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Measurement of the Relative Enthalpy of Pure α-Al_2O_3 (NBS Heat Capacity and Enthalpy Standard Reference Material No. 720) from 273 to 1173 K

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The relative enthalpy of NBS Standard Reference Material No. 720 (99.98 percent pure, single-crystal α-Al_2O_3, a calorimetric heat-capacity standard) was measured over the range 273 to 1173 K by the drop method using a highly precise Bunsen ice calorimeter. Enthalpy data over the same temperature interval were obtained also on the Calorimetry Conference Sample of this substance. These results are believed to be more accurate than similar NBS results on the latter sample published in 1956, and show no significant discontinuity with the NBS data on the same substance that covered the ranges 13 to 380 K and 1173 to 2257 K. The average deviation from the mean for all enthalpy measurements on the SRM 720 sample was 0.017 percent, and the smooth enthalpy values derived from the data were estimated to be accurate to 0.1 percent. The precautions observed in order to minimize measuring errors are described in detail. The data are compared with many sets of the most reliable published data available and new recommended values for the thermodynamic functions of α-Al_2O_3 are presented for the interval 0 to 1200 K.

Key words: Alumina; aluminium oxide; corundum; drop calorimetry; enthalpy; heat capacity standard; specific heat; standard reference material; synthetic sapphire; thermodynamic functions.

1. Introduction

Calorimetric standard substances are necessary in order to facilitate meaningful comparison of different calorimeters or the same calorimeter at different times. One such substance, α-Al_2O_3 ("corundum"), was recommended as a calorimetric heat capacity standard in 1948 by a committee of the Fourth Conference on Low Temperature Calorimetry. It was felt that its ready availability in highly pure form as synthetic sapphire, together with its chemical and mechanical stability, would make it suitable for use from the cryogenic temperature range to near its melting point (2327 K ± 6 K [1][1]). The National Bureau of Standards ("NBS"), as part of its overall responsibility for the maintenance of standards in several areas of science and industry, subsequently undertook the measurement of the heat capacity and enthalpy of a special sample of pure α-Al_2O_3 from approximately 0 to 1200 K [2]. Although the NBS distributed for the Calorimetry Conference, specimens from this sample of α-Al_2O_3 (hereafter called the "Calorimetry Conference Sample") to qualified laboratories, this material was never considered a formal part of the NBS Standard Samples Series.

As the NBS stock of the Calorimetry Conference Sample neared depletion, the question of adopting a more suitable physical form for the synthetic sapphire standard arose. The Calorimetry Conference Sample was in the form of crushed crystals ranging in size from 0.5 to 2. mm. Past experience had shown that the sharp edges and diversity of size of the particles of the old sample often led to considerable difficulty in filling and emptying some sample containers of calorimetrically desirable design. It was felt that cylindrical segments was one form which was compatible with the technology of producing the synthetic sapphire and which promised to avoid the handling difficulty referred to above. The new synthetic-sapphire heat-capacity standard is being incorporated into the NBS Standard Reference Materials Program and will hereafter be referred to as "SRM 720."[2]

This report describes measurements by the "drop" method with a Bunsen ice calorimeter, of the relative enthalpy of SRM 720 from 273 to 1173 K, together with a remeasurement of the Calorimetry Conference Sample. Owing to the improved precision and accuracy

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

[2] All inquiries concerning the availability of this material and details concerning purchases should be directed to the Office of Standard Reference Materials, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234. It is currently supplied, together with a certification of values of its enthalpy and heat capacity in the temperature range 273.15 to 2250 K, at a cost of $56. per unit of 15. grams.

of the present results over those of previous similar NBS measurements on this substance, new light has been shed on the validity of certain corrections to the older NBS data which have been proposed in the literature [10]. Based partly on the present results, a new table of thermodynamic functions for the range 0 to 1200 K has been generated which the authors believe is the most accurate available today. In evaluating the data, use has been made of similar measurements completed recently by other investigators at NBS [22] using a high-temperature (1173 to 2300 K) drop-calorimetric apparatus of entirely different design [3].

2. Samples

Details describing the preparation and analysis of the Calorimetry Conference α-Al_2O_3 have already been given [2]. The new α-Al_2O_3 sample (SRM 720) was produced by the Linde Air Products Company, as was the Calorimetry Conference Sample. Single-crystal rods of pure α-Al_2O_3 were grown using a modification of the Verneuil method [4]. The rods emerged from this process free of any obvious surface contamination and hence in no need of special chemical treatment as was required for the Calorimetry Conference Sample. The individual rods, not all of uniform diameter, were centerless-ground with diamond-impregnated wheels to establish a maximum diameter for the lot (approximately 2. mm). The rods were then bundled and each bundle cut with a diamond-impregnated saw into segments 4. to 6. mm long. No other cleaning process other than removal of grinding residue was carried out. The entire lot, comprising approximately 18 kg of these segments, was then subjected to a thorough visual examination and doubtful pieces (such as those showing discoloration or other possible contamination) were removed.

Specimens for chemical analysis and enthalpy measurement were chosen from the remainder of the lot.[3] Portions of four of these were encapsulated directly for enthalpy measurement. One portion of each of these four SRM 720 specimens was submitted to the Analytical Chemistry Division of the NBS for a qualitative spectrochemical analysis for metallic constituents. A specimen of the Calorimetry Conference Sample was concurrently analyzed by this method. These analyses indicated the purity (by weight) of all specimens to be the same: probably 99.98 percent, with the major impurities being magnesium, calcium, chromium, iron and silicon. An independent analysis was carried out in the same Division of the NBS by atomic absorption spectrometry for magnesium on the surface and throughout the bulk of the SRM 720 specimens. This analysis indicated the surface contamination by magnesium to be 0.0001 percent by weight or less and the bulk of the material to contain 0.001 percent by weight or less. Tests also indicated that adsorbed matter (presumably moisture on the ground surfaces of the SRM 720 sample) did not exceed 0.003 percent by weight. In light of these results, the effect of impurities on the specimen heat capacity in the present measurements is not likely to have exceeded 0.02 percent. This is less than the precision of measurement by at least a factor of two and about an order of magnitude less than the estimated accuracy of measurement. No account of these impurities was taken in processing the data.

3. Calorimetric Procedure

3.1. Calorimeter Proper

In the "drop" method, described elsewhere in great detail [5], a specimen is held in an isothermal zone of a controlled-temperature furnace for a time sufficient to allow it to attain thermal equilibrium. In the series of measurements reported below, it is then dropped into a Bunsen ice calorimeter, which measures the heat liberated by the specimen as it cools to 0 °C. In accurate work the specimen is usually encapsulated together with an inert gas; this procedure prevents any reaction of the specimen with the furnace atmosphere. Then, a second heat measurement at the same initial furnace temperature is made on the empty capsule (or one nearly identical to it), in order to obtain the desired relative enthalpy of the specimen alone (it is assumed that the capsule loses the same amount of heat both times).

The furnace, ice calorimeter and thermometry of this investigation are very similar to those used previously in this laboratory for enthalpy measurements on the Calorimetry Conference Sample [2]. However, the calorimeter has been slightly modified by incorporating glass-tube segments between the calorimeter and the tempering coil ("T" in fig. 6 of [2]) and between the tempering coil and the mercury-accounting system ("B" and "C" in fig. 6 of [2]). Since both these segments are in the form of an inverted "U", they form traps for gas bubbles or water thus assisting in a rapid diagnosis of leaks and improving one's ability to knowledgeably manipulate the calorimetric fluids during assembly and operation. The portion of the mercury transit line within the innermost calorimeter chamber has also been replaced by a glass tube, allowing one to completely clear the transit line for repairs without danger of contaminating the water inside the calorimeter.

One point of technique worth mentioning involves the procedure used to fill the calorimeter. This is now done by using "R" (fig. 6 of [2]) as the evacuation and purified-water port and afterwards introducing mercury from "B" through valve "V" under atmospheric pressure. Great care must be exercised to rid "V" of air before introducing mercury into the calorimeter and to ensure that the mercury does not splash onto the inner calorimeter parts. In this way, as large an amount of mercury as may be desired can be introduced into the calorimeter.

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[3] See section 3.4.a. for details of the sampling procedure followed.

3.2. Thermometry

a. Construction and Application of Thermometer Elements

Since temperature measurement is often the chief source of error in the drop method at high temperatures, considerable care was taken in this investigation to ensure the best possible knowledge of the sample-capsule temperature. In this effort, the control of the furnace temperature, the construction of the thermocouple thermometers and the placement of all thermometer elements were considered.

The central silver core of the furnace which surrounds the sample capsule during temperature equilibration was maintained as nearly as possible at a uniform temperature by the use of three independent heaters (see [5]): besides the main heater, which surrounded the central core, an additional heater surrounded each of the two silver guard segments, one above and one below. The temperature difference between each guard segment and the nearest end of the central silver core was kept less than 0.1 °C as indicated by single-junction chromel-alumel differential thermocouples installed between the guard segments and the core. The drift from any set value of the furnace temperature as indicated by the thermometers in the central core was usually less than 0.01 °C.

The temperature of the silver-core resistance furnace was measured at and below 500 °C with a different, long-stem, encapsulated platinum resistance thermometer than was used in the earlier measurements on the Calorimetry Conference Sample [2]. Above 500 °C, the temperature was measured with each of two new Pt-Pt10Rh thermocouples. In order to verify the thermocouple calibration "in place", both of these thermocouples were also read at and below 500 °C, the range in which the resistance thermometer was considered the primary thermometric element.

The two thermocouples were constructed of 0.015 in o.d. wires of thermocouple-grade Pt and Pt10Rh alloy. A large assortment of these wires was annealed and tested outside the furnace for homogeneity by a temperature-gradient method. This consisted of subjecting each annealed wire at uniformly spaced stations along its length to a much larger temperature gradient than would normally be encountered under operating conditions in the furnace. Wires were chosen from the assortment which yielded, under the above conditions of testing, parasitic emfs no greater than 0.1 μv. Two pairs of these wires were assembled as the two thermocouples. In the furnace, each thermocouple was contained in a length of new Degussa AL 23 alumina tubing and had its junction protected with alumina cement. Both thermocouples and the resistance thermometer were calibrated on IPTS–48, as amended in 1960, by the Temperature Section of the NBS. (All measured temperatures were later converted to IPTS–68.) The resistance thermometer was calibrated at the ice, steam and sulfur points, and was checked at the zinc point with no sensible discrepancy. Its ice point was frequently checked throughout the enthalpy measurements and did not vary from its calibration value.

The resistance thermometer and both thermocouples are introduced at the furnace top. They extend into holes drilled in the silver core parallel to the furnace axis, terminating at midheight of the core (the same height at which the sample capsule is held). Each thermometer element is located at a different azimuth around the silver core, and its immersion in it is sufficient, according to calculation, to allow the element to attain the temperature of the core.

b. Tests of Thermometer and Furnace Performance

"Immersion" tests of all thermometer elements were conducted with the furnace controlled at 400 °C. These tests comprised measurement of the apparent temperature differences between one of the three thermometer elements positioned in its hole at furnace midheight and the other two elements, positioned in their holes, as the latter elements were withdrawn stagewise. This was repeated three times using each time a different one of the elements as the stationary one, and indicated that any temperature difference which may have existed over the upper half of the central silver core was probably less than 0.1 K. The same type of test was conducted with the thermocouples alone at 850 °C, and indicated an apparent temperature difference no greater than 0.2 K over the upper half of the central core.

Intercomparison of the thermocouples and resistance thermometer in place in the furnace at and below 500 °C showed that each of the two thermocouples consistently registered a temperature 0.1 K above that of the resistance thermometer. The resistance thermometer was considered the more reliable of the two types of thermometer in this temperature range and as a result, each thermocouple-determined temperature above 500 °C was corrected by subtracting 0.1 K in processing the raw data.

Though a helium-rich atmosphere is maintained at all times in both the furnace and calorimeter in order to promote temperature equilibration of the capsule, it was felt that a measurement of any temperature difference which might exist (laterally) between a typical sample capsule and the furnace core would be of value in estimating accuracy. Towards this end, one of the two calibrated thermocouples was paired through a common welded junction with a third similarly constructed Pt-Pt10Rh thermocouple and emf readings of each of these couples were taken over the range 0 to 900 °C. This pair of thermocouples was contained in the furnace in the same porcelain tube during comparison. The third couple was then detached, removed from the furnace and its junction attached inside a dummy capsule similar to those used in the measurements on α-Al_2O_3. The capsule was then suspended in exactly the same position in the furnace it normally occupies, and the emf's of both couples were again observed as the furnace assumed constant temperatures in the range 0 to 900 °C. The results indicated that when the temperature of the furnace core was not changing, any temperature difference between the capsule and core at equilibrium was probably always less than 0.1 K and much smaller at the lower furnace temperatures.

How closely a given capsule, initially at room temperature before being lifted into the furnace, reaches temperature equilibrium with the furnace in the time allowed depends upon its composition, contents and the time it has resided in the furnace. (Any appreciable drift of the furnace temperature would, of course, produce additional error, but in practice this drift was negligible.) The time required to reach equilibrium at any temperature can be readily estimated [5, 6] by making at that temperature two enthalpy measurements, one with a grossly inadequate equilibration time. As a result of tests similar to this, up to an hour of equilibration time was allowed in the measurements on α-Al_2O_3 to ensure that the error due to this cause would be safely less than 0.01 percent.

3.3. Sample Containers

The NBS high-temperature enthalpy measurements on the Calorimetry Conference Sample which were reported in 1956 [2] were made with the specimen contained in a capsule composed of the alloy 80 Ni-20 Cr. However, other enthalpy measurements upon this alloy itself in this laboratory [7] later disclosed that it undergoes a solid-solid phase transition of somewhat undetermined character in the vicinity of 600 °C. In order to avoid possible errors in the present α-Al_2O_3 enthalpy data arising from the use of such a capsule material, the present authors decided to adopt a material free of complicating transitions.

The alloy Pt10Rh was chosen. Besides being inert with respect to the sample and the furnace atmosphere (helium), it has no solid-solid transitions of the type thought to introduce errors in enthalpy measurements [8, 14, 15], and maintains structural properties adequate for a capsule material at least up to 1500 °C. Each capsule was constructed from a segment of Pt10Rh tube (1/2 in o.d., 0.008 in wall thickness) with end caps of the same alloy (0.008 in thick) drawn to a cup shape and edge-welded by a heliarc process to the tube segment. The top of each capsule had welded in its center a 1.5 mm o.d. Pt10Rh alloy tube for the purpose of evacuation and introduction of helium gas. Final sealing was accomplished by pinching off and flame-cutting this small-diameter tube, while the absolute pressure of gas in the capsule was held at 1/4 atm.

Implicit in the sample-container design was the consideration that a given container could not be conveniently opened, emptied and resealed. Therefore, all sample and empty capsules were fabricated as nearly as possible to identical dimensions, and each class of capsule component (wall, end caps and evacuation tube) was chosen from contiguous sections of common pieces of stock. Insofar as the stock was homogeneous, each capsule should then contain equal proportions of Pt and Rh. As a further precaution against unsuspected inhomogeneities in the capsule material, two capsules of the seven fabricated were chosen at random to serve as empty capsules (hereafter also referred to as "blanks"). In order to test whether or not the capsules contained significantly different proportions of Pt and Rh, enthalpy measurements on each of the empty capsules were made before the main series of measurements was started.[4] If there were no difference between the enthalpy data for the two empty capsules, it was felt unlikely that there would exist a significant difference between the empty capsule and sample capsule enthalpies.

3.4. Experimental Program

a. Sampling

It was desired that the enthalpy measurements be representative of those one would obtain for any specimen chosen at random from the lot of material known as SRM 720 (18 kg of rod segments in all). Towards this end, the measurements were made on four specimens chosen in the following manner (see fig. 1): The entire lot of rod segments was apportioned into 24 units (designated numerically 1 to 24) of approximately equal mass. Each of these was subdivided into pairs, each pair member ("portion") receiving the same numerical designation as the parent unit. Four groups of six units each were then formed by choosing at random from these 24 numbered units. Each of the four groups thus corresponded to twelve portions of rod segments labeled pairwise and referred to altogether as a "sublot." Each of the four sublots was then halved by eliminating one portion chosen at random from each numbered pair. Five grams of rods was then extracted from each

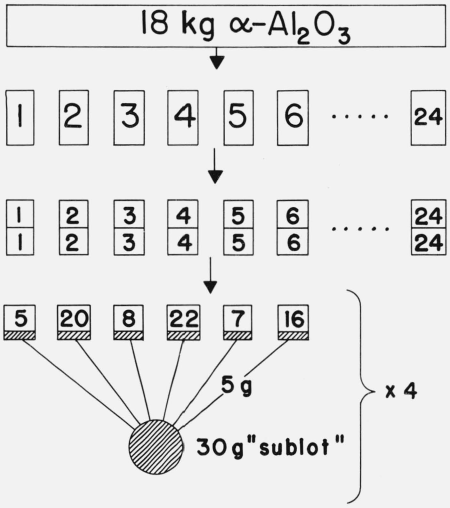

FIGURE 1. *Sampling procedure followed to obtain four random specimens of SRM720.*

See also text, section 3.4.a.

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[4] See section 4.1. for a description and results of this test.

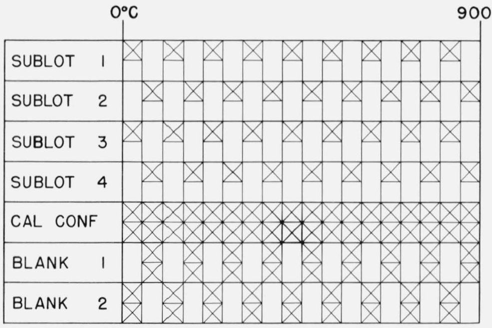

FIGURE 2. *Schedule of measurements.*

Each "X" indicates a single enthalpy measurement. Temperatures are spaced about 50 K apart from 0 to 900 °C. All measurements at any one temperature were completed before proceeding to another temperature.

of the six remaining portions of each sublot and mixed together to yield four 30-g specimens, each characteristic of a different sublot. Hereafter, a reference to "sublot X" will imply "the specimen characteristic of sublot X." Each of four sample containers was then filled with rods from a different one of the 30-g specimens, the remainder of the specimens being retained for chemical analysis. The correspondence between numbers used in the sampling procedure and individual portions of SRM 720 was then dropped and all material save the specimens for measuring and analysis was mixed together. In addition, one sample container was filled with a specimen of the Calorimetry Conference Sample.

b. Schedule of Measurements

It was desirable to complete the enthalpy measurements on the seven capsules (four containing specimens of SRM 720, one containing a specimen of the Calorimetry Conference Sample, and two being blanks) with minimum effort and yet obtain sufficient data to allow analyzing the enthalpy data for any one capsule over the entire temperature range, 0 to 900 °C. Therefore the schedule of measurements described in figure 2 was followed in the main. The enthalpy measurements, indicated individually by "X," were made at temperatures spaced at about 50 K intervals. All measurements at any one temperature required by this program were completed before proceeding to the next temperature (randomly selected from those previously chosen for measurements). At least one duplicate measurement (on the Calorimetry Conference Sample or a blank) was included in each day's work as a daily monitor of precision.

4. Results

4.1. Measurements

Before starting the main series of measurements, a few trial enthalpy measurements were made in an effort to determine whether the blanks and sample containers were sufficiently close in their alloy composition to justify the substitution of enthalpy data on the fabricated blanks for the desired data on the

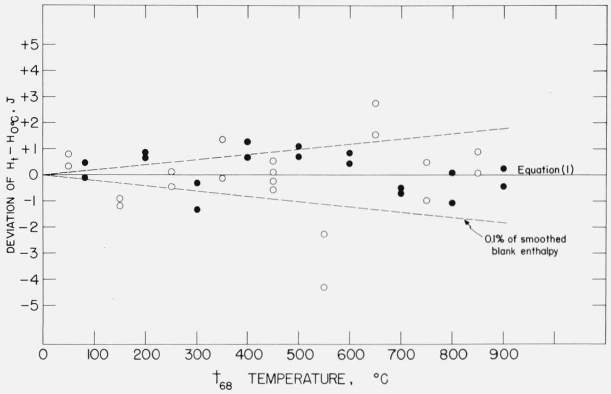

FIGURE 3. *Deviation of Pt10Rh blank enthalpy data from smoothing function (eq (1)).*

●, Blank 1; ○, Blank 2.

(empty) sample containers. If there were a significant difference between the two types of containers, this would not only manifest itself as systematic differences between the enthalpy data for the individual sublots of SRM 720, but might also show up as a difference between the enthalpy data for the blanks themselves. (For example, a variation of 0.1 percent in the rhodium content of the blanks would introduce approximately a 0.1 percent discrepancy among their enthalpy values, which should be easily detectable at 900 °C.)

Triplicate enthalpy measurements on both blanks were made at 900 °C, and indicated that within the precision of thermal measurement (see fig. 3), the two blanks could be considered to have identical compositions. Triplicate enthalpy measurements at 900 °C on each of three of the four SRM 720 sublots were also made, using the enthalpy value for the blank determined above, and these also agreed with each other within the precision of measurement (0.01 percent in this case). With this foundation, the main series of enthalpy measurements was begun.

The enthalpy data for the blanks are given by table 1 and represented in figure 3. Since no irregularities were anticipated in the enthalpy-temperature function of the blanks, it was decided to substitute smoothed blank enthalpy values for the observed blank data in all calculations, thereby reducing the effect of random errors in the blank data. The base line of figure 3 represents the following equation, which was chosen to smooth the data in columns 2, 3, and 4 of table 1:

$$H_t - H_{0\,^\circ\mathrm{C}} = (4.529744)10^{-8}t^3 + (8.068654)10^{-5}t^2 + (1.901653)t - (34.94647)\left(\frac{t}{T}\right).$$

$$H, J;\ T, K = t, ^\circ\mathrm{C} + 273.15, \qquad \text{(IPTS–68)} \qquad (1)$$

The actual enthalpy measurements were made at temperatures differing slightly from those of column 2, and the enthalpy values of columns 3 and 4 include an adjustment averaging 0.1 percent and arrived at using the known masses and specific heats of the two

TABLE 1. *Enthalpy data for two empty Pt10Rh capsules ("blanks")*

Date	Temperature [a]	$H_t - H_{0^\circ\,C}$ (measured)		Measured minus smoothed [c]
		Blank 1	Blank 2 [b]	
1968	°C	J	J	J
15 Oct.	50.00		90.67	+0.79
15 Oct.	50.00		90.21	+0.33
24 Sept.	86.00	156.26		+0.46
24 Sept.	86.00	155.69		−0.11
20 Sept.	150.00		273.57	−1.26
20 Sept.	150.00		273.92	−0.91
19 Nov.	200.00	369.79		+0.64
19 Nov.	200.00	370.00		+0.85
10 Dec.	250.00		464.00	−0.46
10 Dec.	250.00		464.57	−0.11
13 Nov.	300.00	560.37		−0.32
13 Nov.	300.00	559.35		−1.34
9 Oct.	350.00		659.13	+1.35
9 Oct.	350.00		657.64	−0.14
18 Sept.	400.00	756.37		+0.67
18 Sept.	400.00	756.97		+1.27
25 Nov.	450.00		854.99	+0.53
5 Dec.	450.00		854.56	+0.10
5 Dec.	450.00		853.88	−0.58
5 Dec	450.00		854.21	−0.25
6 Nov.	500.00	955.15		+1.09
6 Nov.	500.00	954.75		+0.69
3 Oct.	550.00		1050.18	−4.32
3 Oct.	550.00		1052.21	−2.29
12 Sept.	600.00	1156.64		+0.83
12 Sept.	600.00	1156.24		+0.43
16 Oct.	650.00		1259.54	+1.54
22 Oct	650.00		1260.75	+2.75
15 Nov.	700.00	1360.59		−0.50
15 Nov.	700.00	1360.38		−0.71
10 Oct.	750.00		1465.60	+0.48
10 Oct.	750.00		1464.14	+0.98
13 Sept.	800.00	1570.19		+0.09
13 Sept.	800.00	1569.03		−1.07
2 Oct.	850.00		1676.96	+0.89
2 Oct.	850.00		1676.14	+0.07
26 Sept.	900.00	1783.31		+0.25
26 Sept.	900.00	1782.61		−0.45

[a] International Practical Temperature Scale of 1968 [9].

[b] The masses of Pt, Rh, and He in this capsule were adopted as "standard" values in processing all blank and sample-capsule data.

[c] Derived from eq (1) and columns 3 and 4. See text.

chemical elements in the capsule to reflect these differences.[5] In addition, the "Blank 1" enthalpy values (column 3) have been adjusted (by an average of 0.1 percent) to correct for the small differences between the masses of components of the two blanks.

Table 2 presents the results of the enthalpy measurements on the four specimens of SRM 720 and the Calorimetry Conference Sample. In converting the directly observed quantity (mass of mercury forced into the calorimeter during an experiment) to equivalent energy units, the conversion factor 270.49 J/g(Hg) was used. This factor differs slightly (0.004 percent) from the "ideal" calibration factor [5] in that it accounts for the finite compressibility of the particular ice calorimeter used in this work. The gross (sample-plus-container) heat values were measured at temperatures differing by an average of 0.3 K but no more than 1. K, from the temperatures of column 2. The adjustments to the gross values to account for these temperature differences averaged 0.1 percent and were made using the known mass and best values for the specific heat of the α-Al_2O_3 and each capsule component.[6] Columns 3 and 5 list the corrected gross values for the five specimen-containing capsules, while column 4 indicates on which specimen of the SRM 720 sample the corresponding value in column 3 was obtained. In addition, all gross enthalpy values include an adjustment (averaging 0.2 percent) to account for the difference in the mass of parts of each sample-containing capsule and the empty capsule which was chosen as a "standard." The net measured heats (columns 6 and 8) were obtained by subtracting from each gross value the appropriate smooth blank value (eq (1)), and converting this difference to a molar basis. The blank values constituted from 10 to 15 percent of the gross measured heat.

4.2. Smoothing the Data

As steps toward the goal of finding the best values for the relative enthalpy and other thermodynamic functions of α-Al_2O_3 that are consistent with the data of this investigation, two enthalpy smoothing functions of temperature are derived in this section. The first such function (eq (2)) is the best analytical form found for the 0 to 900 °C enthalpy data for the SRM 720 sample only. From the deviations of all the data (table 2, columns 7 and 9) from this function, it is concluded that the Calorimetry Conference and SRM 720 samples of α-Al_2O_3 are calorimetrically equivalent from 0 to 900 °C. The small systematic deviations of the data from this function are considered but it is not felt that they can with any confidence be attributed to the sample. The second smoothing function (eq (3)) was fit to the present SRM 720 data and other precise NBS enthalpy data on this substance from 150 to 2257 K. It fits the drop calorimeter enthalpy data of the present work substantially as well as the first smoothing function (eq (2)) and yields improved agreement with the results of precise high-temperature adiabatic calorimetry. It has therefore been chosen as a suitable representation of the present NBS data over this extended temperature range. Complete details concerning this second smoothing function are given below.

Several forms of smoothing function for all the enthalpy data from 0 to 900 °C (column 6, table 2) on the SRM 720 sample alone were investigated. The form of eq (2) seemed to fit the data best of all forms tried, and its coefficients were determined by the method of least squares.[7] Three constraints were imposed in the fitting process, namely that the enthalpy relative to 273.15 K should vanish at this temperature and that the first and second temperature derivatives of the enthalpy function at 298.15 K should be equal to the respective values given by the NBS 1956 α-Al_2O_3 data [2]. All data were equally weighted

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[5] The source of specific heat data for making these corrections was [11].

[6] Specific heat data for α-Al_2O_3 were taken from [2]; for capsule components, from [11].

[7] All curve-fitting operations described in this paper were performed on a UNIVAC-1108, programmed in this case in OMNITAB.

TABLE 2. *Enthalpy data (referred to 0 °C) on two samples of pure α-Al_2O_3*

Date	Temperature[a]	Gross measured heat, $H_t - H_{0°C}$			$H_t - H_{0°C}$ (SRM 720)		$H_t - H_{0°C}$ (Cal. Conf.)	
		SRM 720 sample	SRM 720 specimen No.[b]	Cal. Conf. sample[c]	Net meas. heat	Net meas. minus SRM 720 smooth[f]	Net meas. heat	Net meas. minus SRM 720 smooth[g]
1968	°C	J		J	$J\ mol^{-1}$[e]	$J\ mol^{-1}$[e]	$J\ mol^{-1}$[e]	$J\ mol^{-1}$[e]
14 Oct	50.00			484.47			3942.74	−2.31
14 Oct	50.00			484.83			3946.33	+1.28
14 Oct	50.00	611.39	3		3952.44	+7.39		
15 Oct	50.00	667.08	1		3948.61	+3.56		
25 Sept	86.00			864.30			7079.32	−9.79
25 Sept	86.00			865.97			7096.01	+6.90
25 Sept	86.00	1097.05	4		7085.87	−3.24		
25 Sept	86.00	1180.47	2		7079.99	−9.12		
20 Sept	150.00			1591.64			13157.54	−0.87
20 Sept	150.00			1592.46			13165.74	+7.33
24 Sept	150.00	2008.71	3		13140.80	−17.61		
24 Sept	150.00	2199.00	1		13163.18	+4.77		
18 Nov	200.00			2195.05			18244.36	+13.44
18 Nov	200.00			2194.86			18242.46	+11.54
19 Nov	200.00	2791.02	4		18232.19	+1.27		
19 Nov	200.00	3009.20	2		18241.51	+10.59		
9 Dec	250.00			2819.13			23527.82	+1.48
9 Dec	250.00			2818.13			23517.83	−8.51
9 Dec	250.00	3904.14	1		23530.74	+4.40		
10 Dec	250.00	3569.71	3		23534.20	+7.86		
12 Nov	300.00			3464.76			29017.42	+16.80
12 Nov	300.00			3464.62			29016.02	+15.40
13 Nov	300.00	4413.56	4		29004.96	+4.34		
13 Nov	300.00	4760.00	2		29015.27	+14.65		
8 Oct	350.00			4122.59			34620.32	−0.68
8 Oct	350.00			4123.54			34629.82	+8.82
8 Oct	350.00	5226.98	3		34629.25	+8.25		
9 Oct	350.00	5721.27	1		34639.17	+18.17		
18 Sept	400.00			4796.87			40379.30	+16.58
19 Sept	400.00			4796.14			40372.01	+9.29
19 Sept	400.00	6597.22	2		40362.17	−0.55		
19 Sept	400.00	6117.54	4		40364.71	+1.99		
20 Nov	450.00			5479.67			46215.02	+8.24
20 Nov	450.00			5479.99			46218.22	+11.44
20 Nov	450.00	7609.59	1		46211.62	+4.84		
6 Dec	450.00	6951.16	3		46205.93	−0.85		
6 Dec	450.00	6950.75	3		46202.82	−3.96		
5 Nov	500.00			6171.42			52131.78	−6.63
5 Nov	500.00			6171.77			52135.27	−3.14
6 Nov	500.00	7830.44	3		52115.00	−23.41		
7 Nov	500.00	7878.10	4		52125.18	−13.23		
7 Nov	500.00	8497.71	2		52123.09	−15.32		
3 Oct	550.00			6874.61			58154.44	+8.51
3 Oct	550.00			6871.31			58121.47	−24.46
3 Oct	550.00	8727.55	3		58152.84	+6.91		
3 Oct	550.00	9553.62	1		58142.20	−3.73		
12 Sept	600.00			7581.18			64202.19	−17.86
12 Sept	600.00			7582.00			64210.39	−9.66
13 Sept	600.00	9681.84	4		64185.19	−34.86		
13 Sept	600.00	10446.84	2		64196.67	−23.38		
16 Oct	650.00	11541.10	1		70346.35	−6.89		
22 Oct	650.00			8297.90			70342.57	−10.67
22 Oct	650.00			8298.69			70350.46	−2.78
22 Oct	650.00	10539.48	3		70342.88	−10.36		
14 Nov	700.00			9022.33			76550.98	+11.63
14 Nov	700.00			9022.68			76554.48	+15.13
14 Nov	700.00	11529.07	4		76546.03	+6.68		
15 Nov	700.00	12443.30	2		76572.88	+33.53		
10 Oct	750.00	13568.45	1		82798.49	+25.14		
11 Oct	750.00			9752.44			82806.77	+33.42
11 Oct	750.00			9752.49			82807.27	+33.92
11 Oct	750.00	12392.34	3		82815.68	+42.33		
17 Sept	800.00			10482.19			89049.46	−1.57
17 Sept	800.00			10483.14			89058.95	+7.92
17 Sept	800.00	13399.26	4		89051.64	+0.61		
17 Sept	800.00	[d]14446.74	2		[d]88971.56			
1 Oct	850.00			11221.95			95382.28	+13.40

TABLE 2. *Enthalpy data (referred to 0 °C) on two samples of pure α-Al_2O_3* — Continued

Date	Temperature[a]	Gross measured heat, $H_t-H_{0°C}$			$H_t-H_{0°C}$ (SRM 720)		$H_t-H_{0°C}$ (Cal. Conf.)	
		SRM 720 sample	SRM 720 specimen No.[b]	Cal. Conf. sample[c]	Net meas. heat	Net meas. minus SRM 720 smooth[f]	Net meas. heat	Net meas. minus SRM 720 smooth[g]
1 Oct	850.00	…	…	11221.66	…	…	95379.38	+10.50
1 Oct	850.00	14260.10	3	…	95372.38	+3.50	…	…
2 Oct	850.00	15616.47	1	…	95365.82	−3.06	…	…
26 Sept	900.00	16502.65	2	…	101705.48	−18.45	…	…
27 Sept	900.00	…	…	11963.85	…	…	101726.29	+2.36
27 Sept	900.00	…	…	11963.56	…	…	101723.39	−0.54
27 Sept	900.00	15293.80	4	…	101710.81	−13.12	…	…

[a] International Practical Temperature Scale of 1968 [9]. $T, K=t$, °C + 273.15.

[b] Mass of specimen 4 = 13.5440 g; mass of specimen 3 = 13.4534 g; mass of specimen 2 = 14.7566 g; mass of specimen 1 = 14.9045 g. (All masses corrected to a vacuum basis.)

[c] Mass of Calorimetry Conference Sample = 10.2043 g.

[d] This datum not included in smoothing as ice mantle had melted through.

[e] Molecular weight = 101.9612 [12].

[f] Derived from column 6 and eq (2).

[g] Derived from column 8 and eq (2).

save one at 800 °C which was rejected as it resulted from a bad experiment (the ice mantle had melted through).

Equation (2) was then used to calculate the smoothed enthalpies corresponding to the temperatures of column 2, table 2. These were subtracted from columns 6 and 8 to yield columns 7 and 9, respectively.

$$H_T-H_{273.15}=(3.0060629)\ 10^{-3}T^2+(1.2536843)\ 10^2T$$
$$+(7.8733009)\ 10^6T^{-1}-(6.3432750)\ 10^8T^{-2}$$
$$+(1.9579860)\ 10^{10}T^{-3}-(5.5751699)\ 10^4.$$
$$H,\ J\ \mathrm{mol}^{-1};\ T,\ \mathrm{K\ (IPTS{-}68)} \qquad (2)$$

The standard deviation of the SRM 720 data from this equation is 15.7 J mol^{-1}.

The deviations from eq (2) of the enthalpy data for all specimens of SRM 720 are shown also in figure 4. This figure shows, within the precision of measurement, no systematic deviation between the four specimens of SRM 720, and so helps to confirm the homogeneous character of the bulk sample from which the specimens were chosen. Individual fits of the data for each of the four specimens were also tried, but these did not differ significantly from the fit of the combined data. The current enthalpy data on the Calorimetry Conference Sample (table 2) also appear in figure 4 and show that the two samples were calorimetrically indistinguishable over the temperature range 0 to 900 °C. Thus, at least over this temperature range, both the newer standard sample (SRM 720) and the older Calorimetry Conference Sample will serve as equivalent heat capacity standards.

Examination of figure 4 shows that it has not been possible to fit the enthalpy data within the precision of measurement, which was better than 0.05 percent at virtually all temperatures. In fact, the nonsmoothness in the present enthalpy data between 600 and 750 °C appears

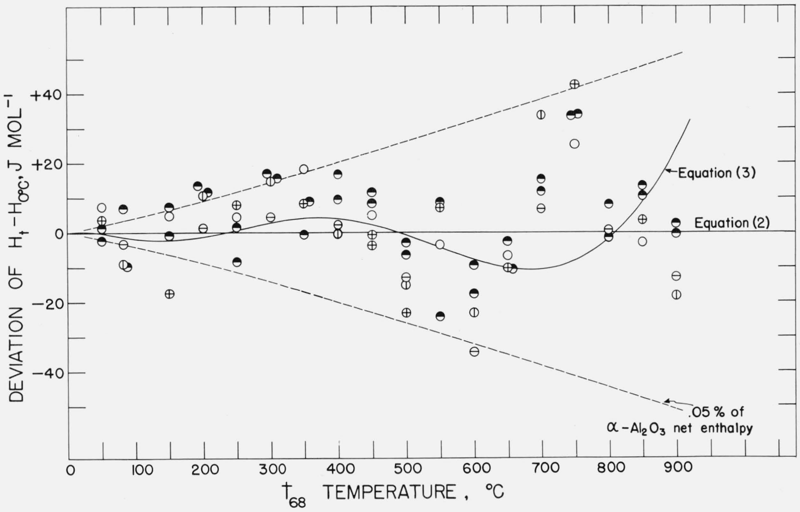

FIGURE 4. *Deviation of α-Al_2O_3 enthalpy data of the present investigation and of eq (3) from least-squares fit of SRM720 data alone (eq (2)).*

SRM720 Sublots: ○, No. 1; ⦶, No. 2; ⊕, No. 3; ⊖, No. 4; ◒, Calorimetry Conference Sample. ———, eq (3).

qualitatively similar to one in the 1956 NBS enthalpy data on the Calorimetry Conference Sample [2]. It is appropriate to examine plausible causes of these small systematic deviations among the different sets of data, in an effort to decide whether these deviations should be accounted for in the final smoothed values, or whether the deviations can be ascribed wholly to systematic error.

In 1963, Ginnings [10] observed that the smoothness of the 1956 NBS α-Al_2O_3 enthalpy data [2] could be considerably improved if it were assumed that all those enthalpy data above 600 °C were in error (too high) by about 100. J mol^{-1}. He reasoned that the sample container material (80 Ni-20 Cr), which is known to undergo a transition near 600 °C, cooled through the transition more rapidly when empty than when containing a sample, as a consequence displaying (when empty) more hysteresis and thus evolving to the calorimeter a *smaller* fraction of the container's (supposed) equilibrium heat of transition. (Any such discrepancy is ordinarily not taken into account in calculating the net heat evolved by the sample alone.) To support his argument, Ginnings noted similar effects in enthalpy measurements using two other container materials undergoing transition in the range of measurement.

The earlier 1947 data of Ginnings and Corrucini [6], also obtained with an 80 Ni-20 Cr sample container and being of equal estimated accuracy and superior precision in relation to the 1956 data, also merit consideration. These earlier data can be interpreted as displaying a similar unsmoothness, of, however, half the magnitude of that observed in the 1956 data. Presumably, the earlier data could also be empirically corrected using Ginnings' reasoning and assuming, in addition, substantially different rates of cooling in the 1947 and 1956 series of measurements.

In 1967, McDonald [27] claimed to have found evidence supporting Ginnings' hypothesis. This came as a result of his remeasurement by drop calorimetry of the enthalpy of pure magnesium from 404 to 1300 K. This remeasurement employed new sample-container materials (Ta and Pt10Rh), eliminating the stainless steel container material used in the previous measurements of McDonald and Stull [54]. However, in the same paper [27] McDonald also published new results on the enthalpy of α-Al_2O_3 above 500 °C which were significantly *higher* (deviating by an average of +0.7 percent from the published NBS results [2]) than previously published results of McDonald and Stull on α-Al_2O_3 which used either stainless steel as a container material [54] or other unspecified types of container material [32, 55] and which were, on the average, with ± 0.3 percent of the NBS results [2] above 500 °C. This would seem at best to call into serious doubt the value of the above evidence for an error from the use of 80 Ni-20 Cr of the sign Ginnings had postulated.

Ginnings' reasoning is qualitatively sound for a container material exhibiting a first-order transition. However, the transition in the alloy 80 Ni-20 Cr is not thought to be of this type; one investigation [7] indicates that as it is heated through its transition temperature, there is no latent heat, yet clearly a rather abrupt translation upward of the heat-capacity curve. (From more precise data, Douglas and Harman [13] noted the same effects in three similar alloys of approximate composition, 76Ni-15Cr-9Fe.) In such a situation one might suppose that whenever the alloy cools too rapidly through the transition region, it may undergo the transition incompletely, as a consequence following an average heat-capacity curve which is closer to the high curve of the high-temperature form, with the evolution of *too much* heat to the calorimeter.

In contrast to the earlier sample-container material, the Pt10Rh used in the present investigation is believed to be free of complicating transitions, yet the nonsmoothness in the present enthalpy data occurs at about the same temperature, and to about 75 percent of the magnitude noted by Ginnings in the 1956 α-Al_2O_3 data. This same behavior can be noted in the enthalpy measurements on one of the blanks of the present work (table 1 and fig. 3); however, substitution of the unsmoothed blank enthalpy values for the smoothed values used in the computation of columns 6 and 8 of table 3 has no appreciable effect upon the systematic deviations of the SRM 720 enthalpy data.

The authors believe that the combined evidence discussed in the foregoing paragraphs is entirely too contradictory to permit attributing, in any of the cases cited, the major part of enthalpy-data nonsmoothness to the use of a container exhibiting a transition. This effectively bars the estimation, using this evidence, of the order of magnitude and even the sign of an error of this type. This is especially true of all samples measured in 80 Ni-20 Cr containers, and leads to the conclusion that Ginnings' "corrected" equation [10] for representing the 1956 NBS α-Al_2O_3 enthalpy data [2] is intrinsically arbitrary and hence not valid.

One conceivable explanation for the nonsmoothness of the data deviations from eq (2) was explored. This nonsmoothness is really quite small, being detectable principally because of the high precision of the present data. A fit to the data was therefore obtained for an empirical combination of Einstein functions, which might be expected to approximate in form more closely the true (unknown) partition function of the α-Al_2O_3; this device, however, failed to yield a smooth function that followed the data more closely than eq (2).

If the nonsmoothness of the data were indeed due to the α-Al_2O_3 samples themselves, one might also expect anomalous behavior of other structure-dependent properties in the same temperature region. It is significant in this context that recent measurements of the electrical conductivity of single-crystal α-Al_2O_3 comparable in purity to that of the present samples [51] have shown no evidence of unexpected behavior between 500 and 800 °C.

The authors believe that more likely contributing causes to the nonsmoothness (in both the present and the 1956 NBS enthalpy data for α-Al_2O_3) are possible systematic error in the realization of the International Practical Temperature Scale of 1968 in these measurements and especially the differences between this Scale and the true thermodynamic one. It may be noted that temperature errors no greater than 0.2 or 0.3 K between 600 and 800 °C could explain the unsmoothness. In fact, the use in the IPTS–68 of a simple quadratic equation to interpolate temperatures in this range may introduce comparable errors, but of unknown magnitude and sign. It is therefore concluded that eq (2) without modification is a suitable representation of the 0 to 900 °C enthalpy data reported in this paper.

In addition to the specific-heat data available from low-temperature calorimetry [2], results have recently become available [22] of very-high-temperature (1173–2257 K) enthalpy measurements on specimens of SRM 720 chosen in the same fashion as those of the present work. An attempt was made to represent some of the NBS low-temperature heat capacity data and all the NBS high-temperature data in a single analytical form. The following expression for the enthalpy of α-Al_2O_3 has been developed by fitting by the method of least squares with a single equation a group of data comprising (1) Enthalpy increments down to 150 K calculated from smoothed low-temperature heat capacity data [2], (2) Enthalpy data up to 1173 K from the present work and (3) Enthalpy data up to 2257 K from the very-high-temperature study referred to above [22]:

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

$$A=+(.66253104)\ 10^8$$
$$B=-(.45423801)\ 10^7$$
$$C=-(.547559893)\ 10^5$$
$$D=+(.257407602)\ 10^3$$
$$E=-(.85751721)\ 10^{-1}$$

H, J mol^{-1}

T, K (IPTS–68) (3)

$$F=+(.42990626)\ 10^{-4}$$
$$G=-(.115191979)\ 10^{-7}$$
$$H=+(.126350649)\ 10^{-11}$$
$$K=+(.25819702)\ 10^6$$

The enthalpy data for α-Al_2O_3 reported in this paper differ from eq (3) by no more than 0.2 percent below 150 °C and by no more than 0.1 percent above 150 °C. The observed data for SRM 720 have a standard deviation from this equation of 21.1 J mol^{-1}.

4.3. Comparison of NBS α-Al_2O_3 Enthalpy and Heat Capacity Data With Data From Various Sources

A comparison of the present NBS thermal data on α-Al_2O_3 with the thermal data of other investigators for this substance will illustrate the improvements in the NBS measurements and the relationship of the present NBS thermal data to the former [2] and the present (table 4) NBS-recommended thermodynamic functions for α-Al_2O_3. This comparison will also provide insight for estimating the overall accuracy of the present NBS enthalpy data for α-Al_2O_3.

Figure 5 compares all NBS enthalpy data between 0 and 900 °C obtained on high-purity α-Al_2O_3 using Bunsen ice calorimeters, with the currently recommended NBS values (table 4, this work). Data are shown for 24 temperatures (indicated by vertical bars which are not to be interpreted as error bounds) and are displaced horizontally by small amounts where necessary to ensure clarity. In addition, two earlier NBS smoothing functions for the enthalpy of α-Al_2O_3 are shown.

These data encompass three different samples of α-Al_2O_3, two different container materials and two different designs of furnace and calorimeter. The three samples of α-Al_2O_3 were obtained over a twenty-year

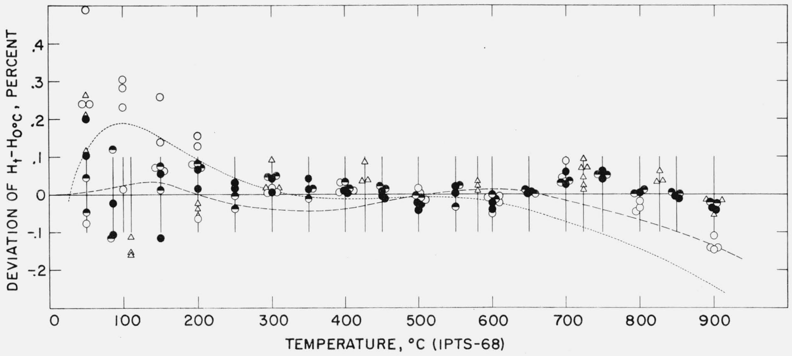

FIGURE 5. *Comparison with table 4 of α-Al_2O_3 enthalpy relative to 0 °C for NBS ice-calorimeter data.*

Base line is table 4; ●, SRM720 sample (this work); ◓, Calorimetry Conference sample (this work); ○, Calorimetry Conference Sample, Furukawa, Douglas et al. (1956) [2] : △, Ginnings and Corruccini (1947) [6]; — — —. Furukawa, Douglas et al. (smoothed values) (1956) [2]; ------, Smooth values of [2] (1956) as corrected by Ginnings (1963) [10]. The vertical bars (not error bounds) locate the common temperature of each group of points.

TABLE 3. *Average spread of NBS enthalpy data for α-Al_2O_3 between 0 °C and 900 °C*

	Ginnings & Corruccini (1947) [6]	Furukawa, Douglas et al. (1956) [2] (Cal. Conf.)	NBS (1970) (this work)	
			(Cal. Conf.)	(SRM 720)
Empty container	1.6 *J*	4.3 *J*	0.8 *J*	0.8 *J*
Container plus sample	1.8 *J*	4.1 *J*	0.7 *J*	1.3 *J*

period from the Linde Air Products Co. Of the second sample obtained (the Calorimetry Conference Sample), two different specimens are represented: the one used in the 1956 NBS enthalpy measurements [2] and the specimen of the present investigation. Four different specimens of the third sample (SRM 720) are represented; see also figure 4. The results of Ginnings and Corruccini [6] as well as those of Furukawa, Douglas et al. [2] were obtained with specimens encapsulated in Nichrome V (80 Ni-20 Cr) whereas Pt10Rh alloy was chosen as the capsule material for the present investigation. Also, Ginnings and Corruccini [6] employed a different design of furnace and calorimeter than has been employed at the NBS starting with the work of Furukawa, Douglas et al. [2].

Notwithstanding these apparatus and sample differences, figure 5 indicates agreement within 0.1 percent among all the enthalpy data save at the extremes of the temperature range. The present enthalpy measurements, however, are more precise than the prior NBS results, as can be seen in table 3. The positive deviation above 650 °C of the currently recommended NBS enthalpy values (table 4) from those of the 1956 NBS table [2] and from Ginnings' proposed corrected values [10] is upheld by the results of recent enthalpy measurements at NBS on α-Al_2O_3 [22] at still higher temperature (1175–2257 K).

In assessing the accuracy of any experimental technique used to measure a specific property, it is of value to have at hand the results of measurements by other reliable investigators of the same property (or one closely related to it) by different techniques. Fortunately, such measurements do exist for α-Al_2O_3. Within the past ten years, dramatic advances in measuring and temperature-control instrumentation have made feasible the operation of high-temperature adiabatic calorimeters. This technique, which has been extended to temperatures at least as high as 1300 K [43], is at a considerable disadvantage at the higher temperatures due to errors arising from radiative heat transfer. Properly designed and operated, however, these calorimeters are capable of yielding in the lower temperature range (say, below 700 K) heat-capacity data of 0.1 percent accuracy.

Three sets of heat capacity data on α-Al_2O_3 (Calorimetry Conference Sample) due to high-temperature adiabatic calorimeters of West and Ginnings (intermittent heating) [16], Martin and Snowdon (continuous heating) [40, 44] and Grønvold (intermittent heating) [17] have been chosen as being probably the most reliable ones in this temperature range. These are compared in figure 6 with heat capacities derived from the present NBS enthalpy data on α-Al_2O_3. The base line of figure 6 is the heat capacity obtained by differentiating eq (2), above. The mean heat capacity values calculated from the present enthalpy measurements at adjacent temperatures and corrected for curvature (solid circles) show an average deviation of 0.23 percent from the base line. The data of Martin and Snowdon [18, 40], which comprise 157 individual heat capacities in the range 295 to 473 K and for which the authors claim 0.1 percent accuracy, are shown in figure 6 in their smooth representation. The deviation of these heat capacity data of Martin and Snowdon from the NBS data of table 4 (solid curve) is less than 0.1 percent below 330 K and slightly more than 0.1 percent above 330 K. It is predominantly positive but can

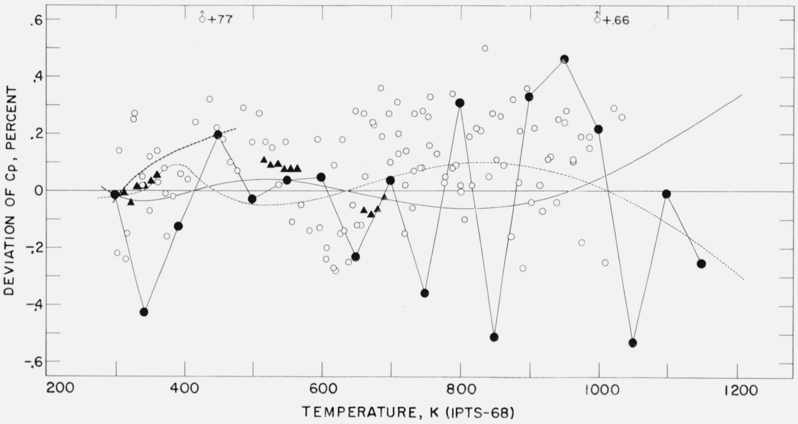

FIGURE 6. *Comparison of NBS drop-calorimeter heat capacity results on α-Al_2O_3 with results of high-temperature adiabatic calorimetry.*

The base line is the heat capacity function derived from eq (2); ●, average Cp, corrected for curvature, from SRM720 data of table 2, this work;------, NBS 1956 recommended values [2]; ————, NBS 1970 recommended values (table 4, this work); ▲, West and Ginnings [16]; ○, Grønvold [17]; ++++++++++ Martin and Snowdon [40].

be considered as being within the individual uncertainties of both sets of data. The heat capacity data of West and Ginnings [16], who used painstaking care to avoid heat-leak errors and to analyze all unavoidable errors, was assigned an overall uncertainty by these investigators ranging from "... less than 0.1 percent in the lower ranges (to) less than 0.2 percent in the upper range." These data deviate from the base line of figure 6 by an average of 0.06 percent. Grønvold's heat capacity data [17], all of which are shown in figure 6, deviate from this base line by 0.17 percent on the average, 75 percent of the data deviating positively. Grønvold claimed 0.3 percent accuracy for these data. One other set of data due to an adiabatic calorimeter of Shmidt and Sokolov [45] is mentioned here for completeness, though not illustrated in figure 6. These authors state no overall uncertainty for their results. Their 33 data, extending from 52 to 714 °C, have a range of ±0.5 percent, and deviate by an average of 0.37 percent from the base line of figure 6, the deviations being mostly positive.

The two curves of figure 6 due to the NBS represent the smooth heat-capacity values recommended in 1956 [2] and those of the present investigation (table 4). Only above 1050 K does the difference between the two sets of values substantially exceed 0.1 percent. The adiabatic heat-capacity data were given no weight in determining the final smooth thermal functions (table 4). Nevertheless, the NBS-recommended specific heat values agree well with these data and can now be considered to be in excellent accord with the results of the best available direct heat-capacity measurements on α-Al_2O_3.

When the first NBS thermal measurements on a standard sample of α-Al_2O_3, were published in 1956 [2], they provided the highest-temperature thermodynamic functions for this substance then available, and there existed in the literature but six series of non-NBS α-Al_2O_3 enthalpy data of near comparability. Since then, numerous investigators, some within the NBS, have published results of enthalpy measurements on α-Al_2O_3 which have extended our range of knowledge of the thermal functions of this substance to the melting point (2327 K±6 K [1]) and higher. In addition, there have been no less than nine efforts since 1956 [11, 24, 46, 47, 48, 49, 50, 53, 56] aimed at correlating all the reliable published α-Al_2O_3 enthalpy and heat-capacity data. Figure 7, which has as its base line the latest NBS-recommended values for the enthalpy of α-Al_2O_3 (table 4) displays the NBS enthalpy data which formed the basis of table 4 along with selected values from the NBS 1956 low-temperature data. Also shown in figure 7 are the results of 14 other enthalpy investigations since 1956 and three of the most reliable sets of results available prior to 1956. Of the compilations, the most recent one is shown, due to Reshetnikov [24], who has proposed a single algebraic function to represent the heat capacity in the range 0 to 2200 K. In selecting sets of data for this comparison, those which consisted solely of "check runs" at a very limited number of temperatures or which showed many values deviating a percent or more from the present NBS results were not included. All data have been expressed on the new temperature scale (IPTS–68) and were referred, where necessary, to 0 °C using enthalpy increments from table 4. The molecular weight of α-Al_2O_3 was taken as 101.9612 and the defined calorie as 4.1840 J.

The data of figure 7 arise from a variety of techniques. The non-NBS enthalpy data (open or partly shaded symbols) has come largely from mixing-type block calorimeters operated either with an isothermal block environment ("isoperibol" calorimeters) [25, 26, 27, 30, 31, 32, 33, 34, 37, 38, 39, 42] or with the temperatures of the block environment controlled to minimize heat transfer ("adiabatic" calorimeters) [26, 29]. There were only two suitable sets of non-NBS data due to Bunsen ice calorimeters available from the literature [36, 41]. The NBS results (wholly shaded symbols) were obtained by analysis of low-temperature adiabatic heat capacity measurements [20], by use of a Bunsen ice calorimeter (this work) and by use of an adiabatic receiving-type calorimeter [3, 22, 23] (essentially a block calorimeter with low block mass and refined shield controls).

A large fraction of the enthalpy data of figure 7 in the range 0 to 900 °C (the operating range of the ice calorimeter used in the present NBS enthalpy measurements) cluster about the current NBS-recommended values (base line). A count of the data in this range shows that somewhat over 50 percent of the (non-NBS) data can be considered as deviating 0.1 percent or less from the NBS values, this figure increasing to 60 percent with the inclusion of the NBS data. Of the two modes of operation of the block-type calorimeters (isoperibol and adiabatic), the adiabatic mode produced in all cases excellent agreement with the NBS results, over 80 percent of all points so obtained deviating less than 0.1 percent from the NBS results. In the isoperibol type of operation, on the other hand, typically 20 percent or less of the results of any given investigator lie within 0.1 percent of the NBS results. Two noteworthy exceptions to this latter generalization are the recent (isoperibol) results of Macleod [26][8] and Oetting [25]. With regard to Oetting's results it should be noted that the NBS values for the enthalpy of α-Al_2O_3 quoted by him [25] resulted from a preliminary analysis of the NBS data for SRM 720 and cannot be expected to agree exactly with the corresponding NBS values derived from table 4. Some enthalpy data above 900 °C have been included in figure 7 to illustrate the high precision of the NBS results above 900 °C and the manner in which these results merge with the data of the present investigation.

4.4. Reliability of Present NBS Data

An estimate of the reliability of the data can be arrived at by taking into account the established precision of measurement (table 2 and fig. 4), the comparisons with the results of other investigators (fig. 6,

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[8] See [35] for a critique on Macleod's methods.

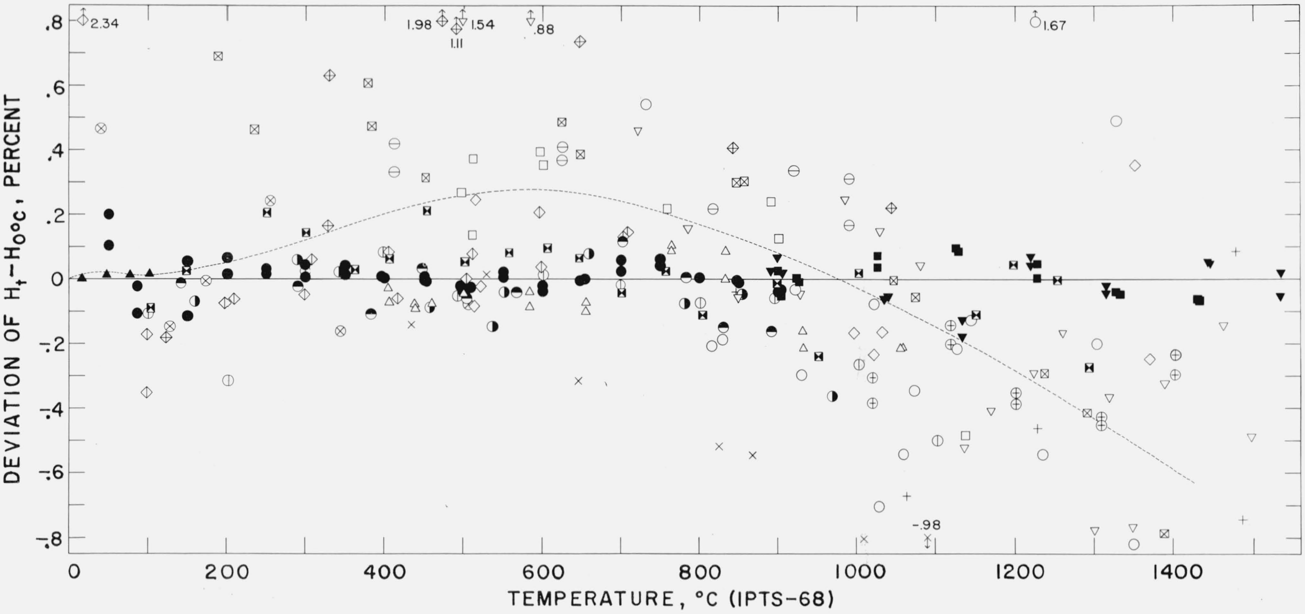

FIGURE 7. *Comparison of α-Al_2O_3 enthalpy data relative to 0 °C with values derived from table 4.*

Selected NBS data upon which table 4 was based are shown along with results of other high-temperature investigators.

Base line: Table 4 (this work).

●	: NBS, sample SRM 720 (this work).		
■	: NBS, sample SRM 720	(1970)	[22]
▲	: NBS, Cal. Conf. sample	(1956)	[20]
▼	: NBS, (West and Ishihara)	(1966)	[23]
----	: Reshetnikov compilation	(1969)	[24]
⧓	; Oetting	(1970)	[25]
◒	: Macleod (adiabatic)	(1967)	[26]
◑	: Macleod (isoperibol)	(1967)	[26]
◈	: McDonald	(1967)	[27]
⊕	: Banashek et al.	(1965)	[28]
△	: Sokolov et al.	(1963)	[29]
□	: Dawson et al.	(1963)	[30]
○	: Kantor et al	(1962)	[31]
◇	: McDonald and Stull	(1962)	[32]
+	: Ferrier and Olette; Olette	(1962, 1956)	[33, 57]
▽	: Kirillin et al.	(1961)	[34]
⦶	: Spedding et al.	(1960)	[36]
⊖	: Margrave and Grimley	(1958)	[37]
◇	: Walker et al.	(1956)	[38]
×	: Shomate and Cohen	(1955)	[39]
⊗	: Oriani and Murphy	(1954)	[41]
⊠	: Shomate and Naylor	(1945)	[42]

particularly) and suspected sources of systematic and random error. The absolute precision of measurement (fig. 4) is relatively constant and independent of temperature, strongly suggesting that random errors are to be associated exclusively with the calorimeter proper. The one and perhaps only source of random error known to be involved in the operation of the furnace—lack of temperature equality between the capsule and furnace—would probably, if it counted significantly in the errors, have introduced a temperature dependence into the precison.

Suspected systematic errors may be categorized as temperature, mass and heat errors. Although precautions were carefully taken to avoid error in each of these categories (consult sec. 3. for further details), no corrections to the data for these suspected errors were made as they were indeterminate as to magnitude and generally in their sign. It is hoped that in the precautions, a pound of prevention has eliminated the need for an ounce of cure.

"Temperature errors" include those stemming from uncertainty in the calibrations of the potentiometer and bridge and in the calibration and use of their associated measuring elements—Pt-Pt10Rh thermocouples and the platinum resistance thermometer. The calibrations of the thermocouple potentiometer and resistance bridge were verified within the range of use of each instrument. The potentiometer was compared with one recently calibrated at the NBS and checks were made on the calibration of the Mueller resistance bridge by measuring a known standard resistance. It is believed that altogether these instruments did not introduce any more than 0.01 percent error into the temperature measurement.

The uncertainty in the thermocouple calibrations (i.e., the success with which IPTS-48, as amended in 1960, was realized during the calibrations in the NBS Temperature Section) was stated not to exceed 0.5 K and is felt to have provided the largest potential source of systematic temperature error—perhaps as large as 0.03 percent. Two independent determinations of the specimen and container masses were made on a calibrated analytical balance, and the capsules were checked for constancy of mass during the course of the experiments. These sources of mass error are not felt to have contributed more than 0.002 percent to the systematic error of measuring enthalpy changes.

Systematic heat errors include a mass item as well: The accounting for mercury forced into the calorimeter during an experiment. This also involves the use of the analytical balance and is subject to an error on the order of 0.001 percent. The calorimeter calibration constant of Ginnings et al. [2, 52] has been used in the reduction of the observed data. This constant expresses the equivalence between heat liberated and mercury forced in during an experiment. It is believed to be uncertain by about 0.01 percent. Finally, there remains the consideration that both the full and empty capsules lose heat during their fall to the calorimeter. Each enters the calorimeter already having suffered a small temperature drop. Elementary considerations show that the difference between the heats so determined is equal to the (desired) difference between the full- and empty-capsule heats at the true furnace temperature provided equal amounts of heat are lost by each capsule during its drop. The absolute magnitude of this heat loss (due to radiation and convection) was roughly estimated to be as high as 0.1 percent of the total heat for a full capsule at 900 °C, but would undoubtedly be much lower at lower temperatures. Assuming a maximum 10 percent difference between the heat loss of the full and blank capsules, due to factors involving the surface emissivity of the capsules and their manner of fall, the error introduced into the net heat values should not exceed 0.01 percent.

That there may be small day-to-day variations in the systematic errors can be seen by considering table 3. The net measured heats of duplicate runs at the same temperature for the Calorimetry Conference Sample (column 8, table 2) have an average range of 0.7 J, whereas the corresponding average for the SRM 720 data (derived from column 6, table 2, assuming an average sample mass) is twice as big: 1.3 J. The significant difference between the two sets of data is that all of the Calorimetry Conference Sample duplicate data were measured on the same days, while of the SRM 720 duplicates, about half consisted of measurements taken on different days.

In light of the foregoing considerations regarding random and systematic errors and comparisons with other reliable data, the error in the enthalpy data of table 4 above 273.15 K is estimated not to exceed 0.1 percent. The heat capacity is estimated to be in error by not more than 0.2 percent.

5. Thermodynamic Functions

Smooth thermodynamic functions were calculated[9] using numerical four-point integration of a single smooth numerical heat capacity function extending from 0 K to the highest temperature of heat measurements (1173.15 K) and thence with a small extrapolation to 1200 K. The thermodynamic functions are given in table 4 (in terms of *joules*) and in the appendix (in terms of *calories*).

Because the present enthalpy data on the SRM 720 sample are subject to somewhat greater uncertainty near the extreme ends of their temperature range (273.15 K and 1173.15 K) than throughout this range, and in light of the complete lack of thermal data below 273.15 K on this particular sample, several compromises were necessary in order to obtain the numerical heat capacity function used in calculating the thermodynamic functions. These will be described with reference to the temperature intervals in which they are applicable.

(1) 0 to 250 K: In order to refer all thermodynamic quantities to the enthalpy and entropy at 0 K, the NBS 1956 heat capacity data on the Calorimetry Conference Sample [20] were used as the numerical heat capacity function over this temperature interval. These were the smoothed, unrounded heat capacity data from which part of table 5 of [2] was derived. It was felt that the use of the Calorimetry Conference Sample thermal data in place of the absent SRM 720 data was justified by the close agreement between the qualitative spectrographic analyses of both these samples (see sec. 2.) and by the close agreement between the present enthalpy data on both of these samples in the temperature interval 273.15 to 1173.15 K (see fig. 4). The data [20] were corrected to account for differences between the temperature scales on which they were expressed[10] and IPTS–68 [9, 19], used in the present investigation, as well as the difference between the 1956 and currently established values for the molecular weight of Al_2O_3 [2, 12].

(2) 250 to 290 K: In this narrow temperature range, heat capacity values were selected from a graphical smooth merging of the 0 to 250 K heat capacity data discussed above and the 290 to 1200 K data referred to immediately below. These heat capacity values differed by no more than 0.005 percent from the data which were so merged.

(3) 290 to 1200 K: Heat capacity values in this interval were chosen by differentiating the composite enthalpy function described above (eq (3)). The data so chosen differ at the highest temperatures by no more than 0.3 percent from heat capacity values derived only from the present NBS ice calorimeter data (eq (2)).

This numerical heat capacity function comprised a total of 152 individual data at the temperatures given in table 4 plus 20 additional evenly spaced temperatures below 50 K. It differed from the 1956 NBS smooth data [2] by no more than 0.05 percent between 190 K and the ice point and by no more than 0.1 percent between 155 and 190 K. The enthalpy increment ($H_{1000\,K}-H_{273.15}$) resulting from the integration agrees exactly (except for rounding error) with the same interval computed directly from eq (3).

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[9] All computations were carried out on a UNIVAC–1108 computer programmed in FORTRAN, and made use of the same thermodynamic relationships employed in the calculation of the 1956 NBS table [2].

[10] Below 90 K, the 1956 data were expressed on the NBS–1939 provisional temperature scale [20, 21], which is numerically 0.01 K higher than the NBS–1955 provisional scale.

TABLE 4. *Thermodynamic functions for* α-*aluminum oxide* [a] (α-Al_2O_3) *solid phase at 1 atm pressure (in JOULE energy units)*

T [b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	$J mol^{-1} K^{-1}$	$J mol^{-1}$	$J mol^{-1} K^{-1}$	$J mol^{-1} K^{-1}$	$J mol^{-1}$	$J mol^{-1} K^{-1}$
0	0	0	0	0	0	0
5	0.001	0.0015	0.0003	0.0004	0.0005	0.00010
10	.009	.0236	.0024	.0032	.0079	.00079
15	.030	.118	.0079	.0106	.0399	.00266
20	.076	.359	.0180	.0241	.123	.00614
25	.142	.881	.0352	.0471	.297	.0119
30	.263	1.874	.0625	.0830	.616	.0205
35	.438	3.582	.102	.135	1.154	.0330
40	.690	6.374	.159	.209	2.006	.0501
45	1.039	10.649	.237	.310	3.292	.0732
50	1.492	16.939	.339	.442	5.157	.103
55	2.070	25.788	.469	.610	7.771	.141
60	2.781	37.86	.631	.820	11.33	.189
65	3.621	53.81	.828	1.075	16.04	.247
70	4.584	74.28	1.061	1.378	22.16	.317
75	5.671	99.86	1.331	1.730	29.90	.399
80	6.899	131.23	1.640	2.135	39.54	.494
85	8.250	169.06	1.989	2.593	51.34	.604
90	9.692	213.88	2.376	3.105	65.56	.728
95	11.22	266.12	2.801	3.669	82.48	.868
100	12.85	326.2	3.263	4.286	102.3	1.023
105	14.56	394.8	3.760	4.954	125.4	1.194
110	16.34	472.0	4.291	5.672	152.0	1.382
115	18.18	558.3	4.855	6.439	182.2	1.585
120	20.08	653.9	5.449	7.253	216.4	1.804
125	22.01	759.1	6.073	8.112	254.8	2.039
130	23.97	874.0	6.723	9.013	297.6	2.289
135	25.95	998.8	7.399	9.954	345.0	2.556
140	27.94	1133.5	8.097	10.934	397.2	2.837
145	29.95	1278.3	8.816	11.950	454.4	3.134
150	31.95	1433.1	9.554	12.999	516.8	3.445
155	33.96	1597.8	10.309	14.079	584.5	3.771
160	35.95	1772.6	11.079	15.189	657.6	4.110
165	37.93	1957.3	11.862	16.325	736.4	4.463
170	39.90	2151.9	12.658	17.487	820.9	4.829
175	41.84	2356.3	13.464	18.672	911.3	5.207
180	43.76	2570.3	14.279	19.88	1008	5.598
185	45.65	2793.8	15.102	21.10	1110	6.001
190	47.51	3026.7	15.930	22.34	1219	6.414
195	49.34	3268.9	16.763	23.60	1334	6.839
200	51.13	3520.0	17.600	24.87	1455	7.274
205	52.89	3780.1	18.439	26.16	1582	7.719
210	54.61	4048.8	19.280	27.45	1716	8.173
215	56.29	4326.1	20.121	28.76	1857	8.637
220	57.94	4611.7	20.962	30.07	2004	9.109
225	59.55	4905.4	21.802	31.39	2158	9.589
230	61.12	5207.1	22.640	32.72	2318	10.08
235	62.66	5516.6	23.475	34.05	2485	10.57
240	64.16	5833.6	24.307	35.38	2658	11.08
245	65.63	6158.1	25.135	36.72	2839	11.59
250	67.05	6489.8	25.959	38.06	3026	12.10
255	68.45	6828.6	26.779	39.40	3219	12.62
260	69.80	7174.2	27.593	40.75	3420	13.15
265	71.12	7526.6	28.402	42.09	3627	13.69
270	72.41	7885.4	29.205	43.43	3840	14.22
273.15	73.20	8114.7	29.708	44.27	3979	14.57
275	73.65	8250.6	30.002	44.77	4061	14.77
280	74.87	8621.9	30.792	46.11	4288	15.32

TABLE 4. *Thermodynamic functions for α-aluminum oxide*[a] (α-Al_2O_3) *solid phase at 1 atm pressure (in JOULE energy units)*—Continued

T[b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	$Jmol^{-1}K^{-1}$	$Jmol^{-1}$	$Jmol^{-1}K^{-1}$	$Jmol^{-1}K^{-1}$	$Jmol^{-1}$	$Jmol^{-1}K^{-1}$
285	76.05	8999.2	31.576	47.44	4522	15.87
290	77.20	9382.4	32.353	48.78	4763	16.42
295	78.32	9771.2	33.123	50.10	5010	16.98
298.15	79.01	10019	33.604	50.94	5169	17.34
300	79.41	10165	33.885	51.43	5264	17.55
305	80.48	10565	34.640	52.75	5524	18.11
310	81.51	10970	35.388	54.07	5791	18.68
315	82.51	11380	36.128	55.38	6065	19.25
320	83.49	11795	36.860	56.69	6345	19.83
325	84.44	12215	37.585	57.99	6632	20.40
330	85.37	12639	38.302	59.29	6925	20.98
335	86.28	13068	39.012	60.58	7224	21.57
340	87.16	13502	39.713	61.86	7531	22.15
345	88.01	13940	40.407	63.14	7843	22.73
350	88.84	14382	41.093	64.41	8162	23.32
355	89.66	14828	41.771	65.68	8487	23.91
360	90.45	15279	42.442	66.94	8819	24.50
370	91.97	16191	43.760	69.44	9501	25.68
373.15	92.43	16481	44.169	70.22	9721	26.05
380	93.41	17118	45.048	71.91	10207	26.86
390	94.78	18059	46.306	74.35	10938	28.05
400	96.08	19013	47.534	76.77	11694	29.24
410	97.32	19980	48.733	79.16	12474	30.42
420	98.50	20959	49.904	81.52	13277	31.61
430	99.62	21950	51.048	83.85	14104	32.80
440	100.69	22952	52.164	86.15	14954	33.99
450	101.71	23964	53.253	88.42	15827	35.17
460	102.68	24986	54.317	90.67	16722	36.35
470	103.60	26017	55.356	92.89	17640	37.53
480	104.48	27057	56.371	95.08	18580	38.71
490	105.33	28106	57.361	97.24	19542	39.88
500	106.13	29164	58.329	99.38	20525	41.05
510	106.90	30229	59.273	101.49	21529	42.21
520	107.64	31302	60.197	103.57	22555	43.38
530	108.35	32382	61.098	105.63	23601	44.53
540	109.02	33469	61.980	107.66	24667	45.68
550	109.67	34562	62.841	109.67	25754	46.82
560	110.29	35662	63.683	111.65	26860	47.96
570	110.89	36768	64.506	113.61	27987	49.10
580	111.46	37880	65.310	115.54	29132	50.23
590	112.02	38997	66.097	117.45	30297	51.35
600	112.55	40120	66.867	119.34	31481	52.47
610	113.06	41248	67.620	121.20	32684	53.58
620	113.55	42381	68.357	123.04	33905	54.68
630	114.02	43519	69.078	124.86	35145	55.78
640	114.48	44661	69.784	126.66	36402	56.88
650	114.92	45808	70.475	128.44	37678	57.97
660	115.35	46960	71.152	130.20	38971	59.05
670	115.76	48115	71.815	131.94	40282	60.12
680	116.16	49275	72.464	133.66	41610	61.19
690	116.55	50439	73.100	135.35	42955	62.25
700	116.92	51606	73.723	137.03	44317	63.31
720	117.64	53952	74.933	140.34	47091	65.40
740	118.32	56311	76.097	143.57	49930	67.47
760	118.96	58684	77.216	146.73	52833	69.52
780	119.56	61069	78.295	149.83	55799	71.54
800	120.14	63466	79.333	152.87	58826	73.53
820	120.69	65875	80.335	155.84	61913	75.50

TABLE 4. *Thermodynamic functions for α-aluminum oxide*[a] *(α-Al_2O_3) solid phase at 1 atm pressure (in JOULE energy units)*—Continued

T[b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	*Jmol⁻¹K⁻¹*	*Jmol⁻¹*	*Jmol⁻¹K⁻¹*	*Jmol⁻¹K⁻¹*	*Jmol⁻¹*	*Jmol⁻¹K⁻¹*
840	121.21	68294	81.302	158.75	65059	77.45
860	121.71	70723	82.236	161.61	68263	79.38
880	122.20	73162	83.139	164.42	71523	81.28
900	122.66	75611	84.012	167.17	74839	83.15
920	123.11	78068	84.857	169.87	78210	85.01
940	123.55	80535	85.676	172.52	81634	86.84
960	123.97	83010	86.469	175.13	85110	88.66
980	124.37	85494	87.239	177.69	88638	90.45
1000	124.77	87985	87.985	180.20	92217	92.22
1020	125.16	90484	88.711	182.68	95846	93.97
1040	125.53	92991	89.415	185.11	99524	95.70
1060	125.90	95506	90.100	187.51	103250	97.40
1080	126.26	98027	90.766	189.86	107020	99.09
1100	126.61	100550	91.415	192.18	110840	100.77
1120	126.95	103090	92.046	194.47	114710	102.42
1140	127.29	105630	92.662	196.72	118620	104.06
1160	127.61	108180	93.261	198.93	122580	105.67
1180	127.93	110730	93.846	201.12	126580	107.27
1200	128.25	113300	94.417	203.27	130620	108.85

H_0° and S_0° are, respectively, the enthalpy and entropy at 0 K and 1 atm pressure of α-Al_2O_3 solid.

[a] Molecular weight = 101.9612 [12].

[b] International Practical Temperature Scale of 1968 [9, 19], T_{68}, K = t_{68}, °C + 273.15

APPENDIX. *Thermodynamic functions for α-aluminum oxide*[a] *(α-Al_2O_3) solid phase at 1 atm pressure (in CALORIE*[c] *energy units)*

T[b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	*cal mol⁻¹K⁻¹*	*cal mol⁻¹*	*cal mol⁻¹K⁻¹*	*cal mol⁻¹K⁻¹*	*cal mol⁻¹*	*cal mol⁻¹K⁻¹*
0	0	0	0	0	0	0
5	0.0002	0.0003	0.0001	0.0001	0.0001	0.00002
10	.0022	.0056	.0006	.0008	.0019	.00019
15	.0072	.0283	.0019	.0025	.0095	.00064
20	.0182	.0858	.0043	.0058	.0294	.00147
25	.0339	.211	.0084	.0113	.0710	.00284
30	.0628	.448	.0149	.0198	.147	.00491
35	.105	.856	.0245	.0323	.276	.00788
40	.165	1.523	.0381	.0501	.479	.0120
45	.248	2.545	.0566	.0740	.787	.0175
50	.357	4.048	.0810	.106	1.233	.0247
55	.495	6.164	.112	.146	1.857	.0338
60	.665	9.049	.151	.196	2.707	.0451
65	.865	12.862	.198	.257	3.835	.0590
70	1.096	17.752	.254	.329	5.295	.0756
75	1.355	23.866	.318	.414	7.147	.0953
80	1.649	31.364	.392	.510	9.451	.118
85	1.972	40.406	.475	.620	12.27	.144
90	2.316	51.117	.568	.742	15.67	.174
95	2.682	63.603	.670	.877	19.71	.207
100	3.071	77.976	.780	1.024	24.46	.245
105	3.481	94.349	.899	1.184	29.98	.285
110	3.906	112.81	1.026	1.356	36.32	.330
115	4.346	133.43	1.160	1.539	43.55	.379
120	4.799	156.29	1.302	1.734	51.73	.431
125	5.260	181.43	1.451	1.939	60.91	.487
130	5.728	208.90	1.607	2.154	71.13	.547

APPENDIX. *Thermodynamic functions for α-aluminum oxide*[a] *(α-Al_2O_3) solid phase at 1 atm pressure (in CALORIE*[c] *energy units)*—Continued

T[b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$
135	6.202	238.72	1.768	2.379	82.46	.611
140	6.679	270.92	1.935	2.613	94.94	.678
145	7.159	305.52	2.107	2.856	108.6	.749
150	7.637	342.51	2.283	3.107	123.5	.823
155	8.116	381.89	2.464	3.365	139.7	.901
160	8.592	423.66	2.648	3.630	157.2	.982
165	9.066	467.81	2.835	3.902	176.0	1.067
170	9.536	514.31	3.025	4.180	196.2	1.154
175	10.000	563.16	3.218	4.463	217.8	1.245
180	10.459	614.31	3.413	4.751	240.8	1.338
185	10.911	667.74	3.609	5.044	265.3	1.434
190	11.355	723.40	3.807	5.340	291.3	1.533
195	11.792	781.27	4.007	5.641	318.7	1.635
200	12.220	841.31	4.207	5.945	347.7	1.738
205	12.640	903.46	4.407	6.252	378.2	1.845
210	13.051	967.70	4.608	6.562	410.2	1.953
215	13.454	1034.0	4.809	6.873	443.8	2.064
220	13.847	1102.2	5.010	7.187	479.0	2.177
225	14.232	1172.4	5.211	7.503	515.7	2.292
230	14.609	1244.5	5.411	7.820	544.0	2.409
235	14.976	1318.5	5.611	8.138	593.9	2.527
240	15.335	1394.3	5.809	8.457	635.4	2.647
245	15.685	1471.8	6.007	8.777	678.4	2.769
250	16.026	1551.1	6.204	9.097	723.1	2.893
255	16.359	1632.1	6.400	9.418	769.4	3.017
260	16.683	1714.7	6.595	9.738	817.3	3.144
265	16.998	1798.9	6.788	10.059	866.8	3.271
270	17.305	1884.7	6.980	10.380	917.9	3.400
273.15	17.494	1939.5	7.100	10.582	950.9	3.481
275	17.604	1971.9	7.171	10.700	970.6	3.529
280	17.894	2060.7	7.360	11.020	1024.9	3.660
285	18.177	2150.9	7.547	11.339	1080.8	3.792
290	18.452	2242.4	7.733	11.658	1138.3	3.925
295	18.720	2335.4	7.917	11.975	1197.4	4.059
298.15	18.885	2394.6	8.032	12.175	1235.4	4.144
300	18.981	2429.6	8.099	12.292	1258.0	4.193
305	19.234	2525.2	8.279	12.608	1320.3	4.329
310	19.481	2622.0	8.458	12.923	1384.1	4.465
315	19.721	2720.0	8.635	13.236	1449.5	4.602
320	19.955	2819.2	8.810	13.549	1516.5	4.739
325	20.183	2919.5	8.983	13.860	1585.0	4.877
330	20.405	3021.0	9.154	14.170	1655.1	5.015
335	20.620	3123.5	9.324	14.478	1726.7	5.154
340	20.830	3227.2	9.492	14.785	1799.9	5.294
345	21.035	3331.8	9.657	15.091	1874.6	5.434
350	21.234	3437.5	9.821	15.395	1950.8	5.574
355	21.428	3544.2	9.984	15.698	2028.5	5.714
360	21.617	3651.8	10.144	15.999	2107.7	5.855
370	21.981	3869.8	10.459	16.596	2270.7	6.137
373.15	22.091	3939.2	10.557	16.783	2323.3	6.226
380	22.326	4091.3	10.767	17.187	2439.6	6.420
390	22.653	4316.2	11.067	17.771	2614.4	6.704
400	22.965	4544.3	11.361	18.348	2795.0	6.988
410	23.261	4775.5	11.648	18.919	2981.4	7.272
420	23.542	5009.5	11.927	19.483	3173.4	7.556
430	23.810	5246.3	12.201	20.040	3371.0	7.840
440	24.065	5485.7	12.467	20.591	3574.2	8.123
450	24.308	5727.5	12.728	21.134	3782.8	8.406

APPENDIX. *Thermodynamic functions for α-aluminum oxide*[a] (α-Al_2O_3) *solid phase at 1 atm pressure (in CALORIE*[c] *energy units)*—Continued

T[b]	C_p°	$H_T^\circ - H_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$
K	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$*K*$^{-1}$
460	24.540	5971.8	12.982	21.671	3996.8	8.689
470	24.761	6218.3	13.230	22.201	4216.2	8.971
480	24.972	6467.0	13.473	22.725	4440.9	9.252
490	25.173	6717.7	13.710	23.242	4670.7	9.532
500	25.366	6970.4	13.941	23.752	4905.7	9.811
510	25.550	7225.0	14.167	24.256	5145.7	10.090
520	25.726	7481.4	14.387	24.754	5390.8	10.367
530	25.895	7739.5	14.603	25.246	5640.8	10.643
540	26.057	7999.3	14.813	25.731	5895.7	10.918
550	26.212	8260.6	15.019	26.211	6155.4	11.192
560	26.360	8523.5	15.221	26.685	6419.9	11.464
570	26.503	8787.8	15.417	27.152	6689.1	11.735
580	26.640	9053.5	15.610	27.615	6962.9	12.005
590	26.772	9320.6	15.798	28.071	7241.3	12.273
600	26.899	9589.0	15.982	28.522	7524.3	12.540
610	27.021	9858.6	16.162	28.968	7811.7	12.806
620	27.139	10129	16.338	29.408	8103.6	13.070
630	27.252	10401	16.510	29.843	8399.9	13.333
640	27.362	10674	16.679	30.273	8700.5	13.594
650	27.467	10948	16.844	30.698	9005.3	13.854
660	27.569	11223	17.006	31.118	9314.4	14.113
670	27.668	11499	17.164	31.534	9627.7	14.370
680	27.764	11777	17.319	31.944	9945.1	14.625
690	27.856	12055	17.471	32.350	10266	14.879
700	27.946	12334	17.620	32.752	10592	15.132
720	28.117	12894	17.910	33.542	11255	15.632
740	28.278	13458	18.188	34.314	11933	16.127
760	28.431	14025	18.455	35.070	12627	16.615
780	28.576	14596	18.713	35.811	13336	17.098
800	28.713	15168	18.961	36.536	14059	17.575
820	28.845	15744	19.201	37.247	14797	18.046
840	28.970	16322	19.432	37.943	15549	18.511
860	29.090	16903	19.655	38.626	16315	18.971
880	29.206	17486	19.871	39.296	17094	19.426
900	29.317	18071	20.079	39.954	17887	19.875
920	29.424	18658	20.281	40.599	18692	20.318
940	29.528	19248	20.477	41.233	19511	20.756
960	29.629	19840	20.667	41.856	20341	21.189
980	29.726	20433	20.851	42.468	21185	21.618
1000	29.821	21029	21.029	43.070	22040	22.041
1020	29.913	21626	21.202	43.661	22907	22.459
1040	30.003	22225	21.371	44.243	23786	22.872
1060	30.091	22826	21.534	44.815	24677	23.281
1080	30.176	23429	21.694	45.378	25579	23.685
1100	30.260	24033	21.849	45.933	26492	24.084
1120	30.342	24639	22.000	46.479	27416	24.479
1140	30.422	25247	22.147	47.017	28351	24.870
1160	30.500	25856	22.290	47.546	29297	25.256
1180	30.577	26467	22.430	48.068	30253	25.639
1200	30.653	27079	22.566	48.583	31220	26.017

H_0 and S_0 are, respectively, the enthalpy and entropy at 0 K and 1 atm pressure of α-Al_2O_3 solid.

[a] Molecular weight = 101.9612 [12].

[b] International Practical Temperature Scale of 1968 [9, 19], T_{68}, $K = t_{68}$, °C + 273.15.

[c] 1 calorie = 4.1840 J.

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