An Automatic Adiabatic Calorimeter for Low Temperatures. The Heat Capacity of Standard Benzoic Acid[1]

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In recent years there has been an increasing interest in the heat capacities of crystals at low temperatures as a means to determine, for example, third law entropies, the purity of materials, and the frequency spectra of the lattice modes of vibration. Numerous methods of measuring the low-temperature heat capacity of the crystal have been reported. In the " adiabatic "-type calorimeter, two operators, at least, and tedious labor are required in order to obtain highly accurate results. The development of electronics in recent years has, however, made it possible to replace manual regulation with automatic control and also manual observation with automatic recording, without any general loss of the claimed accuracy. Stull[2] has, in fact, recently developed such an automatic calorimeter. This report stimulated us to construct such a one-man-operated type low-temperature calorimeter with a high accuracy.

The present paper will report the construction and the operational procedure of this low-temperature calorimeter and will also present the results of our heat-capacity measurement of a standard sample of the benzoic acid crystal, which is used for checking the reliability and accuracy of our results.

Apparatus

Calorimeter and Cryostat.—A schematic cross section of the calorimeter and the cryostat is shown in Fig. 1. The apparatus is of the adiabatic type, consisting of a vacuum-insulated calorimeter surrounded by an adiabatic shield whose temperature is maintained at essentially the same level as that of the calorimeter during heat-capacity measurements. The sample container, A, is made of gold plate, with walls 0.3 mm. thick and with a central re-entrant well into which a combined thermometer-heater is set. In order to obtain good heat conduction between the container and the specimen, six radial fins of platinum 0.1 mm. thick are attached with silver solder to the outside of the well and also to the inside of the container. A brass cap with capillary copper tubing is unsoldered and resoldered in order to change samples.

The calorimeter temperature is measured with a Leeds and Northrup 25-ohm " four

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[1] Reported at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[2] D. R. Stull, *Anal. Chim. Acta*, 17, 133 (1957).

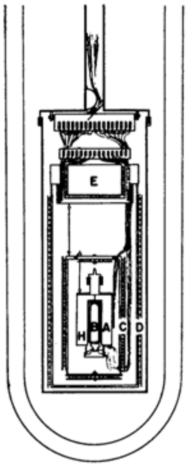

Fig. 1. Schematic diagram of low-temperature adiabatic calorimeter (13—300°K).

lead" platinum-resistance thermometer, 5 mm. in diamerter and 50 mm. long. Around the outside of this thermometer, the calorimeter heater, formed of approximately 100 ohms of #36 B and S constantan wire, for the supply of electrical energy is wound non-inductively and insulated with G. E. adhesive #7031. The surface is coated with gold foil, and the thermometer-heater is set rigidly into the central well of the calorimeter with Wood's metal. Around the protruded bottom of the calorimeter, all the lead wires from the thermometer-heater are wrapped tightly, insulated with the G. E. adhesive, and then soldered to copper lugs. The container is hung from the top of the inner adiabatic shield, C, with three nylon threads, the length of which can be adjusted externally. The empty weight of the container, including the thermometer-heater, is about 100 g.

The inner adiabatic shield is made of brass, 1 mm. thick, and it is chromium-plated on both sides. It consists of three portions, top, sides and bottom. The side portion is fitted with copper lugs to which are connected all the lead wires coming from the container to the outside. All the wires from this connecter are bundled together and wound on the outer surface of the side portion of the shield for four turns and then secured with the adhesive. These wires and the whole of the outer surface of the shield are wrapped with a heater made of #32 B and S constantan wire. The heater is wrapped in three sections. The resistance around the cyrindrical side portion is about 100 ohms, while that of the top and bottom portions is approximately 40 ohms. The entire surface is coated with the adhesive, covered with a heavy grade of aluminum foil.

Difference thermocouples between the container and the inner adiabatic shield are of the Chromel-P constantan type, formed of #38 and #36 B and S wires, and they are placed in seven different positions within the adiabatic shield. The other junctions are gathered together and secured to, but electrically insulated from, the pocket of the sample container.

The inner adiabatic shield is hung with three nylon threads from the upper block, E, which is in turn hung by adjustable nylon cords from the vacuum jacket. This block consists of brass (3 kg.), an embedded constantan heater, copper lugs, and two Chromel-P constantan difference thermocouples whose other junctions are secured to the inner adiabatic shield. Surrounding the inner adiabatic shield, an outer shield, D, is hung with detachable chains from the upper block. The outer shield, 60 mm. in diameter and 250 mm. high, constantan heater and two difference thermocouples whose other junctions are placed on the inner adiabatic shield. In order to obtain good performance in the temperature control of the inner shield, the temperature of the outer shield is kept somewhat below that of the inner shield so as to offer a necessary cold head. All the lead wires from the calorimeter assembly are, after being wrapped to the inner shield, in intimate contact with the upper block and are secured with the adhesive and then passed through a hole to copper lugs attached to the bakelite ring. Hereafter, the wires passed through stainless steel tubing, 25 mm. in diameter and 900 mm. long to the top closure, where they emerge through a vacuum seal made of bees wax.

For the refrigeration, the calorimeter assembly is mounted in the glass dewar, 110 mm. in outer diameter and 1200 mm. long. Liquid nitrogen or liquid hydrogen as a refrigerant is transferred by means of a transfer siphon entering the equipment through the top plate.

Measuring and Control Circuits.—A schematic diagram of measuring and control circuits is given in Fig. 2. The resistance of the thermometer could be recorded continuously on a Leeds and Northrup "High-Precision" resistance recorder, by means of which the temperature of the sample could be read to ±0.01°K at room temperature. When more precision was needed in the temperature measurement, the resistance was measured with a Leeds and Northrup-type G-2 Mueller Bridge in conjunction with a high sensitive galvanometer and lamp scale. At all except the lowest temperatures, the resistance of the thermometer could be read to a precision of one or two parts per ten thousands with this equipment.

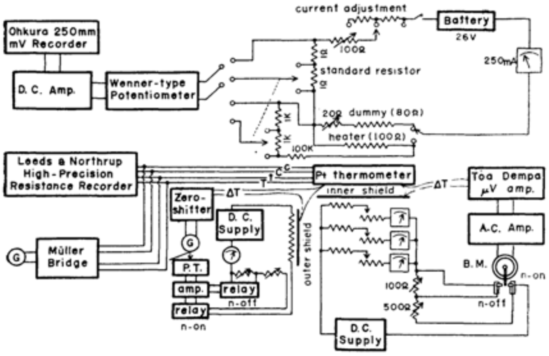

Fig. 2. Circuits diagram for heat capacity measurements.

The electrical energy for heating the calorimeter was supplied by four storage batteries (capacity: 120 amp. hr. at 26 V.). The current was adequately adjusted by means of a six-dial decade resistor and a variable resistor. The current was determined by the potential drop across a 2-ohm (or 1-ohm) series resistor. The potential drop across the calorimeter heater was divided by a 100000-ohm volt box, which had a 100 : 2 (or 100 : 1) ratio certified to 0.01 per cent. These two potential drops were mostly compensated for, respectively, by means of a Leeds and Northrup Wenner potentiometer; the residual differences were, after amplifying by a d. c. amplifier, recorded continuously on a Ōkura 250-mm. voltage recorder. All the necessary standard resistors were contained in a box held at the constant temperature of 32±0.5°C, where the temperature coefficient of the resistance of manganin wire is essentially zero. Since the resistance of the calorimeter heater was not constant over even one heating period, the current and the voltage through and across the heater were recorded alternatively in this period according to Giauque's schedule,[3] i.e., currents at 0.21 τ and 0.79 τ, and the voltage at 0.50 τ, where τ means the total heating period. To allow for the small amount of heat generated in the current leads between the calorimeter and the inner adiabatic shield, one of the potential leads was attached to a terminal on the calorimeter, and the other to a terminal on the inner shield. If the resistances of the current leads are similar, this procedure accounts for that part of the heat generated in them which flows to the calorimeter. When the heater was not energized, the current was kept at the same value as that through the heater by connecting the circuit to a dummy heater composed of fixed and variable constantan resistors. The energy input was automatically started and stopped by an electric timer synchronized with a transistor clock, as is shown in Fig. 3. The input interval was held to integral seconds by synchronizing the heater switch with a relay which was closed once each second. The interval was measured by a counter and was found to be accurate to 0.05% or better.

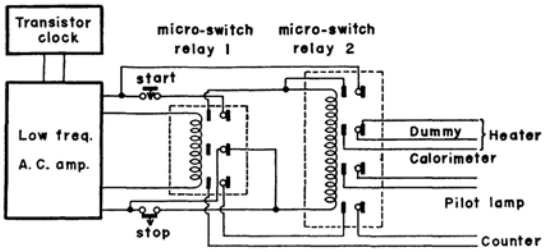

Fig. 3. Circuits of electronic timer.

The precise control of the temperature difference between the calorimeter and the inner shield is essential for accurate measurements in the adiabatic-type calorimeter. For this purpose, a signal from a seven-junction Chromel-P constantan thermocouple which registered any temperature difference between them was fed to a Tôa Dempa AD-4 d.c. amplifier and an a. c. amplifier, the output of the latter amplifier being used to operate a balancing motor (Fig. 4). When the thermocouple thus signaled that the shield was colder than that calorimeter, the balancing motor converted a "normally open" relay to the "closed" state, thus shortening the series resistor in the heater circuit, resulting in an increase in the heater current. In the reverse case, the balancing motor turned off another "normally closed" relay, resulting in zero current. The currents in each step were regulated so as to minimize the "hunting" or temperature swings about the zero point and also to

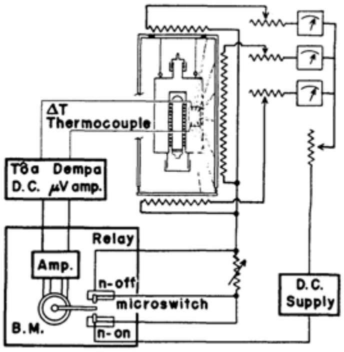

Fig. 4. Control circuits for inner adiabatic shield.

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[3] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

make the length of time spent in the colder state equal to the time spent in the hotter state. The heater current in three parts of the inner shield was separately adjusted to be proportional to the heat capacity of each part. The design of the controller of this type is similar to that of Stull.[2] Manual refinements have been added to permit closer control at the beginning and end of the heating period.

Besides the inner shield, the temperatures of the outer shield and brass block were regulated by another control system. Two-junction Chromel-P constantan thermocouples for detecting any temperature difference between the inner shield and the outer shield and also between the inner shield and the brass block were connected to a highly sensitive galvanometer (the control circuit of the block is not shown in Fig. 2). The light beam from the source was reflected by the mirror of the galvanometer, and then projected on to two photo-transistors, which served to operate two microswitchs attached to heater circuit. By this arrangement, the heater current was adjusted automatically in three steps so as to give no temperature difference between the inner shield and the block. On the other hand, the temperature of the outer shield was adjusted somewhat below that of the inner shield by adding an adjustable bucking potential to the e.m.f. of the difference thermocouple. The temperature of the inner adiabatic shield was kept automatically the same as that of the sample container within ±0.003°K at room temperature and within ±0.01°K at 30°K.

Experimental Procedure

The Calibration of the Platinum Resistance Thermometer in the Temperature Range from 13 to 300°K. — It is necessary to calibrate a working platinum resistance thermometer against the international or the thermodynamical temperature scale, since the accuracy of the measurement of the temperature has an important bearing on the precision claimed for the calorimetry. The procedure for calibrating the thermometer is described below.

Above 90°K, the International Temperature Scale (I.T.S.) has been used as a practical scale of temperature in order to give a greater reproducibility and a far simpler realization of the scale than would otherwise be obtained on the gas scale. On the other hand, in only one part of the scale below 90°K has an agreed method of interpolation been adopted internationally, namely, from 0.5 to 5.2°K a scale based on the vapor pressure temperature scale of He^4.[4] At the National Bureau of Standards a provisional scale has, however, been established in terms of a gas thermometer with the aim of seeking the uniformity of the temperature scales of the various laboratories doing low-temperature work.

For this purpose a series of Pt resistance thermometers has been made by the Leeds and Northrup Company; they were calibrated at the National Bureau of Stndards,* based on the I.T.S. of 1948 between the boiling points of sulfur and of oxygen, and on the NBS scale of Hoge and Brickwedde[5] below the oxygen boiling point. One of these, No. 1510628, was purchased by our University and served as the standard for the calibration of the working thermometers used in our laboratory. The working thermometer, No. 1526483, was calibrated against the standard thermometer by an intercomparison method at any fixed temperature. For this purpose, two thermometers were fixed with Wood's metal into reentrant wells in a copper block. This copper block was hung in the place of the sample container within the inner adiabatic shield of the calorimeter assembly described above. The measurements of the resistance were carried out by the use of the Mueller Bridge with an accuracy of ±0.00001 ohm by keeping the temperature difference between the block and the adiabatic shield as small as possible. Practically all the intercomparison experiments were performed with temperature drifts less than ±0.0001°C/min. of the copper block. The precise R_0 value, the resistance at the ice point, was measured in the conventional manner by the use of the apparatus, which is essentially the same as that described by Stimson.[6]

For the smoothing of the intercomparison data, the resistance differences ΔR between the standard (S) and the working (W) thermometers were plotted against R_s. Fortunately, fairly linear relationship was observed between ΔR and R_s in the measured temperature range, as may be seen in Fig. 5. The scatters of the experimental points from the straight line derived by the method of least squares were nowhere smaller than 0.00007 ohm; they are plotted in Fig. 6. The linear relationship between ΔR and R is to be expected if the "Z function" method proposed by Cragoe[7] can be

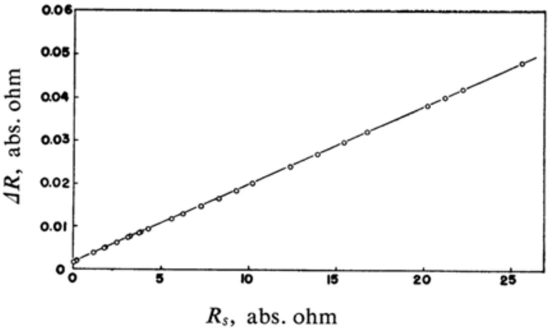

Fig. 5. Plots of $\Delta R(R_x - R_s)$ against R_s.

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[4] H. van Dijk, M. Durieux, J. R. Clement and J. K. Logan, *J. Research Natl. Bur. Standards*, **64A**, 4 (1960).

* We are greatly obliged to Dr. G. T. Furukawa of the N. B. S. for his kindness in making arrangements for the standardization of our thermometer,

[5] H. G. Hoge and F. J. Brickwedde, ibid., **22**, 351 (1939).

[6] H. F. Stimson, ibid., **24**, 209 (1949).

[7] D. R. Stull, *Chem. Eng. News*, **27**, 2772 (1949).

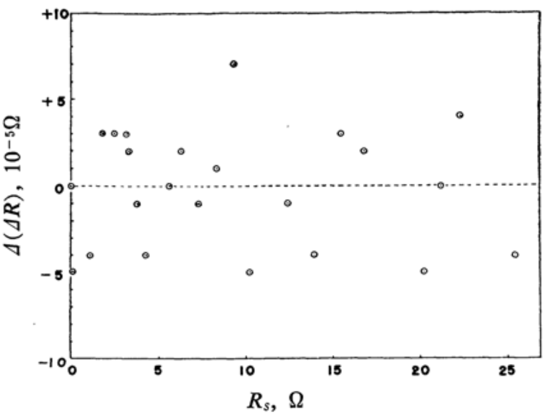

Fig. 6. Deviations of ΔR from straight line derived by the method of least squares.

exactly applied to these thermometers. That is, if the resistances of the two thermometers obey the Matthiessen rule, and if the temperature dependent components of the resistances can be described with the same function of temperature, the linear relationship follows that between ΔR and R.

It was now possible make a resistance-temperature table directly for the working thermometer through the formula: $R_w = R_s(1+A)+B$, the numerical factors, A and B, being determined to be 0.0018325 and 0.001556 respectively. The tabulation was made with intervals of temperature 0.1°K below 90°K and 1°K above 90°K. Also, the temperature variation of the resistance, dR/dT, was tabulated by the formula; $dR_w/dT = (1+A)dR_s/dT$. This value served for making a linear interpolation of the resistance at any temperature.

Measurements of the Heat Capacity. — After setting the sample in the container, the closure was fastened with soft solder. Then helium gas at the desired pressure was introduced through the copper tubing attached to the closure, and the tubing was pinched off so as to keep helium gas tight. The calorimeter was then assembled, and the insulating vacuum space was pumped for several days at room temperature. The pressure was read on a Phillips gauge with a liquid nitrogen trap.

In order to cool the calorimeter, liquid nitrogen was added to the dewar, and helium gas of about 1 mmHg pressure was introduced into the vacuum space. By pumping off the liquid nitrogen in the dewar vessel, the sample was cooled to about 55°K. In the course of this cooling process, the "High-Precision" resistance recorder was operated in such a manner as to draw a continuous cooling curve of the sample, a curve useful for checking the presence of any thermal anomaly that might be encountered. When the measurements were to be made at lower temperatures, liquid hydrogen was introduced into the dewar vessel through a transfer siphon after the liquid nitrogen had been drawn off and the vacuum space flushed with hydrogen gas. A small amount of helium gas was again introduced into the vacuum space; by pumping on the hydrogen bath, the temperature of the calorimeter could be lowered to about 12°K. The in-

TABLE I. SELECTED VALUES OF THE EXPERIMENTAL HEAT CAPACITY OF THE BENZOIC ACID CRYSTAL

0°C=273.15°K Mol. wt. 122.12

T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ joul./deg. mol.
	Series I	
15.25	2.613	6.127
17.60	1.881	8.479
19.66	2.027	10.781
21.59	1.695	12.961
23.41	1.846	14.724
25.56	2.375	17.380
28.15	2.694	20.035
30.69	2.386	22.694
	Series II	
15.25	2.587	6.216
19.40	1.564	10.161
23.11	2.262	14.498
32.94	2.143	25.230
36.86	1.833	29.038
41.35	2.861	32.515
46.83	2.856	37.332
51.34	2.873	40.570
57.04	2.793	44.178
60.06	2.742	45.888
66.31	3.114	49.188
69.14	3.050	50.717
72.74	2.955	52.363
78.17	2.987	54.843
80.83	2.930	56.243
86.25	2.998	58.595
88.92	2.949	59.625
94.55	3.151	61.828
100.15	3.048	63.909
104.78	2.016	65.229
110.17	1.956	67.637
118.90	1.882	70.565
126.06	1.936	73.447
133.10	1.880	75.965
145.37	3.154	80.886
151.12	3.051	82.956
162.52	3.055	88.376
173.82	2.942	91.998
184.75	2.839	96.633
195.96	3.145	101.46
207.80	3.033	106.19
213.60	2.989	108.54
223.67	3.227	112.89
235.94	3.107	118.44
245.17	2.195	122.07
253.63	2.144	125.82
257.81	2.117	127.93
263.97	2.078	130.94
272.05	2.032	134.74
281.31	3.214	139.20
293.85	3.162	144.66
299.99	3.070	147.14
303.55	3.043	148.90

sulating vacuum space was then evacuated, and after the sample showed an upward temperature drift a series of measurements were started.

In an individual measurement, the temperature drift was measured before and after the heating period. The rate of energy input was varied from about 0.01 degrees to 0.2 degrees per minute. A series of measurements in the temperature range from 15 to 310°K usually required about 100—150 hr. Additional runs were made on the empty container over the whole temperature range. To obtain the heat capacity of the sample itself, the heat capacity of the filled calorimeter was corrected for the smooth heat capacity of the empty can.

Experimental Results

In order to verify the performance and the accuracy of this low temperature calorimeter, the heat capacity of the benzoic acid crystal was measured from 15 to 310°K. The sample was obtained through the courtesy of E. J. Prosen of the Chemistry Division of the National Bureau of Standards as a Calorimetry Conference Standard specimen. About 23 g. of this sample was transferred into the sample container.

Figure 7 illustrates an example of heat capacity measurement. In general, the time taken to attain equilibrium after the energy input was between 3 and 5 min. Above 50°K, most of the experiments were carried out with a small thermal leakage, resulting in temperature drifts within ±0.0003—0.0005 deg./min. On the other hand, some experimental difficulties were encountered below 50°K as a result of the decrease in the heat capacities of the specimen and also the increase in the heat exchange between the calorimeter and the surroundings.

The experimental heat capacities, listed in Table I are the ratio of the increment in enthalpy to the increment in temperature, $\Delta H/\Delta T$, and must be corrected for curvature if the differential heat capacities are needed. In the case of the benzoic acid crystal, the correction is for all points less than a change of one in the last figure entered in the table. Also listed in this table are the approximate temperature rise, ΔT, in an individual measurement and T_{av}, the arithmetic mean of the initial and final temperatures. The deviation of each measured point from a smooth curve is plotted in Fig. 8 as a function of the temperature; the dotted lines mean a one per cent deviation. An examination of the figure indicates that the greatest divergence is found below 50°K. The reason for this seems to be the difficulties of maintaining the adiabatic conditions of the calorimeter in this temperature range; the equipment becomes insensitive, and the thermal leakages between the assembly and the surroundings increase, while the heat capacities of the constituent materials decrease progressively as the temperature is lowered.

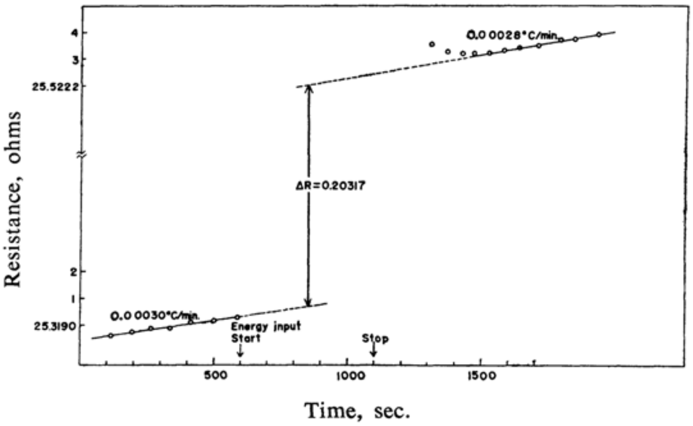

Fig. 7. Typical drift curves before and after an energy input.

I_{av}	35.9495 mamp.	Input energy	67.084 abs. joul.
V_{av}	3.7321 V.	Lost energy	0.068
t	500 sec.	Net input energy (E)	67.016
		R_i	25.31904 ohms/ohms
		R_f	25.52221
		ΔR	0.20317
		$E/\Delta R$	329.85 abs. joul./ohms
		$\dfrac{\Delta R}{\Delta T}$ at $\dfrac{R_i+R_f}{2}$	0.10729 ohm.
		$C_p=\dfrac{E}{\Delta T}=\dfrac{E}{\Delta R}\cdot\dfrac{\Delta R}{\Delta T}$	35.3896 abs. joul./deg.

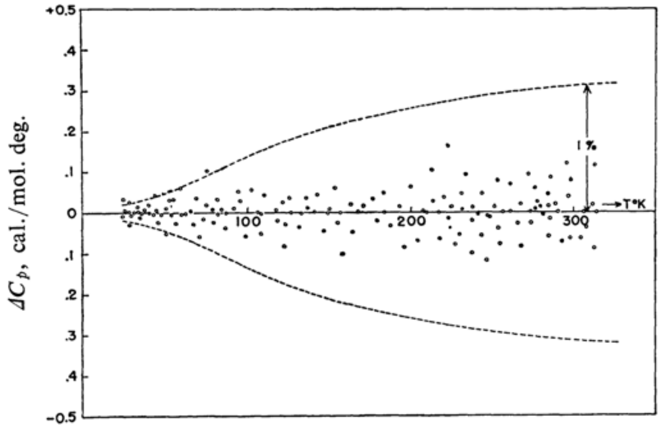

Fig. 8. Deviations of experimental heat capacities of benzoic acid from a smoothed curve.

Above 100°K all the points fall within ±0.5%, and most of them within ±0.3%.

Measurements of the heat capacity of the Calorimetry Conference Standard benzoic acid have hitherto been reported by Furukawa et al.[8], Stout et al.[9], Osborne et al.[10] and by Busey[11]. The smooth curve derived from the present measurements coincides well (within 1%) with their results above 20°K. Remarkable disagreements have been reported among the heat capacity data reported hitherto at temperatures below 20°K. The present data seems to lie between the NBS and Stout data. The increase in the scattering of each measured point, however, makes it impossible to deduce a quantitative conclusion in this temperature range at the present stage.

Summary

An adiabatic calorimeter for the measurements of the heat capacity of a solid and liquid over the temperature range from 13 to 300°K has been constructed. In order to minimize the operating manpower, all the temperature controls were recorded semiautomatically. The energy input was started and stopped automatically by a timer driven by a signal from a transistor clock. The working platinum resistance thermometer was calibrated against a laboratory standard thermometer which had been calibrated by the National Bureau of Standards. In order to verify the performance and the accuracy of this one-man-operated calorimeter, the heat capacity of a Calorimetry Conference Standard sample of benzoic acid crystal has been measured from 15 to 310°K. The results have compared with the data from the NBS and from other laboratories; this comparison served to establish the reliability of this equipment. The estimated errors are ±2% at 20°K, ±1% below 50°K, and ±0.3% above 50°K.

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[8] G. T. Furukawa, R. E. McCosky and G. J. King, *J. Research Natl. Bur. Standards*, **47**, 256 (1951).

[9] A. G. Cole, J. O. Huchens, R. A. Robie and J. W. Stout, *J. Am. Chem. Soc.*, **77**, 2737 (1955).

[10] D. W. Osborne, E. F. Westrum, Jr., and H. R. Lohr, ibid., **77**, 2737 (1955).

[11] R. H. Busey, ibid., **78**, 3263 (1956).