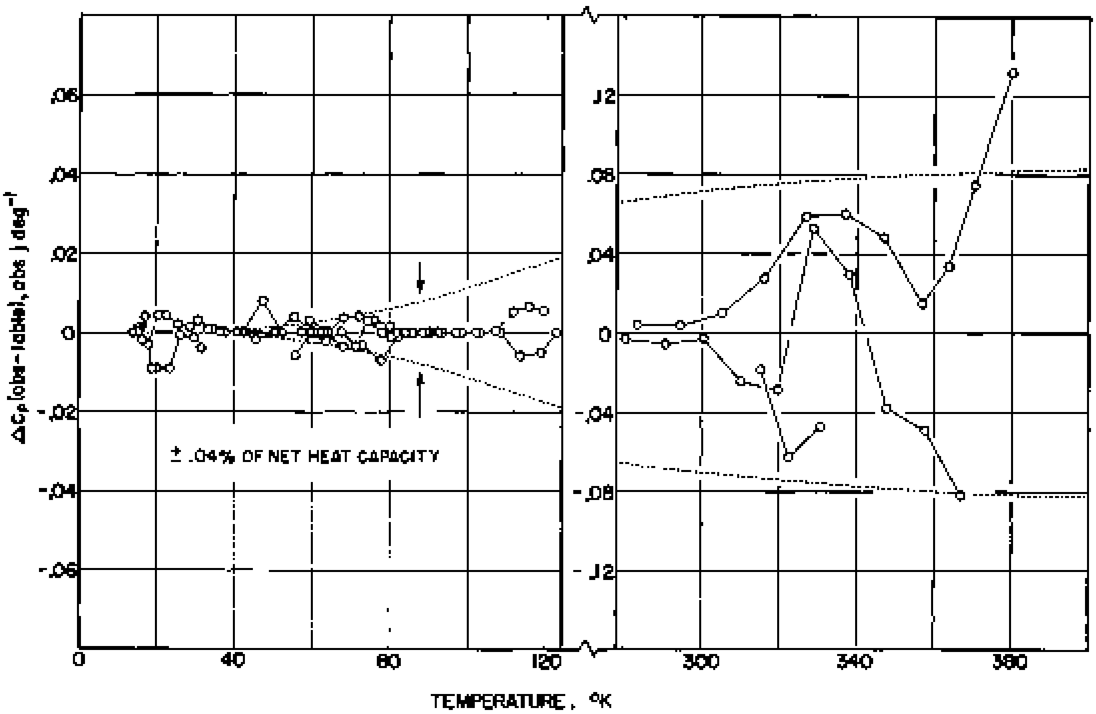

FIGURE 2. *Deviations of the experimental heat capacities (corrected for curvature) of the measurements of series I from smoothed tabular values obtained for the container plus synthetic sapphire.*

The results of the same run are connected by lines. The deviation boundary is given in terms of the net heat capacity (heat capacity of sample).

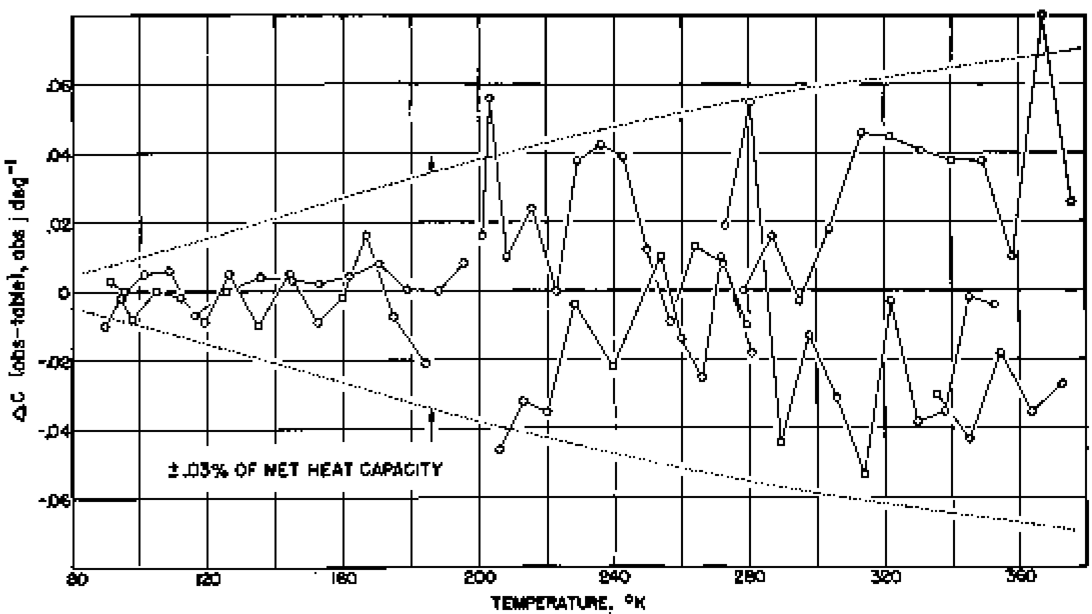

FIGURE 3. *Deviations of the experimental heat capacities (corrected for curvature) of the measurements of series II from smoothed tabular values obtained for the container plus synthetic sapphire.*

The results of the same run are connected by lines. The deviation boundary is given in terms of the net heat capacity (heat capacity of sample).

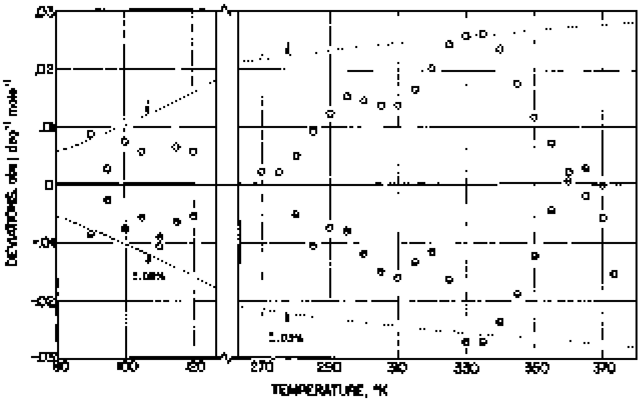

FIGURE 4. *Comparison of the smoothed values of the heat capacity of aluminum oxide obtained in the measurements of series I and II.*

⊖, Series I; ○, Series II

empty container are those obtained previously during the heat-capacity investigation of benzoic acid [1]. (As these data have not been given previously they are reported in this paper.) [4] The deviations of the experimental heat-capacity values (corrected for curvature) of the empty container from the smoothed values, obtained according to the procedure outlined earlier, are shown in figure 1. As the measurements of series I and II contained different amounts of sample, two sets of percentage-deviation boundaries are shown in the figure. Similar deviation plots for the results of the measurements of series I and II are shown in figures 2 and 3, respectively. The deviation boundaries showing the precision of the measurements are given in terms of the net heat capacity. The net heat capacities from the two series of measurements were averaged wherever their temperatures coincided to arrive at the heat-capacity values with the low-temperature adiabatic calorimeter. The smoothed values of the heat capacity of aluminum oxide for the two series are compared in figure 4.

3.3. Reliability and Comparison of the Low-Temperature Results

The sample container A and calorimeter G, in which the low-temperature heat-capacity measurements on aluminum oxide described in this paper were made, were tested earlier by determining the heat capacity of water from 274° to 332° K. The maximum variation of 14 experiments on water was 0.02 percent from the very accurate values previously published by Osborne, Stimson, and Ginnings [13]. A comparison has been described previously [2] of the heat-capacity results obtained on n-heptane, in a similar calorimeter in which the results agreed with the maximum variation of 0.15 percent from the values between 5° and 90° C published by Osborne and Ginnings [14]. In the test experiments from 274° to 332° K with water the heat capacity of the sample was about 2 to 3 times greater than that of the aluminum oxide sample in the same temperature range. Consequently, any constant heat leak that may have been present would cause the percentage inaccuracy in the aluminum oxide experiments to be 2 to 3 times greater than that of the water experiments. Between 5° and 90° C the heat capacity of the aluminum oxide sample was 30 to 50 percent greater than that of the n-heptane sample, but at 14° K the heat capacity of the aluminum oxide sample was only one one-hundredth of that of the n-heptane sample.

The precision of the low-temperature heat-capacity measurements on aluminum oxide is shown in the deviation plots of figures 1, 2, 3, and 4. Figures 2 and 3 show that the precision of the measurements of series I and II are about the same. In figure 4, although the two series of measurements were made in the same calorimeter and container and the conditions in the calorimetric system were made as nearly identical as possible, the results deviate slightly and systematically from each other, those of series II in general being higher than those of series I. These small systematic deviations are attributed to the possibility that portions of thermocouple and electric lead wires were in contact with the container, resulting in small differences in the heat capacity of the system. Also, there is a possibility of small errors in accounting for the slight differences in the mass of the container for the different series of measurements. The two series of results are, however, in good agreement.

Considering the precision obtained and various known sources of systematic error, the uncertainty in the values of the heat capacity above 90° K was estimated to be ±0.1 percent. Below 90° K, the uncertainty increases to much larger values from various contributing factors. In the measurements of series I, the net heat capacity decreased from about 43 percent of the gross (container plus sample) heat capacity at 90° K to 10 percent at 14° K. A platinum resistance thermometer having 25.5 ohms at the ice point will be 0.036 ohm at 13° K and changes in resistance by only 0.0059 ohm between 13° and 14° K. This difference at the best can be determined only to 0.00002 ohm or 0.003 deg. As given in table 2, the temperature interval of heating in this region was about 0.6 deg. The thermocouples used in detecting the temperature difference between the shield and the sample container become very insensitive at the lower temperatures, also the thermal conductivity of the copper leads is over 10 times that at room temperature. Considering these factors, a precision of about 0.5 to 1 percent is all that can be expected from the measurements at the lowest temperature (see fig. 2), consequently at 14° K the heat-capacity value obtained for aluminum oxide is believed to be uncertain by as much as 10 percent.

In figure 5 are compared various published heat-capacity values of aluminum oxide with those of the present measurements. The results of Parks and Kelly [15] are about 7 percent higher at 90° K and 0.1 percent lower at 290° K. The results re-

[4] Figure 1 of this reference [1] should be disregarded. The deviation plot of the measurements on an empty container of another heat-capacity investigation was inadvertently introduced. This oversight, however, does not affect the results given in this reference.

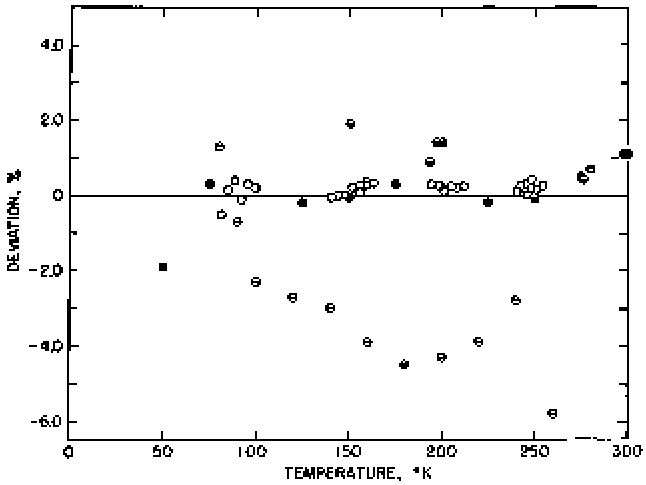

FIGURE 5. *Comparison of the values of heat capacity obtained by means of the low-temperature adiabatic calorimeter with those of other investigators.*

●, Kerr et al.; ⊖, Simon and Swain; ⊖, Parks and Kelly; ○, Morrison.

ported by Simon and Swain [16] are generally higher at the lower temperatures and lower at higher temperatures. Except in the lowest temperature range, the values reported by Kerr et al. [17] are in good agreement. Recently Morrison [18] made heat-capacity measurements on a sample of Calorimetry Conference aluminum oxide. His results are in excellent agreement with the measurements presented in this paper.

4. High-Temperature Calorimetry

4.1. Method and Apparatus

The heat capacity measurements in the high-temperature range (0° to 900° C) were made by the "drop" method. In brief, this method is as follows. The sample, sealed in its container, is suspended in a furnace until it comes to a constant known temperature. It is then dropped into a Bunsen ice calorimeter, which measures the heat evolved by the sample plus container in cooling to 0° C. In order to account for the heat capacity of the container and the heat lost during the drop, a similar experiment is made with the empty container at the same temperature. The difference between the two values of heat is a measure of the change in enthalpy of the sample between 0° C and the temperature in the furnace. From enthalpy values of the sample so determined, for a series of temperatures, the heat capacity can be derived.

Many of the details of the ice calorimeter and furnace and their operation have been given in previous publications [5, 6, 19]. More details will be given here, in addition to a repetition of some details given earlier, because reprints of an earlier publication [19] are no longer available. Figure 6 shows a schematic diagram of the furnace and ice calorimeter. A central well, A, made of an alloy having low thermal conductivity, is provided to receive the container with the sample. The lower part of this well is surrounded by two coaxial Pyrex vessels, P. The inner vessel contains the ice-water system in which ice melts when heat is added. The outer vessel insulates the inner vessel from the surrounding ice bath, E. The vessels are sealed to the metal caps by Apiezon "W" wax, and the space between them is filled with dry carbon dioxide at the pressure of the atmosphere. A specially designed gate, G, prevents a transfer of heat by radiation from above the calorimeter down through the central well. An ice mantle, I, is frozen around the central well in the inner vessel by introducing a tube filled with solid carbon dioxide (dry ice) into the well. The shape of the ice mantle and the rate of freezing are controlled by adjusting the amount of dry ice in the tube and the thermal contact between this tube and the well. The ice mantle is frozen around the central well and the copper vanes, F, the vanes serving to speed thermal equilibrium in the inner vessel. The vanes, central well, and metal caps are tinned to avoid contamination of the pure air-free water in the inner vessel. The inner vessel is connected to the outside through mercury, M, which connects to the beaker of mercury, B, and glass capillary, C. When heat is added to the inner vessel containing the ice mantle and surrounding water, ice melts, causing mercury to be drawn into the calorimeter. This amount of mercury is proportional to the heat added, the proportionality constant being a fundamental physical constant which was determined by electrical calibration experiments. One gram of mercury was found to be equivalent to 270.48 ±0.03 absolute joules.[7]

There are several details of the construction of the ice calorimeter which will be mentioned here as an aid to those making ice calorimeters of similar design. The mercury-water interface is located in the bottom part of the inner vessel for two reasons. First, the area of the interface is large, so that for a given influx of heat, the level of mercury in the calorimeter changes very little. The calorimeter and its contents are slightly compressible, so that a change in pressure in the calorimeter results in a change in volume that must be distinguished from the change in volume due to heat input. With the present calorimeter, the effect of this change in pressure is only 0.004 percent of the calibration factor. A second reason for locating the mercury-water interface in the bottom of the calorimeter is to avoid danger of breaking the inner glass vessel when freezing an ice mantle. During this freezing, the metal cap is colder than 0° C so that if there were water in the small tube leading from this vessel, ice might form to block the tube. During an experiment, any mercury entering the ice calorimeter must be at the temperature of the latter. Coil T serves this purpose, acting as a reservoir holding more mercury than is used in any experiment.

[7] This factor (which is for the "ideal" ice calorimeter with no change in pressure during an experiment) differs slightly from the previously published [19] value of 270.46, due to a correction of the circuit constants applicable in all the calibration experiments.

The calorimeter well, inside the inner glass vessel, will be considered in two parts. In the lower part, short copper sleeves (8 mm high and 1 mm thick) were fitted around the central well to separate the copper fins during assembly. These copper sleeves help also to distribute the heat from the sample over a greater part of the ice mantle. In the upper part of the calorimeter, thin copper-nickel alloy sleeves were used instead of copper to minimize heat conduction upward.

Particular care must be taken in the design of the wax seals between the glass cylinders and the metal caps. First, the metal caps should preferably be made with a material having a low temperature coefficient so that the distance between the glass and metal can be made small, making the wax joint stronger. The glass should be ground to a true cylindrical shape where it fits inside the metal cap. A tolerance on this fit should be allowed for differential expansion over 50 to 100 deg C. For the most accurate results, it seems to be better to keep the calorimeter at the ice temperature at all times. One ice mantle can be used over a period of several days if precaution is taken to protect the top of the ice mantle from excessive melting due to defective ice bath above it. It must be emphasized that the best operation of the ice calorimeter is obtained when the water in the calorimeter is pure and free from dissolved gas. A bubble of gas in the calorimeter cannot be tolerated for accurate work. It is believed desirable to avoid small crevices in the construction of the calorimeter. Proper tinning of metallic parts of the calorimeter should accomplish this as well as avoid contamination of the water.

The furnace is shown in position over the ice calorimeter in figure 6. It is designed to minimize temperature gradients in the region where the container (with sample) is suspended. In this way, it is possible to assume the temperature surrounding the container to be the temperature of the container. The furnace heater was made in three separate sections corresponding in elevation to the three silver cylinders, which were located inside the alundum, as indicated by J, K, and L. By maintaining the cylinders J and L at the same temperature as the cylinder K, the temperature gradient in K can be made negligible. The silver cylinders are supported by porcelain spacers, Y, having low thermal conductivity. Coaxially with the silver and porcelain cylinders are Inconel tubes which serve to enclose the sample container and its suspension wire (A. W. G. No. 32 Nichrome V), so that an atmosphere of helium can be used in the furnace tube, as well as in the calorimeter well, in order to minimize the time required for the sample container to come to thermal equilibrium with its surroundings.

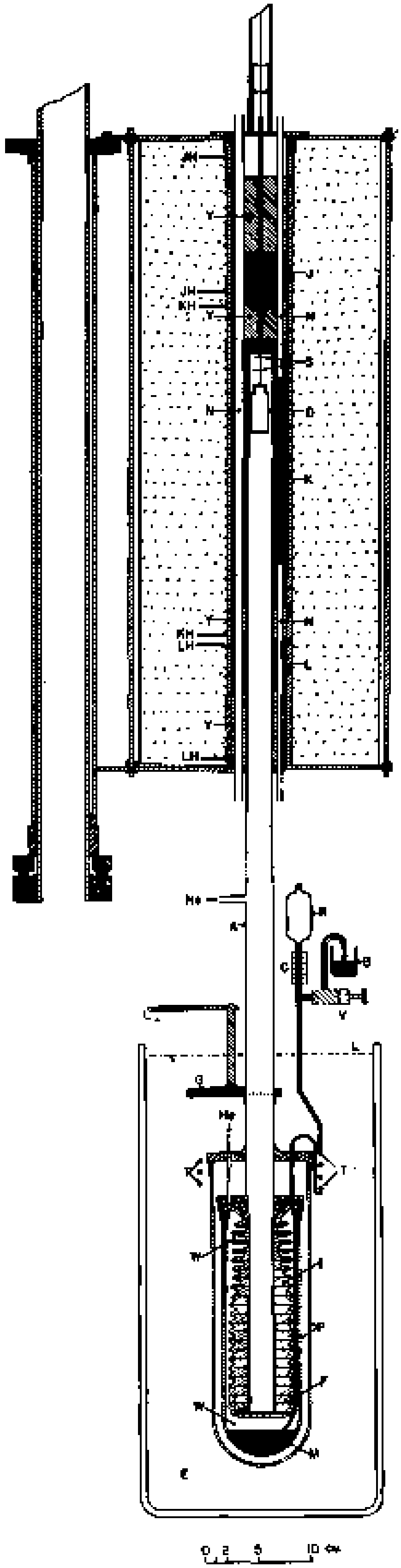

FIGURE 6. *Diagram of the furnace and ice calorimeter.*

A, Calorimeter well; B, beaker of mercury; C, glass capillary; D, sample container; E, ice bath; F, copper vanes; G, gate; I, ice mantle; JH, KH, LH, furnace heater leads; J, K, L, silver cylinders; M, mercury; N, Inconel tubes; P, Pyrex vessels; R, mercury reservoir; S, platinum shields; T, mercury "tempering" coil; V, needle valve; W, water; Y, porcelain spacers.

Figure 6 shows some of the vertical holes, N, drilled through the silver and porcelain and placed 90 deg apart azimuthally. These holes contain the platinum resistance thermometer, the platinum-rhodium thermocouple, and the differential thermocouples between the end silver cylinders, J and L, and the central cylinder K. In one of these holes are placed three small auxiliary heaters, located at the elevations of the three silver cylinders. With these heaters, it is possible to avoid troublesome lag in the main heater and to control the central silver cylinder to 0.01 deg. The end silver cylinders are maintained within a few tenths of a degree of the central silver cylinder.

The suspension of the container, D, in the furnace and its drop into the calorimeter is similar to that described earlier [5, 6]. The braking starts after the container enters the calorimeter. The weight of the falling system is kept constant in all experiments. Two thin platinum shields, S, are attached to the suspension wire just above the container in order to make heat transfer upward (after the drop) essentially the same whether or not there is a sample in the container.

Up to and including 600° C, a strain-free platinum resistance thermometer is used to measure the temperature of the central silver cylinder that surrounds the sample container. Between 600° and 900° C, a platinum–platinum–10 percent rhodium thermocouple is used. Both thermometer and thermocouple are calibrated frequently.

Because the temperature of the sample container is not directly measured, it is necessary to allow sufficient time for the container to reach the temperature of the silver cylinder. Two types of tests are made to prove that the time is adequate. First, the minimum time is estimated from test experiments with the sample container suspended in the furnace a relatively short time. Second, in the regular experiments, the time intervals in the furnace are always varied so that any significant trend in the results with time will be detected.

4.2. Results

The results of all the individual measurements with the furnace and ice calorimeter are given in table 4. (No values were discarded.) These measurements were on only one specimen of aluminum oxide, taken from the Calorimetry Conference sample whose preparation is described in section 2. Specific considerations in arriving at the values tabulated will now be discussed.

The furnace temperatures are given in column 1 of the table. At and below 600°C these are as indicated by a strain-free platinum resistance thermometer calibrated at the Bureau. Ice-point readings of the thermometer, taken several times during the series of measurements on aluminum oxide, showed an over-all change equivalent to only 0.005 deg. This makes it seem unlikely that a much greater change occurred in the temperatures indicated by the thermometer in the range above the ice point. Recent tests at different depths of immersion in the furnace led to the belief that with the immersion that was normally used, the thermometer was brought to the temperature of its surroundings, which included the sample, within 0.1 deg even at 600°C.

TABLE 4. *Experimental results using the drop method*

Furnace temperature,[a] t	Measured heat[b]: Empty container	Measured heat[b]: Container $+Al_2O_3$	Enthalpy change of the Al_2O_3, $H_t-H_{0°C}$: Observed	Enthalpy change of the Al_2O_3, $H_t-H_{0°C}$: Calculated from eq (2)	Enthalpy change of the Al_2O_3, $H_t-H_{0°C}$: Observed minus calculated
°C	abs j	abs j	abs j g⁻¹	abs j g⁻¹	abs j g⁻¹
50.00	267.7 270.6 269.1 268.0	903.6 900.0 902.0 902.0	38.76	38.72	+0.04
100.00	540.9 544.8 546.6 547.9	1,887.0 1,890.6 1,889.9 1,890.9	82.21	82.18	+.03
150.00	833.3 833.3 833.3 ----------	2,946.5 2,942.4 2,942.6 2,944.0	129.21	129.25	−.04
200.00	1,127.9 1,127.5 1,125.0 1,126.7 1,129.2 1,129.5 1,133.8	---------- 4,054.3 4,053.5 4,052.1 4,047.9 ---------- ----------	178.96	178.96	.00
300.00	1,730.1 1,730.9 1,731.0 1,734.4 1,735.7 1,730.5	---------- 6,380.4 6,379.9 6,379.8 ---------- ----------	284.55	284.53	+.02
400.00	2,355.2 2,357.6 2,352.0 2,354.7	8,825.1 8,823.8 8,823.5 ----------	396.03	395.97	+.05
500.00	3,002.3 2,999.0 2,998.7 2,997.3 2,999.3	---------- 11,352.0 11,353.5 11,354.6 ----------	511.42	511.53	−.11
600.00	3,671.3 3,661.3 3,668.6 3,667.1	13,956.2 13,951.5 13,954.4 13,955.3	629.79	630.14	−.35
699.4	4,376.2 4,371.4 4,378.0 4,376.2	16,836.1 16,838.5 16,841.9 ----------	760.70	760.32	+.38
796.9	5,093.3 5,093.4 5,092.0	19,302.5 19,301.1 19,306.0	869.91	869.80	+.11
896.3	5,836.1 5,835.8 5,834.9 ----------	22,066.3 22,061.6 22,066.6 22,066.3	993.09	993.25	−.16

[a] International Temperature Scale of 1948 [9].
[b] Mass of aluminum oxide, 16.3346 g.

For the temperatures above 600°C it was necessary to rely on the electromotive force of a platinum–90 percent platinum-10 percent rhodium–thermocouple. Throughout the measurements on aluminum oxide there was no essential change in the electromotive force of this thermocouple found for a given resistance of the thermometer, and hence presumably no essential change in the thermocouple calibration. This was over the range up to 600°C, where the two instruments were frequently compared in order to detect any sudden shift in the calibration values of either. In addition, the thermocouple was calibrated up to 900°C at the Bureau independently of this thermometer at the beginning and again at the end of the measurements on aluminum oxide. There were thus in effect three independent calibrations of the thermocouple, any two of which disagreed in their temperature indications by amounts which were approximately the same at the different temperatures. The two calibrations made before and after the enthalpy measurements indicated for a given electromotive force a temperature respectively 0.1 deg higher and (above 500°C) 0.5 deg higher, approximately, than indicated by the comparisons with the thermometer in the furnace. (Even if the thermocouple calibration did not really change during this interval, a discrepancy of 0.5 deg is well within the tolerance within which these calibrations are certified.) Although the comparisons with the thermometer were not made above 600°C, the depth of immersion and temperature gradients of the thermocouple were naturally more like those during the enthalpy measurements. Therefore the thermocouple calibration adopted above 600°C was made to conform to the results of these comparisons with the thermometer in the furnace, by taking the temperatures to be 0.1 deg lower than indicated by the initial thermocouple calibration or, what is the same, 0.5 deg lower than indicated by the final thermocouple calibration.

The results of individual heat measurements are given in columns 2 and 3. For each temperature these are listed in the order in which they were determined, and no entry in column 2 has a specific relation to any entry in column 3. These values are based on a corrected calibration factor of the ice calorimeter of 270.48 absolute joules per gram of mercury (see section 4.1) and have been corrected as fully as possible except for the heat lost in the drop into the calorimeter. This heat loss very nearly cancels out in subtracting the values of column 2 from those of column 3 to obtain the net heat due to the aluminum oxide sample.

The corrections that were applied to the heat values are all minor. All masses were corrected to a vacuum basis. The small calorimeter heat leaks (averaging about 2 j/hr) were found by interpolation from rate measurements before and after the run. In a few cases it was necessary to correct for very small deviations from the nominal furnace temperatures. Though the sealed container was filled with helium at 1 atm pressure at room temperature, the internal pressure increased up to 4 atm at the highest temperatures; however, the correction of the heat change to that at a constant pressure of 1 atm was shown thermodynamically to be well within the experimental error, and was neglected. The small differences in masses of all metallic parts of the falling system between the runs on the empty container and those on the container with sample were corrected for, as was also the helium displaced by the volume of the sample. The capsule was weighed at the beginning of each day, and corrected for the small increases due to oxidation by traces of oxygen in the helium atmosphere in the furnace, using the differences in enthalpy between Fe and Fe_3O_4 [20]. These are adequate for the present purpose because the corrections are extremely small. The total correction for these inconstant masses of materials averaged 0.02 percent, and did not exceed 0.05 percent of the net heat due to the sample.

The observed heats due to the aluminum oxide alone are listed in column 4. Each such value is the difference between the corresponding mean values for the same temperature in the two preceding columns divided by the mass of the sample. Smoothed values of relative enthalpy were obtained by using these unsmoothed values to derive, by the method of least squares, the coefficients of an empirical equation. Considering that the precision, in terms of absolute joules per gram, is almost independent of temperature, each value in column 4 was given equal weight. The resulting equation, giving in absolute joules per gram the enthalpy of aluminum oxide at t° C in excess of the enthalpy at 0° C as found by the high-temperature measurements only, is

$$H_t - H_{0°C} = 1.447978t - 1.6777\,(10^{-6})t^2 - 460.915\,\log_{10}\,[(t+273.16)/273.16]. \qquad (2)$$

(As discussed in section 5, this equation does not agree exactly with the final values of heat capacity between 0° and 125° C adopted in this paper and given in table 5.)

Values calculated from this equation are listed in column 5 of table 4 and the agreement with the observed values is shown in column 6.

There are obvious advantages of expressing the results of such measurements by a simple empirical equation, especially for convenience of interpolation and for analytical derivation of other properties. The three constants of eq (2) were derived from 11 experimental values. Nevertheless, it should be pointed out that this equation represents the unsmoothed data without appreciable trends with temperature, and therefore is probably as reliable as any numerically derived representation of the high-temperature results. The deviations (column 6), which vary from 0.10 percent at 50° to 0.02 percent at 896° C and average 0.03 percent, are of the same order of magnitude as the precision indicated by the individual runs. In fact, the form of eq (2) has been found [21] to represent in this temperature region precise enthalpy data of a number of crystalline substances, including aluminum oxide, more closely than several other similar three-constant forms of equation that have been proposed for general use.

4.3. Reliability and Comparison of the High-Temperature Results

Evidence as to the probable accuracy of the values of relative enthalpy given by eq (2) and of heat capacity given by its derivative can be obtained from three sources: (1) the reproducibility or precision of the measurements, (2) an examination of the likely systematic errors, and (3) the agreement among different observers.

Taking into proper statistical account the effect of the precision at a given temperature in the individual runs on the empty container and also those on the container with sample, the probable error (precision) of the mean unsmoothed net enthalpy of aluminum oxide at a given temperature, relative to that at 0° C, can be shown from the data of table 4 to average ± 0.05 abs j g^{-1}, the maximum being twice this great. This corresponds to a variation from ± 0.10 percent at 50° C to ± 0.01 percent or less at 300° C and above.

It is noteworthy that the absolute magnitude of this precision (i. e., in absolute joules per gram) is approximately constant and shows no systematic variation with temperature. This indicates that the accidental error probably arose largely in the performance of the ice calorimeter, only a small part being attributable to the furnace variables whose effect would normally be expected to be strongly dependent on temperature. As the heat capacities of most substances do not change by large factors between 0° and 900° C, it follows that the present high-temperature apparatus is capable of measuring a mean heat capacity over a specified temperature interval almost as precisely at high as at low temperatures, even though at high temperatures the determination may be based on a similar difference between two very large heat quantities. These facts strongly suggest also that the precision of measuring with the ice calorimeter the enthalpy *per unit mass*, at one given furnace temperature, could be increased greatly by proportionately increasing the size of sample measured.

In the present measurements on aluminum oxide, the mean unsmoothed heat capacity between two successive temperatures (50 to 100 deg apart) is found to have a precision corresponding to a probable error averaging approximately ± 0.1 percent. The differences between the unsmoothed values and those calculated from eq (2) are comparable, except for the range 600° to 700° C, where the difference is ± 0.6 percent. This single relatively large difference may be due to the joining of thermometer and thermocouple temperature scales in this region. Otherwise, the heat capacity of aluminum oxide varies so regularly that the smoothing accomplished by eq (2) can reasonably be expected to have reduced the effect of accidental errors on the accuracy of the final values.

Various sources of systematic error with the ice calorimeter and furnace were examined. Uncertainties in measuring the temperature on the International Temperature Scale are thought not to have introduced major error except in the region above 600° C, where the necessary dependence on thermocouple readings may have led to errors at 900° C as high as 0.05 percent in the relative enthalpy and 0.2 percent in the heat capacity. The heat lost in the drop into the calorimeter is estimated to have reached 0.5 percent of the total heat measured at 900° C. While this should have been nearly the same with or without the sample present, it is possible that the variation of the emissivity of the container surface in these two cases may have caused an error of as much as 0.1 percent in the heat capacity at this highest temperature. Other sources of error, such as varying amounts of oxide on the container, impurity in the sample, and uncertainties in the mass of sample and the ice-calorimeter calibration factor, are so small that their combined effect on all enthalpy and heat-capacity values is thought not to have exceeded 0.02 to 0.03 percent.

Two comparisons may be made with results of other observers which are accurate enough to be significant here. In the first place, as pointed out later in this paper (section 5 and figure 8), the heat-capacity values calculated from eq (2) are slightly higher in the temperature region of overlap than the somewhat more accurate values determined with the low-temperature adiabatic calorimeter. A maximum difference of approximately 0.25 percent occurs at about 50° C, but has decreased to approximately 0.1 percent at 100° C. In the second place, over-all checks on the accuracy of the furnace and ice calorimeter, described elsewhere [2], were carried out by measuring the mean heat capacity of water between 0° and 25° C and between 0° and 250° C. These results are lower by 0.05 ± 0.14 percent and by 0.02 ± 0.02 percent, respectively, than the corresponding results obtained earlier at this Bureau of use of two precise adiabatic calorimeters [13, 22].

Considering the foregoing evidence on reliability, an estimate was made that the values of relative enthalpy given by eq (2) can be assigned an uncertainty corresponding to a probable error of ± 0.2 percent. Similarly, it is believed that the probable error representing the uncertainty in heat capacity calculated from eq (2) may be considered to increase from ± 0.2 percent at 100° C to ± 0.4 percent at 800° C. Below 100° C and above 800° C there must be somewhat increased uncertainty in the heat-capacity values obtained from eq (2), owing to the added uncertainty in the derivative of an empirical function near the ends of its range of validity.

Most of the measurements of heat capacities at high temperatures are made by the "drop" method, giving enthalpies referred to either 0° C or room temperature. It is for this reason that the results of the high-temperature measurements on aluminum oxide are compared to the results of other investigators on the basis of the observed enthalpy difference over a large temperature interval, rather than the derived true heat capacities. (The results of the low-temperature measurements of enthalpy were compared on the basis of true heat capacities because the experiments were made over a temperature interval of only a few degrees, so that the results required only very little correction to yield true heat capacities.) Figure 7 gives the deviations of indi-

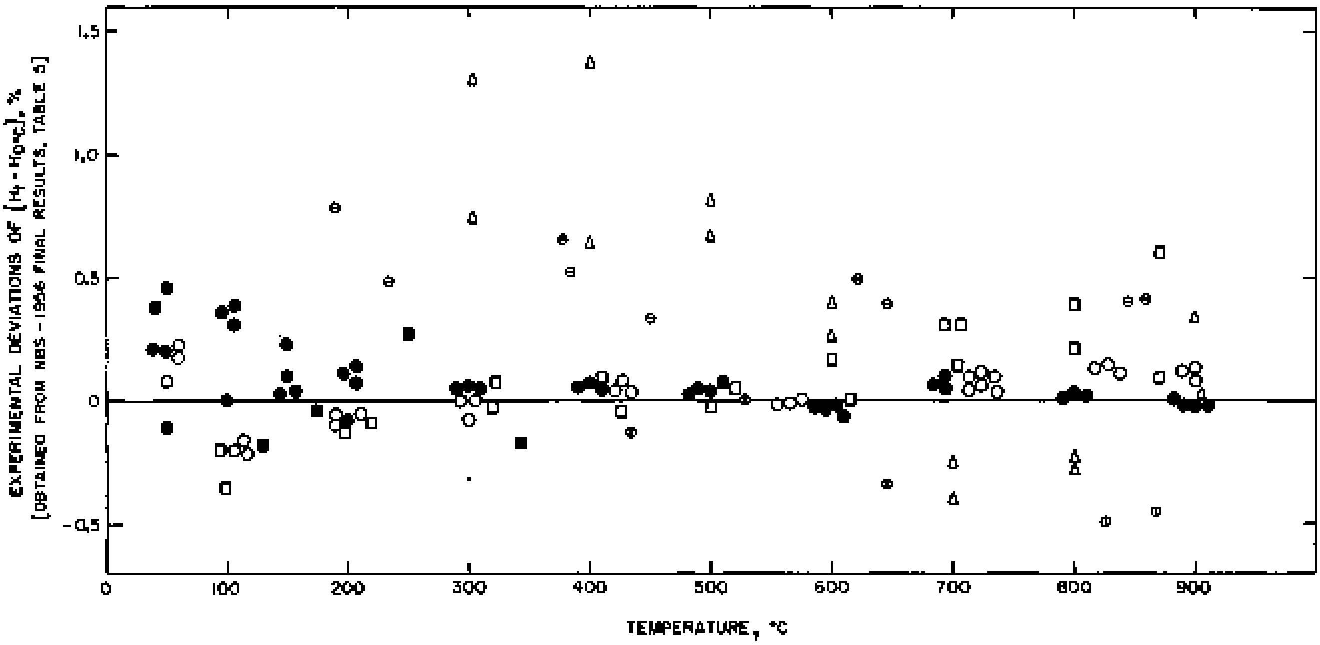

FIGURE 7. *Comparison of the enthalpy, relative to 0° C, of aluminum oxide obtained from table 5 with those from individual high-temperature investigations.*

(Some of the observed points have been displaced horizontally by small amounts in order to avoid the confusion of overlapping. For each of the two sets of NBS data, all observed points for a given temperature are based on the mean empty-container value observed in the same set at that temperature.) ——, 6H9M20L12, NBS–1956 (smoothed); ●, NBS-drop method (1956); ○, NBS-drop method (1947); ■, Oriani and Murphy; □, Grand and Walker; △, Egan, Wakefield, and Elmore; ⊖, Shomate and Naylor; ⦶, Shomate and Cohen.

vidual experimental results of different investigators at high temperatures from the final NBS smoothed values of H_t-H_0 °C obtained from table 5 given later in this paper. In the cases where the measured enthalpy changes were referred to 25° C, the NBS results were used to convert them to the 0° C reference. No attempt has been made to include the results of all investigators because the earlier measurements are generally less accurate. Only measurements reported in the past 20 years are shown. References to earlier high-temperature measurements on aluminum oxide are given in a previous publication [5].

The smoothed results above 100° C, given later in table 5 and serving as the base line in figure 7, are based mostly on eq (2), which was derived from only the present measurements which used the drop method. At temperatures approaching 0° C, values derived from eq (2) are considered to be less accurate than those derived from measurements using the adiabatic calorimeter. There are differences as large as 0.15 percent between the smoothed results using the adiabatic and drop methods in this temperature range where both methods were used. The small positive trend of the deviations of the NBS–1956 results (using drop method) at the lower temperatures are due to the acceptance in this region of the results using the adiabatic calorimeter. A discussion of the relative "weighting" of the two sets of results in this region in formulating table 5 is given later.

In figure 7, the agreement between the NBS results in 1947 [5] and the present results (NBS–1956) is considered generally satisfactory, considering that the 1947 results were obtained with entirely different calorimetric equipment believed to be less accurate. Although the estimated accuracy of the NBS–1947 results was 0.2 percent (except below 100° C), the two sets of results agree within about 0.1 percent except near 100° C. The six experiments of Oriani and Murphy [23] agree with the NBS results with an average deviation of about 0.2 percent, which seems to be about the precision of their measurements. The measurements of Shomate and Naylor [24] are consistently higher than the NBS results, averaging about 0.5 percent. On the other hand, Shomate and Cohen [25], with a different apparatus, agree with the NBS measurements at 400° to 500° C but are 0.5 percent lower between 800° and 900° C. The measurements of Egan et al. [26] start near 300° C about 1 percent higher than those of NBS, the difference decreasing at the higher temperatures. The measurements of Walker et al. [27] agree with the NBS measurements with an average deviation of about 0.2 percent.

All measurements shown in figure 7 except those of Shomate and Naylor were made on samples of synthetic sapphire prepared by Linde Air Products Company and have a probable purity of 99.98 to 99.99 percent. Shomate and Naylor used a sample of natural sapphire. It seems very unlikely that the impurities in the sapphire samples would affect the results shown by as much as 0.1 percent so that the variations in the results by the different observers are probably due to variations in experimental techniques.

5. Final Compilation of Smoothed Thermodynamic Functions

In arriving at a compilation of smoothed values representing the results of both the high-temperature measurements and the low-temperature measurements, it was necessary to decide on "best" values in the temperature range (0° to 100° C) where both methods were used. The differences between the results using the two methods were small, amounting to a maximum of 0.15 percent on $(H_t-H_{0^\circ\,C})$ and 0.25 percent on C_p. Considering that 50° C was the lowest temperature at which measurements were made with the drop method, the equations for $(H_t-H_{0^\circ\,C})$ (eq (2)) and C_p (derivative of eq (2)) which were based *entirely* on the high-temperature results, agree remarkably well with the low-temperature results in the temperature range above 0° C. The authors believe that below 350° K, the results using the adiabatic calorimeter are the more accurate and should be taken as the best NBS results. At higher temperatures, the accuracy of the results using the drop method is more comparable with that using the adiabatic method. Therefore, the drop-method results are given increasing weight above 350° K. The relative weighting is shown in figure 8, which shows deviations of smoothed heat capacity values from the final smoothed values given in table 5. At 400° K and above, the heat capacities in table 5 are based on the high-temperature measurements (eq (10) given later). Below 350° K, the heat capacities are based on the smoothed results using the adiabatic calorimeter. The "compromise" range is from 350° to 400° K.

Table 5 lists smoothed values of the common thermodynamic properties of α-aluminum oxide—heat capacity, enthalpy, entropy, and Gibbs free energy—at a standard pressure of 1 atm and at round temperatures sufficiently close to permit easy interpolation. To be consistent with the data as given in this paper and on which they are based, the values of table 5 are given in terms of the absolute joule as the unit of energy.[5] The values of table 5 below the experimental range (below 13° K) were extrapolated using a Debye heat-capacity function fitted to the experimental values at the lowest temperatures. The equation used was

$$C_p^\circ = 0.937D\left(\frac{198}{T}\right). \qquad (3)$$

D symbolizes the Debye function and $198/T$ its argument. Although the Debye function gives heat capacity at constant volume, it was considered that C_p was sufficiently close to C_v for the present purpose. In the upper temperature range, though measurements were actually made only up to 1,170° K, the properties are given in table 5 up to 1,200° K, their regularity in this temperature range probably justifying the short extrapolation.

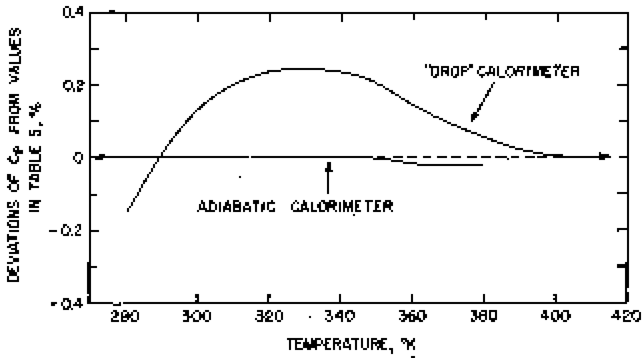

FIGURE 8. *Comparison of smoothed heat capacities obtained by the two methods with the final values given in table 5.*

In order to make the values of table 5 internally consistent, except for small discrepancies caused by rounding, one more significant figure is given than is justified by the accuracy of the measurements. The thermodynamic properties were derived directly from the heat-capacity values below 400° K and from the enthalpy equation above this temperature. It should be noted that in the derivation of the thermodynamic properties it was assumed that the temperature scale employed coincides with the thermodynamic temperature scale (with 0° C=273.16° K, see footnote 4). The two scales are known to differ by small amounts which have not yet been evaluated, and to this extent small errors in the properties are introduced. In deriving the Gibbs free-energy function, it was necessary to assume that the absolute entropy at 0° K is zero, which is probably a safe assumption in the case of a simple ionic crystalline solid such as aluminum oxide.

The values of heat capacity, enthalpy, entropy, and Gibbs free energy were derived using the following thermodynamic relations:

$$C_p^\circ = \left(\frac{\partial H^\circ}{\partial T}\right)_p, \qquad (4)$$

$$H_T^\circ - H_{0^\circ K}^\circ = \int_0^T C_p^\circ dT, \qquad (5)$$

$$S_T^\circ - S_{0^\circ K}^\circ = \int_0^T C_p^\circ dT/T, \qquad (6)$$

$$F_T^\circ - H_{0^\circ K}^\circ = (H_T^\circ - H_{0^\circ K}^\circ) - T(S_T^\circ - S_{0^\circ K}^\circ). \qquad (7)$$

As mentioned earlier, the thermodynamic properties below 400° K were derived from the heat-capacity values, eq (5) and (6) being evaluated by tabular integration, using four-point Lagrangian integration coefficients. Below 13° K, the equations were evalu-

[5] Because it has long been the custom in the applications of chemical thermodynamics to express energies in calories, it was recommended by the Eighth Calorimetry Conference (at Chicago, Illinois, September 11-12, 1953) that the *defined* thermochemical calorie (H=4.1840 abs j) be used in such cases. The four properties of table 5 can readily be converted to this energy unit, if one wishes, by division by this conversion factor.

TABLE 5. *Thermodynamic properties of α-aluminum oxide[a] at 1 atm pressure*

°K=°C+273.16°

T	C°_p	$H^\circ_T-H^\circ_{0^\circ K}$	$S^\circ_T-S^\circ_{0^\circ K}$	$-(F^\circ_T-H^\circ_{0^\circ K})$
°K	abs j deg^{-1} mole^{-1}	abs j mole^{-1}	abs j deg^{-1} mole^{-1}	abs j mole^{-1}
0	0	0	0	0
5	.001	.0014	.0004	.0006
10	.009	.0235	.0031	.0075
15	.030	.1181	.0105	.0394
20	.076	.3588	.0241	.1232
25	.147	.8807	.0471	.2968
30	.253	1.8730	.0829	.6140
35	.438	3.581	.1352	1.151
40	.691	6.374	.2095	2.006
45	1.040	10.650	.3098	3.291
50	1.492	16.941	.4419	5.154
55	2.070	25.792	.6102	7.770
60	2.779	37.86	.8198	11.33
65	3.620	53.80	1.0745	16.04
70	4.582	74.26	1.3773	22.15
75	5.668	99.83	1.7296	29.90
80	6.895	131.19	2.1229	38.63
85	8.248	168.98	2.5915	51.32
90	9.802	213.79	3.1037	65.54
95	11.22	266.04	3.6684	82.45
100	12.84	326.2	4.285	102.3
105	14.54	394.0	4.952	125.4
110	16.32	471.7	5.669	151.9
115	18.16	557.9	6.435	182.2
120	20.06	653.4	7.246	216.3
125	21.99	758.5	8.106	254.7
130	23.96	873.4	9.007	297.5
135	25.96	998.1	9.948	344.8
140	27.96	1132.9	10.928	397.0
145	29.97	1277.7	11.944	454.2
150	31.98	1432.6	12.994	516.6
155	33.99	1597.5	14.078	584.2
160	35.99	1772.4	15.186	657.3
165	37.97	1957.4	16.324	736.1
170	39.94	2152.2	17.487	820.6
175	41.88	2356.7	18.673	911.0
180	43.79	2571	19.88	1007
185	45.68	2795	21.10	1110
190	47.53	3028	22.35	1218
195	49.35	3270	23.61	1333
200	51.14	3521	24.88	1455
205	52.89	3781	26.16	1582
210	54.60	4050	27.46	1716
215	56.26	4327	28.76	1857
220	57.92	4613	30.07	2004
225	59.53	4906	31.39	2157
230	61.10	5208	32.72	2318
235	62.63	5517	34.05	2486
240	64.13	5834	35.38	2658
245	65.59	6158	36.72	2839
250	67.01	6490	38.06	3025
255	68.40	6828	39.40	3219
260	69.76	7174	40.74	3420
265	71.08	7526	42.09	3627
270	72.37	7886	43.43	3840
273.16	73.16	8115	44.27	3979
275	73.62	8250	44.77	4061
280	74.84	8621	46.10	4288
285	76.03	8998	47.44	4522
290	77.19	9381	48.77	4762
295	78.31	9770	50.10	5010
298.16	79.01	10018	50.94	5169
300	79.41	10164	51.42	5263
305	80.47	10564	52.75	5524
310	81.51	10969	54.06	5792
315	82.52	11379	55.38	6066
320	83.50	11794	56.68	6345
325	84.46	12214	57.98	6630
330	85.39	12639	59.28	6924
335	86.29	13068	60.57	7223
340	87.18	13501	61.86	7530
345	88.04	13939	63.14	7844
350	88.88	14382	64.41	8161
360	90.52	15279	66.94	8818
370	92.06	16192	69.44	9500
380	93.51	17120	71.91	10207
390	94.88	18062	74.36	10938
400	96.18	19017	76.78	11694
410	97.39	19985	79.17	12474
420	98.54	20965	81.53	13277

TABLE 5. *Thermodynamic properties of α-aluminum oxide[a] at 1 atm pressure*—Continued

°K=°C+273.16°—Continued

T	C°_p	$H^\circ_T-H^\circ_{0^\circ K}$	$S^\circ_T-S^\circ_{0^\circ K}$	$-(F^\circ_T-H^\circ_{0^\circ K})$
°K	abs j deg^{-1} mole^{-1}	abs j mole^{-1}	abs j deg^{-1} mole^{-1}	abs j mole^{-1}
430	99.64	21956	83.86	14104
440	100.68	22957	86.16	14954
450	101.69	23969	88.44	15827
460	102.63	24991	90.68	16723
470	103.54	26021	92.90	17641
480	104.41	27061	95.09	18581
490	105.24	28109	97.26	19543
500	106.04	29166	99.39	20526
510	106.81	30230	101.49	21530
520	107.54	31302	103.57	22554
530	108.25	32381	105.63	23603
540	108.93	33467	107.66	24668
550	109.59	34559	109.66	25755
560	110.21	35658	111.64	26861
570	110.82	36764	113.60	27987
580	111.40	37875	115.53	29133
590	111.96	38991	117.44	30298
600	112.50	40114	119.33	31482
610	113.03	41241	121.19	32684
620	113.53	42374	123.03	33905
630	114.02	43512	124.85	35145
640	114.49	44654	126.65	36402
650	114.95	45802	128.43	37678
660	115.39	46953	130.19	38971
670	115.82	48109	131.93	40282
680	116.23	49270	133.65	41608
690	116.63	50434	135.35	42954
700	117.02	51603	137.03	44318
720	117.76	53950	140.33	47090
740	118.46	56312	143.57	49929
760	119.12	58688	146.74	52832
780	119.74	61077	149.84	55798
800	120.32	63477	152.88	58827
820	120.88	65889	155.86	61913
840	121.40	68312	158.78	65059
860	121.90	70745	161.64	68264
880	122.37	73188	164.45	71525
900	122.81	75640	167.20	74841
920	123.24	78100	169.90	78212
940	123.64	80569	172.56	81637
960	124.03	83046	175.17	85114
980	124.39	85530	177.73	88643
1000	124.74	88021	180.24	92223
1020	125.07	90520	182.72	95850
1040	125.39	93025	185.15	99530
1060	125.69	95530	187.54	103260
1080	125.98	98050	189.89	107030
1100	126.25	100570	192.21	110860
1120	126.52	103100	194.49	114730
1140	126.77	105630	196.73	118640
1160	127.01	108170	198.93	122590
1180	127.24	110710	201.11	126600
1200	127.46	113260	203.25	130640

[a] Molecular weight, 101.96 [28].

ated analytically, using the Debye heat-capacity function (eq (3)). The relation

$$-(F^\circ_T-H^\circ_{0^\circ K})=\int_0^T (S_T-S^\circ_{0^\circ K})dT \qquad (8)$$

served to check the interconsistency of the tabular integration.

Above 400° K the thermodynamic properties are based entirely on the high-temperature results as expressed by eq (2), except for additive constants (in the enthalpy, entropy, and Gibbs free energy) dependent on the low-temperature results. The corresponding equations for the region above 400° K, derived from eq (2) (except for evaluation of the integration constants from the values tabulated for 400° K), are as follows:

Relative enthalpy in the range 400° to 1,200° K, in absolute joules per mole:

$$H_T^\circ - H_{0^\circ K}^\circ = 148.5704T - 1.7106(10^{-3})T^2$$

$$-46994.87 \log_{10} T + 82{,}146.1. \quad (9)$$

Heat capacity in the range 400° to 1,200° K, in absolute joules per degree per mole:

$$C_p^\circ = 148.570 - 3.421\ (10^{-3})T - 20{,}409.6/T. \quad (10)$$

Entropy in the range 400° to 1,200° K, in absolute joules per degree per mole:

$$S_T^\circ - S_{0^\circ K}^\circ = 342.0960 \log_{10} T - 3.421\ (10^{-3})T$$

$$+20409.6/T - 863.032. \quad (11)$$

Gibbs free energy in the range 400° to 1,200° K, in absolute joules per mole:

$$-(F_T^\circ - H_{0^\circ K}^\circ) = 342.09600\ T \log_{10} T$$

$$+46994.87 \log_{10} T - 1011.6024\ T$$

$$-1.71059\ (10^{-3})\ T^2 - 61{,}736.5. \quad (12)$$

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