JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 69C, No. 1, January–March 1965

An Adiabatic Calorimeter for the Range, 10 to 360 °K

K. F. Sterrett,[1] D. H. Blackburn, A. B. Bestul, S. S. Chang, and J. Horman

(July 21, 1964)

A low temperature adiabatic calorimeter and cryostat assembly is described for measuring heat capacities in the temperature range 10 to 360 °K. A combination of Dewar and tank system is used as refrigerant containers. The temperature of the adiabatic shield is automatically controlled to within a millidegree of that of the calorimeter vessel. This apparatus offers facilities for rapid cooling to about 50 °K and long term adiabatic control for conditioning of a sample and, thus, is especially suitable for measurements on glass, where long equilibration time is sometimes involved.

Data on the empty calorimeter vessel and on the Calorimetry Conference standard sample of synthetic sapphire are presented as a measure of the precision and the accuracy of the apparatus.

1. Introduction

A new adiabatic calorimeter and cryostat assembly with an automatic shield control has been constructed to determine heat capacity and glass transition data for various inorganic and organic glasses from 10 to 360 °K. This paper describes in detail the design and operation of this low temperature calorimeter assembly and presents an experimental evaluation of its precision and accuracy.

Although the general calorimetric design is similar to that of a number of authors [1–4],[2] the sample vessel used in this apparatus has been constructed especially for measurements on glass. Hence, the adiabatic shield and automatic shield control [5] designs were chosen for (a) versatility in producing a desired thermal history of the glass sample, and (b) reliability over long periods of continuous operation necessary for studying "kinetic effects" associated with the glass transition. Older work [6,7] on the heat capacity of glasses at low temperatures in the transition region has mostly relied upon the use of isothermal calorimetry combined with manual operating procedures.

To evaluate the reproducibility and to estimate the accuracy of this apparatus, heat capacity measurements were performed on the empty sample vessel and on the Calorimetry Conference standard α-Al_2O_3 sample [8]. Previous work on samples of the same material were reported by Furukawa, Douglas, McCoskey, and Ginnings [8] of the Heat Division, by Morrison and Patterson [9], and by Edwards and Kington [10]. Kerr, Johnston, and Hallett [11] also made measurements on a synthetic sapphire similar in origin to our standard.

[1] Present address: Northrup Space Laboratories, Hawthorne, Calif.
[2] Figures in brackets indicate the literature references at the end of this paper.

2. Description of the Apparatus

2.1. Calorimeter and Cryostat Assembly

a. Sample Vessel

The 150 ml cylindrical sample vessel (fig. 1) was constructed with 0.015 in. copper sides, a 0.010 in. copper top and a 0.020 in. Monel bottom. The Monel bottom was silver soldered to the central copper reentrant well and to the copper cylinder which forms the outside of the vessel. A false 0.010 in. copper bottom held insulated binding posts for the heater and thermometer leads and was soldered with indium-tin eutectic to the vessel below

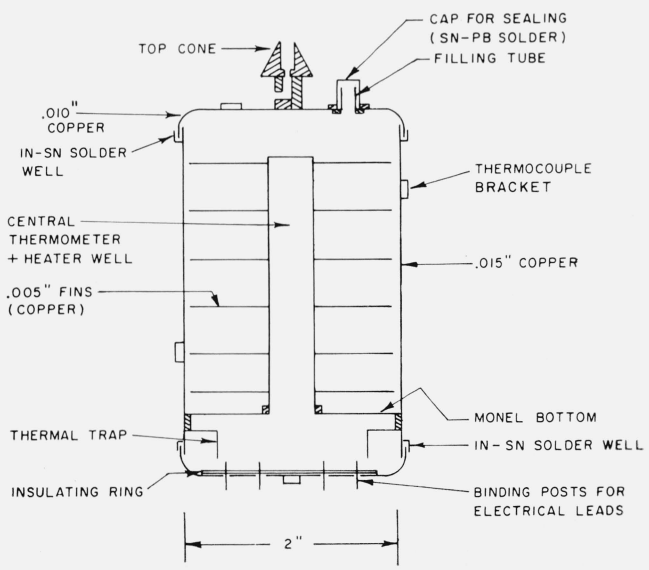

FIGURE 1. *Sample vessel.*

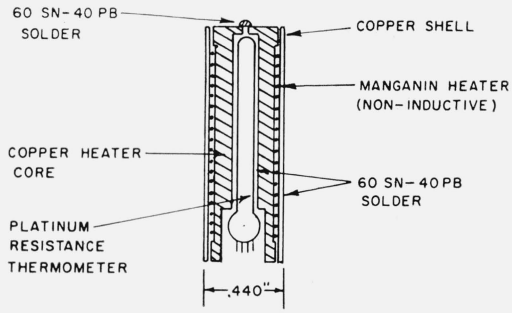

FIGURE 2. *Central well components.*

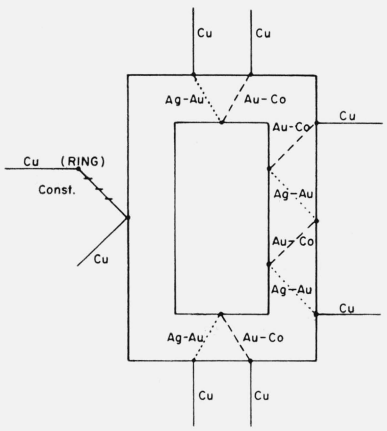

FIGURE 3. *Thermocouple schematic.*

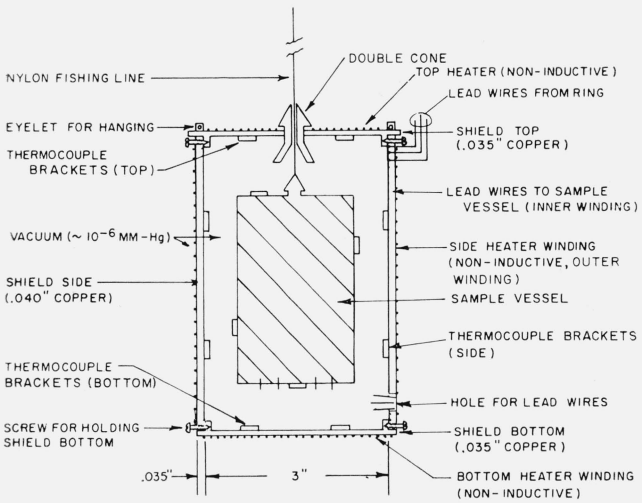

FIGURE 4. *Detail of adiabatic shield (showing sample vessel in measuring position).*

the Monel bottom. The top was designed to be soldered in place with this indium-tin eutectic after the vessel was packed with a sample. The entire sample vessel was gold-plated to minimize heat exchange by radiation. Six removable gold-plated fins, 0.005 in. thick × 0.500 in. i.d. × 1⅞ in. o.d., with raised edges and half-circle shaped holes and flaps were spring fitted to the central reentrant well in order to provide faster distribution of heat throughout the sample.

The central reentrant well components (fig. 2) contained a 25-ohm platinum resistance thermometer and a 180-ohm heater. The platinum resistance thermometer was an encapsulated four-lead, strain-free type described by Southard and Milner [12].

The heater consisted of #34 AWG [3] single cotton and enamel (S.C.E.) insulated manganin wire wound noninductively on a copper spool and insulated with several coats of G.E. #1696 high temperature varnish. The varnish was baked overnight at 150 °C after each application. The electrical leads from the thermometer and heater ran from the central well to the thermal trap, where they were wound around twice in 0.008 in. grooves. The winding was held in good thermal contact in the grooves with G.E. #7031 varnish. This winding prevented heat leakage along the leads during and immediately after a heating period when thermal gradients exist within the sample vessel. The leads then were connected to the binding posts mentioned above.

The central well components (fig. 2) were assembled using 60 tin-40 lead solder. The small hole at the top of the copper heater core, which let air escape during assembly of the thermometer into the core, was closed with a plug of the same solder. The assembly was then soldered within the central reentrant well of the sample vessel.

Two small U-shaped brackets were silver soldered to the side of the sample vessel. One junction of a multiple-junction difference thermopile used for controlling the adiabatic shield (fig. 3) was inserted into each bracket and was held by small copper wedges. Similar brackets were mounted on the top and false bottom. The junctions were electrically insulated from the copper sample vessel by mica "sandwiches." This type of mounting and insulation was described by R. B. Scott et al. [13].

A 60° cone was silver soldered at the center of the sample vessel top. This cone anchored the nylon suspension and also made thermal contact through the double adiabatic-shield cone to the helium tank when the sample vessel was cooled to liquid helium temperatures.

To aid in the distribution of heat, helium gas was introduced into the sample vessel at a slight overpressure through a 3/16 in. o.d. copper tubing which was soft-soldered to a tube fitting at the top of the sample vessel. The tubing was pinched off and sealed immediately with a drop of soft solder.

b. Adiabatic Shield and Control Thermocouples

The adiabatic shield (fig. 4) consisted of a 0.035 in. thick, 5.5 in. long copper can, gold plated. It was cylindrical with flat ends surrounding the sample vessel. The top and bottom were firmly attached to the side by means of two 56 screws. When the shield was in measuring position, it was suspended

[3] Hereafter, the numeral preceded by the # mark denotes the American wire gage number.

by three nylon lines attached to eyelets on the shield top. A 60° double cone which was an integral part of the top provided thermal contact between the sample vessel and the liquid helium tank as described above.

Differential thermocouples (fig. 3) between the calorimeter vessel and shield in conjunction with three independently controlled electrical heaters wound on the top, side, and bottom of the shield enabled the maintaining of the shield at the temperature of the sample vessel. Four thermocouple brackets were soft-soldered to the interior of the side, two to the top, and two to the bottom. The thermocouple junctions were attached to these brackets as described in the previous section.

The differential thermocouple consisted of two or more (Ag+0.37 at. percent Au) versus (Au+2.1 at. percent Co) junctions. This choice of thermocouple gave a greater thermoelectric power at low temperatures than a (Cu) versus (Constantan) thermocouple [14]. To keep the thermal conductivity low, especially at low temperatures, the silver alloy was used instead of (Cu) between the shield and sample vessel. The thermoelectric power of this "normal" silver is approximately the same as that of (Cu). All junctions were welded with a condenser discharge type welder.

The heater on the side shield was noninductively wound in a series of 0.012 in. spiral grooves machined in the side shield. It consisted of about 500 ohms of #30 S.C.E. Constantan wire which was thermally bonded to the metal with G.E. #7031 varnish. A layer of aluminum foil was placed over the heater to reduce heat loss by radiation. Beneath this heater thirty #34 copper lead wires and two #34 Constantan thermocouple wires were bonded to the side shield in another set of 0.008 in. grooves. These lead wires wrapped around the shield six times and passed into the interior through a hole near the bottom.

The heaters on the top and bottom shield consisted of about 125 ohms of #30 S.C.E. Constantan wire which was noninductively wound into a disk. A special coil winder was built to produce this flat winding. The flat coil was transferred to the copper shield top and then was varnished into place with G.E. #7031.

c. Floating Ring

Thirty-two #36 Formvar, double silk insulated copper wires were wound and varnished on a 1 in. wide $\times 2\frac{3}{4}$ in. diam. copper ring. These lead wires came from the helium tank where they were equilibrated at the helium tank temperature, to the ring where a 150 ohm noninductive #34 Constantan heater was used at temperatures above 200 °K to bring them to the temperature of the adiabatic shield. A single junction Cu versus Constantan thermocouple on the side shield (fig. 4) and a similar thermocouple junction on the ring sensed the temperature difference.

The floating ring was thermally insulated from the helium tank by three 1 in. long $\times \frac{3}{16}$ in. diam. plastic spacers. Each spacer also held one end of a nylon line which supported the adiabatic shield in the measuring position. An insulating ring attached to the copper floating ring contained 32 copper binding posts which connected the leads from the adiabatic shield to those from the floating ring.

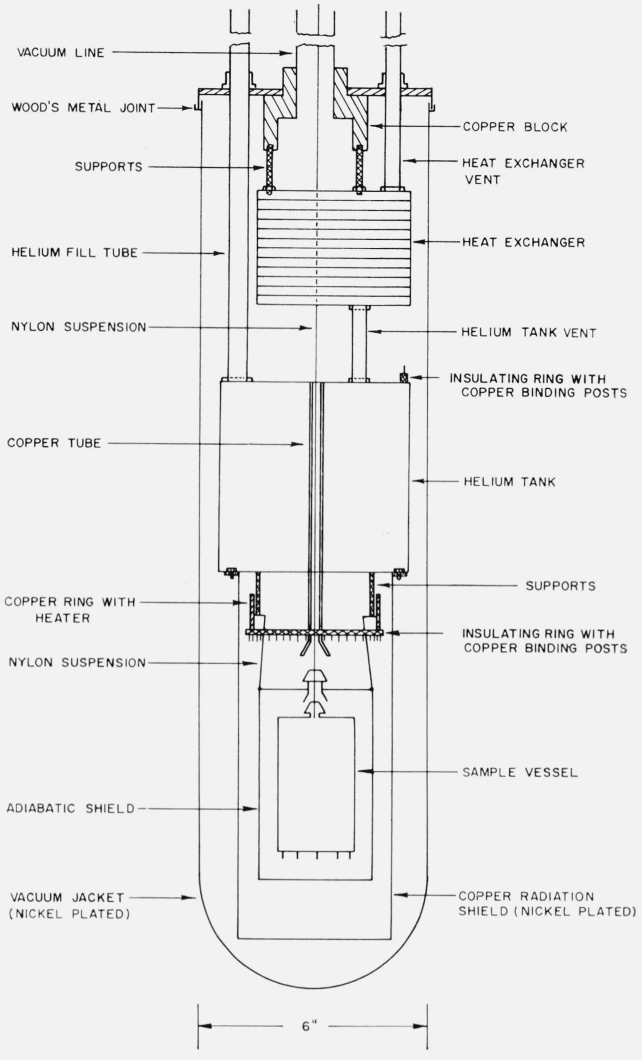

FIGURE 5. *Low temperature adiabatic calorimeter.*

d. Helium Tank and Radiation Shield

The internal coolant container (fig. 5—helium tank) held liquid helium or liquid nitrogen, depending upon the temperature range desired. By pumping on the coolant through the 0.5 in. diam. $\times$ 0.010 in. wall Monel "fill" tube while the $\frac{3}{8}$ in. diam. $\times$ 0.004 in. wall Monel vent tube was closed, temperatures can be obtained below the normal boiling points of liquid helium and liquid nitrogen.

The tank was constructed from 0.040 in. wall copper and was 5 in. long $\times$ 5 in. diam. Thirty-two #36 copper wires were wrapped six times around the tank in 0.008 in. grooves. The leads were varnished in these grooves and were connected to copper binding posts mounted in a plastic strip at the top of the tank. This procedure assured thermal equilib-

rium of the leads at the tank temperature to prevent heat from leaking to the floating ring and adiabatic shield assembly.

Six 10-32 threaded studs at the bottom of the helium tank were used to hold a nickel-plated copper radiation shield, 8.5 in. long × 4 in. diam. × 0.015 in. wall. The thirty-two #36 wires which were varnished to the helium tank entered the radiation shield through a small slot and then wrapped around the floating ring.

A ½ in. diam. × 1/16 in. wall copper tube with a 60° cone at the lower end extended from the top of the helium tank to 2 in. below the bottom of the helium tank. This 60° cone provided thermal contact to the shield and the sample vessel through the operation of the mechanical heat switch described in section 2.1.h.

A 3/32 in. o.d. × 0.015 in. wall Monel tube (not shown in fig. 5) led from the top of the helium tank to outside the cryostat. This tube served as a pressure measuring line when the pressure above the refrigerant was lower than atmospheric.

e. Heat Exchanger

When liquid helium was used as the coolant, the "boil-off" helium gas passed through the vent tube (fig. 5) to the interior of a 1/16 in. wall × 4 in. o.d. copper can containing ten copper fins, 0.010 in. thick × 3.75 in. o.d. × 2 in. i.d. These fins were soft soldered to the interior walls of the can. Around the outside of this can thirty-two #34 copper leads were wrapped and varnished with G.E. #7031 in 0.010 in. grooves. This design equilibrated the leads at a temperature somewhere between the boiling point of helium and the temperature of the nitrogen bath surrounding the vacuum jacket. It reduced the heat leak along the leads to the helium tank and thus served to diminish the liquid helium "boil-off" rate. This heat exchanger is similar to the "helium economizer" described by Westrum et al. [1].

f. Copper Block

A copper block, 2.5 in. diam., shown in figure 5, was silver soldered to the top flange of the brass vacuum jacket. Thirty-two #34 copper lead wires came down the vacuum line to this block where they were thermally bonded using G.E. #7031 varnish. This equilibration of the leads at the outer bath temperature minimized heat leakage along the leads from room temperature to the components inside the vacuum jacket.

Bundles of leads of about 12 in. length formed a full turn of loose helix between two adjacent components inside the vacuum jacket; namely, between the adiabatic shield and the binding posts on the floating ring, the ring and the helium tank, the binding posts on the tank and the heat exchanger, and the exchanger and the copper block.

g. Vacuum Jacket

A 24 in. long x 6 in. diam. x 1/16 in. wall nickel-plated, brass tube with a hemispherical spun bottom surrounded the components mentioned above. The spun bottom was silver soldered to the tube. The top of this tube was soldered with Wood's metal to a flange which held the interior parts. A vacuum of 1–3 x 10^{-6} mm Hg was maintained when desired for heat insulation within the brass tube.

h. Windlass and Mechanical Heat Switch

The internal bellows assembly from a ¾ in. Veeco high vacuum valve was employed as a convenient and compact windlass which caused contact between the 60° mating cones on the helium tank, adiabatic shield and sample vessel. This mechanical heat switch provided thermal contact between the sample vessel and the helium tank without using helium gas to destroy the insulating vacuum.

The valve assembly consisted of a sylphon bellows, an O-ring bonnet seal and an adjustment screw for raising and lowering the bellows. The effective length of the bellows was doubled by passing the sample vessel suspension over a pulley mounted on the plunger and then tying the suspension to an eyelet at the top of the heat exchanger.

i. Nitrogen Dewar

A 36 in. long x 8¼ in. i.d. stainless steel Dewar held in a brass container surrounded the vacuum jacket. The brass can was counterweighted so that it could slide easily on steel elevator rails. An O-ring was used at the top of this can as a vacuum seal.

2.2. External Electrical Equipment

a. Calorimeter Heater and Thermometer Circuits

The resistance of the platinum thermometer was determined by measuring the potential drop across and the current passing through the thermometer. A Rubicon #2773 Double Six-Dial Thermofree potentiometer calibrated by the Electricity Division was used to observe the potential across the thermometer on one set of its dials. The other set was used to measure the potential drop across a standard resistor in series with the thermometer. The double potentiometer was also used to measure the electrical energy dissipated by the heater during heating periods by observing the potential drop across the heater and that across a standard resistor in series with it. Voltage dividers made of standard resistors were used to reduce the voltage to within the range of the potentiometer (0.1111110 V). The balance indicating instrument was a Rubicon #3550 photoelectric galvanometer, the output of which was observed on a 25–0–25 microammeter connected in series in a resistance network to provide suitable overall sensitivity.

b. Interval Timer

The NBS standard frequency line supplied 60 cycles at 2 V which was amplified to 110 V to power the interval timer. The clutch of the timer was energized from the 110 V a-c general laboratory supply by the same switch that supplied power to the calorimeter heater.

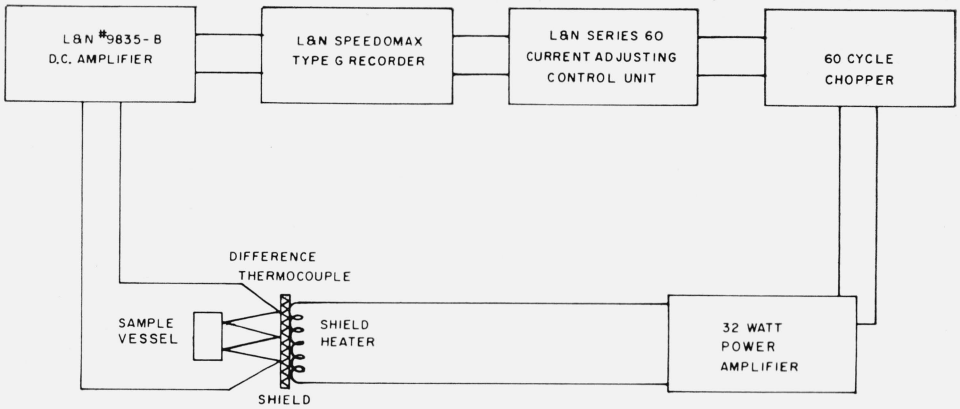

FIGURE 6. *Automatic shield control.*

c. Automatic Shield and Floating Ring Control Circuits

The automatic adiabatic shield control was similar to that used by the Heat Division [5]. It consisted of the thermocouple arrangement described earlier, three each of Leeds & Northrup 9835–B d-c amplifiers, Speedomax G recorders and Series 60 C.A.T. control units. In each channel the control signal generated by the C.A.T. unit was converted into ac by a 60-cycle chopper before feeding into a 32-W power amplifier from which power for heating the corresponding shield was generated (fig. 6). The deviation of shield temperature from the control point was usually within about 0.001 to 0.002°. Temperature differences in the order of 0.005 to 0.01° occurred momentarily at the beginning and the end of a heating period. The momentary departure from zero at "on" and "off" was so small that no correction for the heat input was necessary.

The floating ring was controlled manually with a box-type galvanometer as the indicator and with 110 V a-c variable transformers supplying heater power.

2.3. Vacuum Systems

Three vacuum systems were used with the calorimeter. They provided vacuum of 1–3 x 10^{-6} mm Hg for heat insulation, means for reducing the temperature of the refrigerants in the Dewar and in the helium tank, and the ability to fill the space in the vacuum jacket with helium heat exchange gas to cool the sample vessel when helium was used as refrigerant.

3. Temperature Scale

The platinum resistance thermometer was calibrated by the Temperature Physics Section of the Heat Division, above 90 °K in accordance with the International Practical Temperature Scale of 1948 [15] and between 10° and 90 °K with the NBS–1955 provisional scale, which is maintained by a set of platinum resistance thermometers which had been compared with a helium-gas thermometer. This provisional scale is 0.01° lower than the NBS–1939 scale [16].

4. Measurement Procedures

In both the α-Al_2O_3 and the empty sample vessel determinations a small quantity of helium gas was sealed in the sample vessel to shorten the internal thermal equilibration time. The sealed vessel was then checked for leaks with a helium mass spectrograph and hung in place in the cryostat with nylon fishing line. Thermocouples, electrical leads, radiation shield, and outer vacuum jacket were attached before the apparatus was cooled to the desired Dewar bath temperature with 10 to 20 cm Hg helium exchange gas in the vacuum jacket. After equilibration at the Dewar bath temperature the exchange gas was pumped out and heat capacity determinations were begun.

A special cooling procedure was used for the liquid helium range determinations; namely, (1) precooling with solid nitrogen around the vacuum jacket, (2) restoration of high vacuum within the vacuum jacket, (3) raising of the windlass to provide thermal contact between sample vessel, adiabatic shield and helium tank, (4) filling helium tank with liquid helium, (5) waiting a few hours for equilibration at 4 °K, and (6) lowering the windlass to obtain thermal insulation. The supply of liquid helium from one filling of the helium tank was sufficient for cooling and about 15 hr of experimental determinations.

5. Heat Capacity Measurements

Heat capacities of the empty sample vessel and of the vessel loaded with sapphire sample were determined from 10 to 360 °K. The results were tabulated in tables 1 and 2, respectively. Data represented were corrected for curvature. The correction was, in general, less than 0.1 percent of the apparent heat capacity. The temperature rise per heating interval was about 1 to 4° below 30 °K, 4 to 6° from 30 to 80 °K, and 5 to 9° above 80 °K.

The observed heat capacity data were fitted by means of least squares to an equation with Debye and Einstein terms programmed by the Heat Measurements Section [17]. Deviations of data

TABLE 1. *Principal experimental data for the heat capacity of the empty sample vessel*

C_p	T	ΔT
	Series I	
J/deg	°*K*	°*K*
72.174	302.129	4.761
72.400	306.994	4.934
72.643	311.917	4.911
	Series II	
19.899	52.043	5.994
23.782	57.549	5.018
26.970	62.296	4.427
30.188	67.353	5.673
33.397	72.753	5.126
36.208	77.680	4.727
38.589	82.258	4.432
38.953	82.900	6.735
42.070	89.379	6.226
42.037	89.276	7.265
44.903	96.302	6.787
47.396	102.904	6.418
49.526	109.177	6.129
51.396	115.189	5.896
53.041	120.989	5.704
54.543	126.609	5.537
52.685	119.735	6.201
	Series III	
0.3920	10.546	1.049
.6657	13.468	4.452
1.1732	16.997	2.531
1.6305	19.214	1.820
2.1121	21.110	1.911
2.8698	23.534	2.883
3.9794	26.469	2.945
5.5982	29.990	4.071
7.8032	34.066	4.056
10.334	38.110	4.021
13.439	42.817	5.385
17.041	47.988	4.950
21.150	53.834	6.741
	Series IV	
0.3979	10.735	1.548
.5289	12.289	1.533
.6971	13.864	1.505
.9058	15.392	1.517
1.1565	16.898	1.467
1.4477	18.388	1.471
1.7874	19.873	1.474
2.3313	21.862	2.467
3.1493	24.346	2.482
4.1300	26.836	2.479
5.3848	29.577	2.986
6.9580	32.573	2.978
8.7349	35.609	3.082
10.647	38.643	2.978
12.979	42.152	3.959
15.714	46.111	3.957
18.515	50.078	3.977
21.313	54.062	3.990
24.076	58.054	3.990
	Series V	
23.409	57.093	3.972
26.135	61.066	3.976
28.750	65.036	3.963
31.208	69.019	4.002
34.102	73.983	5.927
37.420	79.951	6.006
40.468	85.936	5.963
46.480	100.394	5.456
48.472	106.036	5.828
50.388	111.924	5.948
52.195	117.948	6.100
53.894	124.503	6.008
55.304	129.877	5.687
56.614	135.697	5.951
59.015	147.609	6.217
60.095	154.008	6.435
61.099	160.510	6.567
62.053	167.074	6.560
63.743	180.180	6.514
64.496	186.951	7.029
65.203	193.929	6.932
65.898	200.934	7.078

TABLE 1. *Principal experimental data for the heat capacity of the empty sample vessel*—Continued

C_p	T	ΔT
	Series VI	
J/deg	°*K*	°*K*
63.781	181.111	7.319
65.362	196.145	8.280
66.827	212.509	8.087
67.518	220.551	7.999
68.095	228.513	7.925
68.664	236.397	7.852
	Series VII	
62.993	174.541	8.794
63.981	183.262	8.648
64.919	191.843	8.515
65.761	200.301	8.396
66.511	208.643	8.292
67.209	216.600	7.987
67.741	224.553	7.918
68.318	232.429	7.843
	Series VIII	
68.978	243.327	7.395
69.559	250.689	7.326
69.972	257.989	7.272
70.429	265.234	7.217
70.766	272.428	7.171
71.169	279.573	7.121
69.394	246.974	4.768
69.745	251.706	4.741
70.049	256.437	4.714
70.418	261.141	4.686
70.814	271.719	4.627
71.020	276.343	4.610
	Series IX	
72.544	310.048	5.537
72.877	315.549	5.505
72.919	321.055	5.497
73.383	326.524	5.457
72.628	313.204	5.491
72.997	318.668	5.458
73.055	324.127	5.446
73.505	329.271	5.391
73.634	335.150	5.372
73.874	339.533	5.349
	Series X	
72.455	307.322	5.410
72.655	312.725	5.384
	Series XI	
71.202	281.346	5.526
71.431	286.898	5.501
71.743	292.381	5.473
72.123	297.472	5.421
72.223	302.888	5.408
72.474	307.981	5.365
72.682	313.665	5.400
73.007	319.058	5.371
73.153	325.117	5.355
73.350	329.782	5.335
73.551	335.117	5.314
73.730	340.468	5.378
73.965	346.128	5.883
74.182	352.139	6.150
74.446	358.505	6.538

TABLE 2. *Heat capacity data for sample vessel containing synthetic sapphire sample*

T	ΔT	$C_{p\ \text{total}}$	$C_p\ Al_2O_3$
		Series I	
°K	°K	J/deg	J/deg/mole
10.908	1.553	0.4123	0.010
12.554	1.939	.5743	.019
16.613	2.628	1.172	.041
20.606	5.358	2.122	.078
25.456	4.349	3.861	.153
30.449	5.631	6.346	.272
36.793	7.050	10.504	.515
42.775	4.912	15.134	.864
47.765	5.071	19.418	1.267
52.831	5.063	24.059	1.807
		Series II	
61.852	4.849	32.766	3.071
63.953	3.850	34.850	3.429
67.952	4.153	38.824	4.173
72.016	3.598	42.918	5.019
79.084	3.066	50.166	6.682
82.068	2.899	53.225	7.756
85.474	6.076	56.766	8.375
90.695	2.469	62.126	9.921
		Series III	
76.972	4.757	47.939	6.128
81.864	5.029	52.979	7.381
84.823	6.101	56.105	8.228
90.311	2.580	61.753	9.819
116.260	1.780	88.326	18.595
118.022	1.742	90.226	19.313
		Series IV	
96.546	5.061	68.067	11.71
102.199	6.244	73.881	13.57
108.197	5.747	79.994	15.63
113.743	5.340	85.829	17.70
119.886	6.943	92.097	20.00
126.580	6.442	98.942	22.59
133.229	6.876	105.55	25.17
139.889	6.444	112.27	27.88
146.889	7.566	119.15	30.70
154.230	7.115	126.28	33.74

TABLE 2. *Heat capacity data for sample vessel containing synthetic sapphire sample*—Continued

T	ΔT	$C_{p\ \text{total}}$	$C_p\ Al_2O_3$
		Series V	
°K	°K	J/deg	J/deg/mole
154.837	6.985	126.88	33.96
162.007	7.354	133.55	36.79
169.569	7.783	140.08	39.83
177.166	7.405	147.28	42.75
184.408	7.073	153.53	45.51
191.346	6.796	159.43	48.14
198.666	7.839	165.17	50.70
206.352	7.534	171.20	53.42
213.751	7.264	176.90	56.00
221.771	8.767	182.48	58.53
238.598	8.189	193.99	63.80
		Series VI	
205.015	4.258	170.30	53.01
211.700	9.106	175.22	55.23
220.632	8.775	181.57	58.10
229.248	8.473	187.52	60.82
237.578	8.207	193.35	63.49
245.660	7.972	198.53	65.86
266.072	8.277	210.58	71.35
274.230	8.069	215.13	73.50
282.280	7.873	219.44	75.49
289.906	7.700	223.21	77.22
297.546	7.547	226.81	78.87
		Series VII	
242.519	8.941	196.71	65.04
249.961	9.493	200.70	66.84
259.270	9.203	206.54	69.54
266.884	6.077	210.72	71.45
260.867	8.409	207.39	69.92
269.134	8.194	212.43	72.15
277.198	8.005	216.67	74.20
286.847	8.558	221.59	76.47
		Series VIII	
308.929	6.985	231.78	81.15
315.828	6.895	235.39	82.84
322.649	6.820	238.05	84.06
336.049	6.652	243.60	86.62
340.584	6.650	245.23	87.37
347.161	6.569	247.30	88.31
353.623	6.468	250.16	89.65

points from the equation were shown in figures 7 and 8 for the empty vessel and the loaded vessel, respectively. The deviations were, in general, confined within the envelope formed by the solid lines representing 0.1 percent of the observed heat capacity. The larger deviations near 90 °K probably resulted from the imperfection of the two temperature scales used.

A peritectic decomposition of the γ-phase of indium-tin alloy was proposed to occur below 80 °C, although no thermal effect for the reaction was found [18]. No thermal anomaly was observed in the heat capacity measurements.

Molal heat capacity values for α-Al_2O_3 were also listed in table 2. The Calorimetry Conference standard synthetic sapphire sample weighing 199.913 g (in vacuo) was used. The molecular weight (1961) of alumina was taken as 101.9612. Adjustments were made for the differences in the amount of helium, copper, and solders used between the measurements of the empty and of the loaded vessel.

Deviations of the observed heat capacity values of α—Al_2O_3 from those of Furukawa et al., are shown in figure 9. The heat capacity of the empty sample vessel represented 95 to 85 percent of the total heat capacity of the loaded vessel from 10 to 50 °K, 85 to 65 percent from 50 to 100 °K, 65 to 40 percent from 100 to 200 °K, and from 40 to 30 percent from 200 to 360 °K. Hence deviations below 50 °K were not shown due to the unfavorable contribution from the empty vessel. The dash-line represented molal heat capacity values derived from the two equations with Debye and Einstein terms for the empty and the loaded vessel. The values at rounded temperatures were listed in table 3. Deviation of this curve from the data of Furukawa et al., varied between zero to +0.08 percent for the temperature range from 100 to 360 °K. From 100 to 50 °K, the deviation was of the order of 0.2 to 0.4 percent, and from 50 to 10 °K, 2 to 10 percent. Hence, with estimated uncertainty of 0.1 percent in the measurement of the total heat capacity (figs. 7 and 8), the agreement between the smoothed observed heat capacity and that of Furukawa et al., was remarkable. If the sample vessel were loaded with an appropriate amount of a typical glass, e.g., vitreous sodium tetraborate [19], the precision and accuracy should be markedly improved due to the more favorable

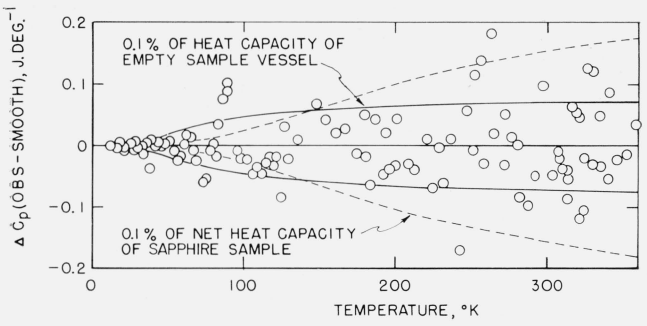

FIGURE 7. *Heat capacity of empty sample vessel, deviations of experimental data from a smooth curve.*

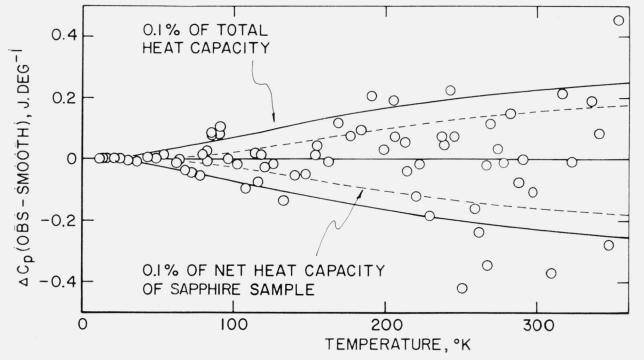

FIGURE 8. *Heat capacity of loaded sample vessel, deviations of experimental data from a smooth curve.*

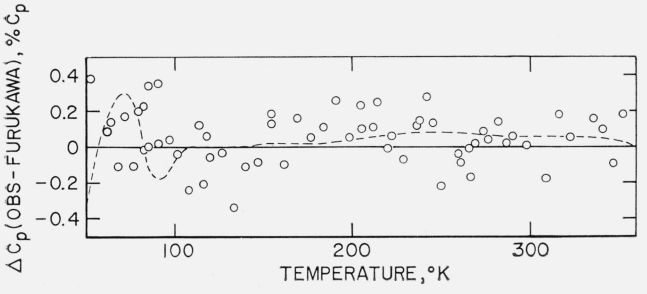

FIGURE 9. *Deviation of observed heat capacity of synthetic sapphire from the data of Furukawa et al.* [8]

contribution from the empty sample vessel toward the total heat capacity of the loaded vessel.

It was found that the EMF selector switch of the double potentiometer was of the "make-before-break" type, such that during the switching operation a shunt of very low resistance was effectively put across either the thermometer or the heater during temperature or power measurements respectively. Thus, a portion of the experimental error might be attributed to either the resulting upsetting of the steady-state of the thermometer current or inaccuracy in the evaluation of energy input. In some of the later runs of the loaded calorimeter vessel, by means of a different voltage divider arrangement, this type of error was minimized in the power measurement. However, these data points showed

TABLE 3. *Heat capacities of synthetic sapphire*

T	C_p	T	C_p
°K	J/deg/mole	°K	J/deg/mole
10	0.010	190	47.54
20	.067	200	51.16
30	.246	210	54.63
40	.674	220	57.96
50	1.487	230	61.14
60	2.782	240	64.18
70	4.595	250	67.07
80	6.904	260	69.81
90	9.670	270	72.42
100	12.83	280	74.89
110	16.32	290	77.23
120	20.06	300	79.45
130	23.96	310	81.56
140	27.96	320	83.55
150	31.99	330	85.44
160	36.00	340	87.22
170	39.94	350	88.92
180	43.80	360	90.52

scattering of the same order as the others. Hence, the deviation produced by the usual fast switching operation of the double potentiometer was assumed to be less than 0.1 percent. Nevertheless, experimental error resulting from this source could be completely eliminated by changing the switching arrangements to a "break-before-make" type [20]. Other possible sources of systematic error are being investigated.

6. References

[1] E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, J. Chem. Phys. **21,** 419 (1953).

[2] R. A. Ruehrwein and H. M. Huffman, J. Am. Chem. Soc. **65,** 1620 (1943).

[3] H. M. Huffman, Chem. Rev. **40,** 1 (1947).

[4] T. M. Dauphinee, D. K. C. McDonald, and H. Preston-Thomas, Proc. Roy. Soc. **221A,** 167 (1954).

[5] G. T. Furukawa and M. L. Reilly, publication pending.

[6] G. E. Gibson and W. F. Giauque, J. Am. Chem. Soc. **45,** 93 (1923).

[7] G. S. Parks, S. B. Thomas, and D. W. Light, J. Chem. Phys. **4,** 64 (1936).

[8] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. NBS **57,** 67 (1956) RP2694.

[9] J. A. Morrison and D. Patterson, Trans. Faraday Soc. **52,** 764 (1956).

[10] J. W. Edwards and G. L. Kington, Trans. Faraday Soc. **58,** 1313 (1962).

[11] E. C. Kerr, H. L. Johnston, and N. C. Hallett, J. Am. Chem. Soc. **72**, 4740 (1950).

[12] J. C. Southard and R. T. Milner, J. Am. Chem. Soc. **55,** 4384 (1933).

[13] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Res. NBS **35,** 39 (1945).

[14] R. L. Powell, M. D. Bunch and R. J. Corruccini, Cryogenics **1,** 139 (1961).

[15] H. F. Stimson, J. Res. NBS **65A,** (Phys. and Chem.) No. 3, 139 (1961).

[16] H. J. Hoge and F. G. Brickwedde, BS J. Res. **22,** 351 (1939).

[17] G. T. Furukawa and M. L. Reilly, publication pending.

[18] F. N. Rhines, W. M. Urquhart and H. R. Hoge, Trans. Am. Soc. Metals **39,** 69 (1947).

[19] E. F. Westrum, Jr., and G. Grenier, J. Am. Chem. Soc. **79,** 1799 (1957).

[20] G. T. Furukawa and S. S. Chang (to be published).

(Paper 69C1–181)