

Enthalpy, Specific Heat, and Entropy of Aluminum Oxide from 0° to 900° C

By Defoe C. Ginnings and Robert J. Corruccini

Apparatus consisting of a furnace and ice calorimeter has been used for the measurement of enthalpies at high temperatures by the "drop" method. The enthalpy (referred to 0° C) of a sample of aluminum oxide (corundum) has been determined in the range 0° to 900° C. Derived values of specific heat and entropy are given.

I. Introduction

Substances whose thermal properties are accurately known are frequently useful in calorimetry. For example, benzoic acid is used in combustion calorimetry for determining the so-called energy equivalent of the calorimeter. This avoids electric-energy calibration of the calorimeter and, being a substitution method, eliminates those experimental errors that remain the same in all combustion experiments.

Similar use of a substitution method in heat-capacity measurements may be convenient in some cases, especially with calorimeters used in the method of mixtures. Here, the energy equivalent of the calorimeter would be determined by experiments with a standard substance having accurately known heat capacity.

More often, perhaps, observers would find it desirable to utilize experiments with the standard substance to give an indication of the accuracy obtained by them and to provide a guide toward improvement of instrumental technic. In the past, water, because of the many accurate investigations of its properties, has served these functions more often than any other substance.

A material whose enthalpy and heat capacity were accurately determined over a very much larger temperature range than is possible with water would constitute a desirable calorimetric standard substance. This material would preferably be a crystalline solid without transitions or changes of state up to, say, 1,600° C. It should be nonvolatile, nonhygroscopic, chemically stable in air, and should not absorb carbon dioxide. It

also should be of high purity, and the uncertainty involved in correcting the results for the impurities should be considerably less than the error of the accurate thermal data that would establish the substance as a standard. The heat capacity per unit volume (specific heat times density) should be high. There is ample evidence that introduction of mechanical effects, such as strains due to cold-working, cause small but appreciable changes in the thermal properties of metals. Hence it seems desirable at present to eliminate malleable substances, including most metals, from the list of prospects.

Among the most promising possibilities, then, are the oxides of Be, Mg, Al, and Zr, provided they are not so finely divided as to adsorb moisture from the air. This paper presents the results in the range 0° to 900° C of an investigation that was undertaken to determine the suitability of α -Al₂O₃ (corundum)¹ for use as the above-mentioned standard substance, this material having been tentatively chosen because of its commercial availability in high purity.

II. Experimental Procedure

1. Sample

The sample of Al₂O₃ was synthetic sapphire obtained from the Linde Air Products Co. in the form of polished rods, 2.5 mm in diameter and 36 mm long. The weight of the sample used was 8.0406 g, corrected for buoyancy. A spectrographic

¹ The so-called β -form is an impure alumina, whereas the γ -form, prepared from precipitated alumina, is metastable, transforming to corundum at about 1,000° C.

analysis performed after the completion of the heat measurements indicated 0.02 to .03 percent impurity. No correction for the impurity was applied as it was largely SiO_2 , which, in this temperature range, has a specific heat very close to that of Al_2O_3 . It seems probable that the specific heat of this sample was the same as that of the pure material within less than 0.01 percent. A 1.4-g portion of the sample was ignited at $1,000^\circ\text{C}$ for 1 hour without detectable loss of mass (0.1 mg).

2. Apparatus

The apparatus, shown in figure 1, consisted essentially of a furnace and an ice calorimeter. The sample (contained in a sealed capsule) was heated to a known temperature in the furnace and dropped into the calorimeter that measured the heat evolved in cooling the sample to 0°C . The heat content of the empty capsule, together with the small heat loss during the drop, were accounted for in separate "blank" experiments. The ice calorimeter is described elsewhere [1].²

The furnace was mounted in such a way that it could be swung aside from its position over the calorimeter. It consisted of an Alundum tube, *A*, 1-in. in inside diameter and 18 in. long, having a Chromel winding and surrounded by insulation. The upper end of the furnace tube was stoppered by a fired-talc plug, *E*, $2\frac{1}{2}$ in. long. Auxiliary heating elements, *B*, covered a 3-in. length at each end of the furnace core. Proper apportioning of power to these end-heaters resulted in a more nearly isothermal environment within the furnace. The supplying of power to the upper end-heater was guided by the indications of a thermocouple whose principal junction was located in the upper part of the furnace tube. As there could be no obstruction to the fall of the capsule, the temperature could not be observed within the lower part of the furnace tube. The power required by the lower end-heater at various temperatures was determined by separate experiments in which a thermocouple junction was located in the lower part of the furnace tube. This junction was then removed. Tests made at temperatures up to $1,000^\circ\text{C}$ with thermocouple junctions located at various points within the furnace indicated that under optimum conditions, gradients of only a few

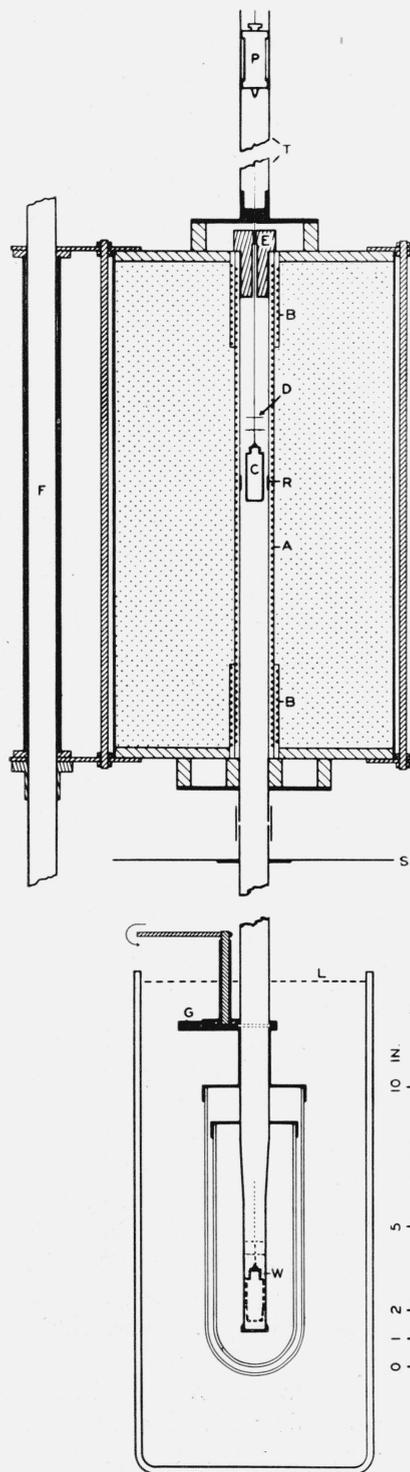


FIGURE 1.—Schematic diagram of high-temperature enthalpy apparatus.

A, Main heating element; *B*, end-heaters wound on short lengths of Alundum tube; *C*, capsule; *D*, shields; *E*, fired-talc plug; *F*, pipe supporting the furnace; *G*, gate mechanism; *L*, level of ice bath; *P*, plunger; *R*, silver ring; *S*, shield to protect ice bath from furnace radiation; *T*, tube 34 in. long; *W*, calorimeter well. Dotted figure shows position of capsule after fall. Details of ice calorimeter are omitted.

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

tenths of a degree an inch still existed in that region where the sample would be suspended. Power for the furnace was supplied through a constant-voltage transformer and was regulated manually.

The sample was contained in a Nichrome-5 capsule (fig. 2) having a screw cap of the same metal and a gold gasket for sealing. The capsule had a mass of 8.6 g (capacity of 7 ml) and was assembled by welding the bottom to the machined upper part at *A*. The gold gasket, *G*, was 0.3 mm thick. The capsule was filled with helium before sealing. A new gasket was used each time the capsule was to be sealed. The capsule (*C*, fig. 1)

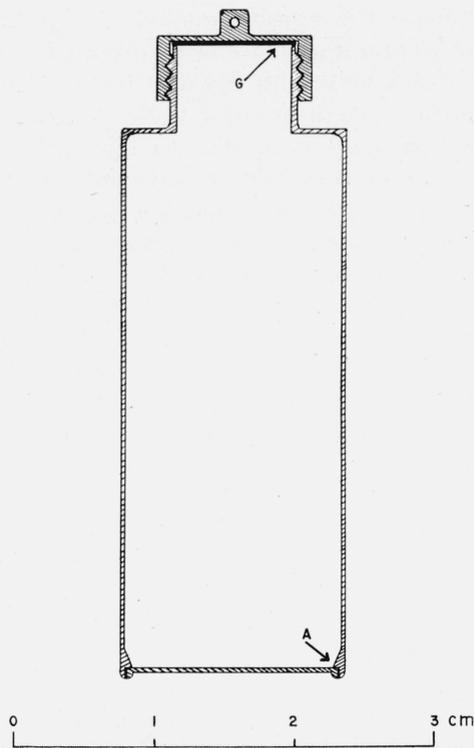


FIGURE 2.—Capsule.

A, Weld; *G*, gold gasket.

was suspended about midway in the furnace by a No. 32 B & S Chromel wire, the upper end of which was attached to a plunger, *P*, in a long vertical tube, *T*, situated on top of the furnace. The provision for releasing the system of capsule, wire, and plunger in practically free fall and slowing its drop by means of an air cushion once the capsule has entered the calorimeter was similar to that devised by Southard [2].

The function of the gate, *G*, was to intercept radiation down the well to the calorimeter. Its effectiveness is indicated by the fact that there was no observable difference in the calorimeter heat-leak rate with the furnace in place at 900° C or with it swung aside. The gate was held open for 2 seconds during each drop. A negligible amount of heat entered the calorimeter during this interval (about 0.1 cal with the furnace at 700° C) and would in any case have been accounted for in the blank experiments. Figure 3 shows how the gate carries the suspension wire against the wall of the calorimeter well in closing. This provides for intercepting any heat conducted along the suspension wire from the furnace.

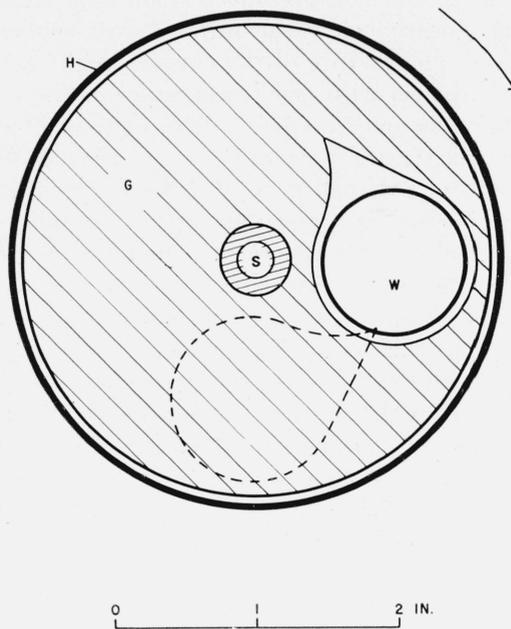


FIGURE 3.—Calorimeter gate in open position viewed from above.

G, Gate; *H*, housing; *S*, spindle; *W*, calorimeter well. Dotted line shows position of hole in gate after gate has been closed by rotation in direction of the arrow.

The temperature of the capsule and contents was measured by a platinum : platinum-10-percent rhodium thermocouple, whose principal junction was fused into a silver ring (*R*, fig. 1) consisting of a section of silver tube 12 mm long with a wall thickness of 0.5 mm. This ring fitted tightly within the Alundum furnace core and was located in such a way that the capsule would be within it when suspended in the furnace. Its purpose was (1) to provide for a rigid attachment

of the thermocouple junction that would not be easily dislocated by shock or thermal expansion, (2) by means of its high-thermal conductivity to provide some integration of the temperature around the furnace wall, and (3) to attach the thermocouple junction thermally to the furnace wall, thus preventing the temperature of the junction from being affected by conduction of heat along its leads. The effect of such conduction had been noted as a response of the thermocouple to variations in the temperature of that part of the furnace through which the leads pass. The effect was eliminated by installation of the silver ring.

The existence of temperature gradients in the furnace, together with the fact that the capsule when in the furnace presents a small solid angle to a cold surface below the furnace exit, suggested that the temperature of the capsule might not be quite identical with the temperature of the nearby thermocouple junction. The method of calibration of the thermocouple was such as to offset this effect, at least in part. This consisted in comparing the thermocouple with a second platinum: platinum-10-percent rhodium thermocouple whose principal junction had been placed within a dummy capsule approximating in size, shape, and thermal conductivity the real capsule, and the dummy capsule being inserted into the furnace from the bottom and located in the position that the real capsule would occupy in use. This second thermocouple was certified at the Bureau by comparison with a standard platinum: platinum rhodium thermocouple. In addition, it was calibrated directly at the steam and sulfur points.

All electromotive-force readings were made with a Wolff thermocouple potentiometer, the calibration of which was checked during the measurements. Although the emf of the thermocouple could be measured to within $0.1 \mu\text{v}$ (0.01°) and the furnace could be held constant to within a few hundredths of a degree, the measurement of temperature of the sample was probably not accurate to better than one-tenth degree up to 500°C . and several tenths at 900°C .

In addition to the measurement of the temperature in the furnace, it was necessary to allow sufficient time for the capsule and its contents to come to effective equilibrium with the furnace. This time was estimated early in the series of

experiments. With simplifying assumptions, it may be shown that

$$\log_{10} \left[\frac{Q_0 - Q}{Q_0} \right] = -\frac{t}{K},$$

where Q_0 is the heat evolved in any experiment in which the capsule has been in the furnace long enough before dropping to reach effective equilibrium, and Q is the heat evolved with a shorter time, t , in the furnace, the latter being held at constant temperature. The constant, K , which is evaluated by two such experiments, is equal to the time required for the temperature difference between capsule and furnace to be reduced by a factor of one-tenth. In the blank experiments, the capsule was held in the furnace at least 20 minutes before being dropped, whereas in the experiments with Al_2O_3 , at least 45 minutes was allowed. In most cases, these times exceeded $4K$, so that any error due to failure to reach thermal equilibrium should have been less than 0.01 percent. In addition, occasional longer experiments (noted in table 1) were made with no consistent difference in the results.³

In addition to measuring the temperature of the sample in the furnace, it is also necessary to account for any loss of heat from the sample (a) in falling from the furnace to the calorimeter or (b) up the calorimeter well, while cooling in the calorimeter.

(a) Calculations indicate that in a drop at $1,000^\circ\text{C}$, the capsule may lose as much as 30 or 40 cal by radiation and convection to surroundings other than the calorimeter. This loss will be slightly less in the case of the empty capsule as compared to capsule plus sample, the difference depending upon the coefficient of heat transfer within the capsule and its contents. It has been calculated that, for a sample of average heat capacity, the above-mentioned difference will not exceed about 1 cal or about 0.05 percent of enthalpy of the sample and probably is less than 0.01 percent in experiments below $1,000^\circ\text{C}$. An additional error is possible if the rate of fall is not reproducible. The velocity of the capsule at a point just below the furnace exit (near S , fig. 1)

³ It was also necessary to allow sufficient time after the drop for the capsule and contents to come to the temperature of the ice calorimeter. In this case, however, it was possible to observe directly in each experiment the time necessary to come to equilibrium. This time was on the average 26 minutes for the empty capsule and 66 minutes for the experiments with the Al_2O_3 . These times included, of course, the time for the calorimeter itself to come to equilibrium.

TABLE 1.—Results of individual experiments

Blank experiments				Sample plus capsule			
Temperature	Date	Mass of mercury ^a	Deviation from mean	Temperature	Date	Mass of mercury ^a	Deviation from mean
° C		<i>g</i>	<i>g</i>	° C		<i>g</i>	<i>g</i>
50.3	Nov. 23, 1945	^d 0.7043	−0.0004	50.3	Apr. 29, 1946	^{b d} 1.8646	0.0009
		.7035	−.0012			1.8629	−.0008
		.7064	.0017			1.8640	.0003
	Mean	0.7047			Mean	1.8637	
110.5	Nov. 26, 1945	^d 1.5759	.0014	110.5	May 1, 1946	^d 4.2945	−.0005
		1.5730	−.0015			4.2947	−.0003
		1.5747	.0002			4.2958	.0008
	Mean	1.5745			Mean	4.2950	
200.7	Nov. 23, 1945	2.9331	−.0046	200.7	Apr. 30, 1946	^d 8.2733	.0008
		2.9383	.0006			8.2716	−.0009
		2.9395	.0018			8.2725	.0000
	Nov. 28, 1945	^d 2.9425	.0048	Mean	8.2725		
		^d 2.9369	−.0008				
		2.9383	.0006				
		2.9354	−.0023				
	Mean	2.9377					
300.9	Nov. 26, 1945	4.5078	−.0007	300.9	May 2, 1946	^b 12.9940	.0024
		^b 4.5085	.0000			12.9876	−.0040
		4.5093	.0008			12.9939	.0023
	Mean	4.5085			Mean	12.9916	
426.7	Nov. 27, 1945	^d 6.5521	−.0014	426.7	Apr. 26, 1946	^d 19.2351	−.0019
		6.5532	−.0003			19.2348	−.0022
		6.5552	.0017			19.2411	.0041
	Mean	6.5535			Mean	19.2370	
579.0	Nov. 27, 1945	9.1462	.0012	579.0	Apr. 25, 1946	27.1301	.0022
		9.1438	−.0012		May 3, 1946	27.1257	−.0022
		9.1451	.0001		^d 27.1280	.0001	
	Mean	9.1450			Mean	27.1279	
723.8	Nov. 21, 1945	^b 11.8546	.0061	723.8	Apr. 25, 1946	^d 35.0452	−.0095
		11.8485	.0000		May 3, 1946	35.0531	−.0016
		11.8459	−.0026		May 6, 1946	35.0641	.0094
	May 15, 1946	^c 11.8346	−.0139	May 9, 1946	^c 35.0234	−.0313	
		11.8502	.0017		35.0480	−.0067	
		11.8470	−.0015		35.0588	.0041	
		11.8469	−.0016	May 10, 1946	^e 35.0588	.0041	
	Mean	11.8485			Mean	35.0547	
826.0	May 15, 1946	^d 13.8146	−.0040	826.0	May 7, 1946	40.7804	−.0028
	May 16, 1946	13.8153	−.0033		40.7812	−.0020	
	^d 13.8258	.0072	40.7880		.0048		
	Mean	13.8186			Mean	40.7832	
898.7	May 16, 1946	^d 15.2381	−.0006	898.7	May 8, 1946	44.8931	.0035
		15.2359	−.0028		44.8818	−.0078	
		^d 15.2421	.0034		44.8940	.0044	
	Mean	15.2387			Mean	44.8896	

^a Corrected for buoyancy.

^b These experiments were weighted slightly less because of unsteady heat leak.

^c Experiments discarded on suspicion of moisture in calorimeter well.

^d Time in furnace on these experiments was at least 20% more than on those of same group not so marked.

^e CO₂ flow-rate in calorimeter was about three times as great as usual.

was determined by suspending a magnet below the capsule and measuring with a cathode ray oscilloscope the emf produced in a coil through which the magnet fell when the plunger was released. The velocity was found to be reproducible within the uncertainty of the measurement, which was about 2 percent. Also, it was within 2 percent of the velocity of free fall of the magnet in air. During the heat measurements, the weight of the falling system was kept constant, regardless of the weight of sample, by means of small weights that could be added to or removed from the plunger.

(b) Approximate calculations indicated that the loss of heat up the calorimeter well by radiation and conduction from the hot capsule after its fall was quite small for temperatures up to 1,000° C. However, the convection loss remained unknown, and for the purpose of minimizing it as well as the other upward losses, there was employed a system of thin, horizontal platinum shields (*D*, fig. 1) of the same diameter as the capsule and spaced about ½ in. apart on the suspension wire immediately above the capsule. The effectiveness of the shields was tested by drop experiments at 725°, in which the number of shields was varied while maintaining the heat capacity of the system constant. The heat evolved was about 2,000 cal for each experiment. In going by steps from one to four shields, the total range of variation in the heat transferred to the calorimeter in each experiment was 0.7 cal, the variation being largely random. With no shields the heat transferred to the calorimeter was less by 5 cal. Thus one shield appeared to be adequate for confining the convection. In the experiments with Al₂O₃, two shields were employed.

III. Results

The results of 31 experiments with the sample and 35 blank experiments are given in table 1. The blank experiments were made at the same series of temperatures as the experiments with sample. In this table are listed the masses of mercury taken into the ice calorimeter in the respective experiments. Two classes of corrections have been applied to these masses. These corrections are small and therefore are not listed separately. The first class comprises corrections for slight deviations from ideal calorimetric behavior, that is,

for heat leak and the change in position of the mercury meniscus between the beginning and end of an experiment. These corrections were roughly independent of the magnitude of the heat involved in an experiment, and each kind averaged only about 0.002 g of mercury (equivalent to about 0.1 cal). The second class of corrections accounted for small differences in the amount of gas and gold contained in the capsule in the experiments with the sample as compared with the blank experiments and also accounted for small variations in capsule weight resulting from slow surface oxidation of the Nichrome wire at temperatures above 800°. These corrections, when lumped together, were approximately proportional to the amount of heat in an experiment and averaged about 0.04 percent of the net mercury intake (that due to sample alone).

In table 2 the conversion of experimental data to enthalpy of Al₂O₃ is completed by using 64.638 cal/g of mercury (1 cal=4.1833 int. j) for the "apparent" calibration factor of the ice calorimeter [1]. An arbitrary enthalpy-temperature curve was drawn through the data of table 2, values were read off at even temperature intervals, and the results were smoothed. The deviations of the observed enthalpies from the smoothed values before rounding off the latter are given in the last column of table 2.

TABLE 2.—*Computation of enthalpy—Comparison with smoothed values*

Temperature, <i>t</i>	Net mass of mercury ^a	Enthalpy ^b $H_{obs.} - H_0$	Enthalpy observed minus smoothed
° C	g	cal. g ⁻¹	Percent
0	-----	0	-----
50.3	1.1590	9.317	-0.03
110.5	2.7205	21.870	.02
200.7	5.3348	42.886	.11
300.9	8.4831	68.195	-.05
426.7	12.6835	101.962	-.02
579.0	17.9829	144.564	-.05
723.8	23.2062	186.553	.01
826.0	26.9646	216.767	.03
898.7	29.6509	238.362	.00

^a From table 1: Means from column 7 minus means from column 3.

^b Mass of sample=8.0406 g; "apparent" calibration factor of ice calorimeter=64.638 defined calories per gram of mercury.

Values of specific heat, $C_p = (\partial H / \partial T)_p$, were obtained from the smoothed enthalpy data by the method of Rutledge [3]. The entropy (re-

ferred to 0° C), $S]_0^t = \int_0^t (C_p/T) dt$, was calculated by using Simpson's rule. The smoothed values of enthalpy and the derived quantities are given in table 3.

TABLE 3.—Enthalpy, specific heat, and entropy of Al_2O_3 at even temperature intervals

[1 cal=4.1833 int. j; 0° C=273.16° K]

Temperature	$H]_0^t$	C_p	$S]_0^t$
° C	Cal g ⁻¹	Cal g ⁻¹ deg ⁻¹ C	Cal g ⁻¹ deg ⁻¹ K
0	0	0.1731	0
20	3.56	.1830	0.01259
40	7.32	.1922	.02498
60	11.25	.2007	.03714
80	15.34	.2085	.04906
100	19.58	.2157	.06074
120	23.96	.2224	.07218
140	28.47	.2285	.08337
160	33.10	.2341	.09431
180	37.84	.2392	.10499
200	42.67	.2438	.11542
220	47.59	.2480	.12560
240	52.59	.2518	.13554
260	57.66	.2552	.14524
280	62.80	.2583	.15470
300	68.00	.2611	.16393
320	73.25	.2637	.17293
340	78.54	.2660	.18171
360	83.88	.2681	.19028
380	89.26	.2701	.19865
400	94.68	.2719	.20682
420	100.14	.2736	.21480
440	105.63	.2753	.22260
460	111.15	.2769	.23023
480	116.70	.2784	.23770
500	122.28	.2799	.24502
520	127.89	.2813	.25219
540	133.53	.2827	.25922
560	139.20	.2840	.26611
580	144.90	.2853	.27287
600	150.62	.2865	.27950
620	156.36	.2877	.28600
640	162.13	.2888	.29238
660	167.92	.2899	.29865
680	173.73	.2909	.30481
700	179.56	.2919	.31086
720	185.41	.2928	.31681
740	191.28	.2937	.32266
760	197.16	.2945	.32841
780	203.06	.2953	.33406
800	208.97	.2960	.33962
820	214.90	.2967	.34509
840	220.84	.2974	.35048
860	226.80	.2981	.35579
880	232.77	.2988	.36102
900	238.75	.2995	.36617

IV. Discussion of Results

1. Reliability

An index to the reproducibility, or "precision", of the enthalpy measurements is given by the deviations from the mean (table 1). The average deviation of this type was 0.015 percent in the experiments with the sample. Another index is given by the deviations of the mean observed values of enthalpy from the "smoothed" values (table 2). The average deviation of this type was about 0.035 percent. In addition to the accidental errors there must be considered the possibility of systematic errors. For example, the calibration factor of the calorimeter may be in error by 0.02 percent [1]. The possibility of error in the measurement of temperature has already been discussed as well as the error attached to the heat loss in dropping. From consideration of these and other errors, the authors believe that the smoothed values of enthalpy given in table 3 do not differ by more than 0.2 percent from the true values, except below 100° C, where the relative sensitivity of the apparatus and method is less. This estimate of error is supported by measurements of the enthalpy of liquid water⁴ at 254° C using the same apparatus, with the exception of the capsule. The results were within 0.04 percent of what may be considered an accepted value [4].

In addition to the error in the determination of enthalpy, an error of about the same magnitude has been introduced in determining the derived quantities of specific heat and entropy. These quantities also possess an increased uncertainty above 850° C due to the difficulty of determining the derivative of a function near its end.

2. Comparison with Other Investigations

The specific heats near 0° C could have been adjusted so as to conform more nearly to the low-temperature measurements of Parks and Kelley [5] and Simon and Swain [6], which extend up to near 20° C. However, the results in table 3 are already within, at the most, 0.9 percent and on the average 0.5 percent of the five determinations of the above authors in the range of overlap. As the deviations are not greater than the estimated

⁴ These measurements will be described in more detail in a paper on *p*-xylene which will follow in another journal.

error of any of the investigators concerned, and as the present results fall below those of Parks and Kelley and above that of Simon and Swain, no attempt was made at any adjustment.

There have been several high-temperature measurements on Al_2O_3 . For comparison, these results have been placed on the basis employed in this paper, that is, mean specific heats or enthalpies between high temperatures and room temperature have been converted to enthalpies referred to 0°C by using data in table 3. These adjustments are small in all cases and are not subject to sufficient uncertainty to materially affect the comparisons among different authors.

Figure 4 shows the derived specific heats from

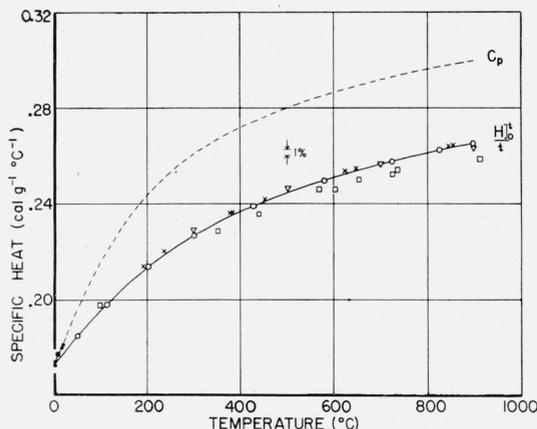


FIGURE 4.—Comparison of mean and true specific heats of Al_2O_3 with those from some other investigations.

C_p , NBS (derived); ●, Parks and Kelley; ■, Simon and Swain; $\frac{H_0^t}{t}$, —, NBS (smoothed); ○, NBS (observed); ×, Shomate and Naylor; ▽, von Gronow and Schwiete; □, Roth and Bertram.

table 3 compared with the observed specific heats of Parks and Kelley, and Simon and Swain. The mean specific heat, H_0^t/t , is also plotted showing results of selected investigators for comparison. Use of the quantity H_0^t/t rather than H_0^t serves better to show up differences between investigators as well as irregularities in the work of any one investigator. The results of von Gronow and Schwiete [8] and Shomate and Naylor [9] are within 1 percent of those of this investigation, whereas the results of Roth and Bertram [10] are within 2 percent, with one exception. Observed data of the above authors were used in plotting figure 4, except for von Gronow and Schwiete, who published only smoothed results.

No weight is attached to the work of Cohn [11], Kolosovski and Skoulski [12], Newman and Brown [7], Miehr, Immke, and Kratzert [13], Wilkes [14], Esser, Averdick, and Grass [15], Lyashenko [16], Auzhbkovich [17], Cherbov and Chernyak [18], or earlier investigators because of obvious defects in experimental methods and/or sample. The results of the above authors differ by several percent on the average from those of this investigation, being lower for the most part, except from 100° to 200°C , where they cluster about the results of this investigation.

V. Conclusions

The results of the present investigation indicate that Al_2O_3 in the form of synthetic sapphire (corundum) is admirably suited to serve as a standard of heat capacity in the range 0° to 900°C . There is no apparent reason why it should not serve equally well in the range 0°K to 0°C , and from 900°C up to at least $1,600^\circ\text{C}$.

VI. References

- [1] D. C. Ginnings and R. J. Corruccini, *J. Research NBS* **38**, 583 (1947) RP1796.
- [2] J. C. Southard, *J. Am. Chem. Soc.* **63**, 3142 (1941).
- [3] G. Rutledge, *Phys. Rev.* **40**, 262 (1932).
- [4] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research NBS* **18**, 389 (1937) RP983.
- [5] G. S. Parks and K. K. Kelley, *J. Phys. Chem.* **30**, 47 (1926).
- [6] F. Simon and R. C. Swain, *Z. physik. Chem. [B]* **28**, 189 (1935).
- [7] A. B. Newman and G. G. Brown, *Ind. Eng. Chem.* **22**, 995 (1930).
- [8] H. E. von Gronow and H. E. Schwiete, *Z. anorg. allgem. Chem.* **216**, 185 (1933).
- [9] C. H. Shomate and B. F. Naylor, *J. Am. Chem. Soc.* **67**, 72 (1945).
- [10] W. A. Roth and W. W. Bertram, *Z. Elektrochem.* **35**, 297 (1929).
- [11] W. Cohn, *J. Am. Ceram. Soc.* **7**, 475 (1924).
- [12] N. A. Kolosovskii and I. Skoulski, *Bul. Soc. Ch m.* [4] **47**, 136 (1930).
- [13] W. Miehr, H. Immke, and I. Kratzert, *Tonind. Ztg.* **50**, 167 (1926).
- [14] G. B. Wilkes, *J. Am. Ceram. Soc.* **15**, 72 (1932).
- [15] H. Esser, R. Averdick, and W. Grass, *Arch. Eisenhüttenw.* **6**, 289 (1933).
- [16] V. S. Lyashenko, *Metallurg* **10**, 85 (1935).
- [17] A. E. Auzhbkovich, *Legkie Metal.* **5**, 23 (1936).
- [18] S. I. Cherbov and E. L. Chernyak, *J. Applied Chem. (USSR)* **10**, 1220 (1937).

WASHINGTON, November 29, 1946.