[CONTRIBUTION NO. 313 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heat Capacity of Lead Sulfate

BY EUGENE GEORGE HAAS[1] WITH GEBHARD STEGEMAN

The results of the investigation here reported represent a part of the measurements of the thermal properties of lead sulfate which the authors are undertaking. Through a private communication from C. T. Anderson of the United States Bureau of Mines at Berkeley it was learned that he had previously made some measurements of the heat capacity of lead sulfate. The values obtained by him agree with those here reported in the middle range of temperatures, but differ somewhat at the upper and lower values. A consideration of the possible causes of the differences in the measured values led to a second standardization of the calorimeter thermometer, and the heat capacity of the empty calorimeter was also redetermined. These measurements show agreement with the original values within the experimental error. The standard cell also indicated no change in potential on comparison with a new one. The cause of the discrepancy was therefore not discovered.

Apparatus

The apparatus and its arrangement was substantially the same as that devised by Gibson and Giauque.[2] The diagram submitted as Fig. 1 will be self explanatory. Some difficulty was experienced with welded steel joints, so the vacuum can and cover were cut from a piece of solid steel shafting. All joints except the bolted one were thus avoided. A pressure of 0.00001 mm. could be maintained without difficulty by means of two mercury diffusion pumps in series, backed up by an oil pump.

The calorimeter was made from copper tubing cut to 0.5 mm. in thickness. A center post of small-bore copper rod was soldered to eight copper vanes of paper thickness. The vanes were also soldered to the inside of the calorimeter. Two caps of sheet copper were screwed to the ends of the center post till they fitted snugly on the ends of the copper tube. The caps were then soldered in position. A small opening was provided for filling. The calorimeter after being filled was placed in a vacuum desiccator and was alternately exhausted and filled with hydrogen several times. The opening was then quickly sealed with solder. The measurement of the temperature drop after energy input was greatly facilitated in this way. Two minutes were sufficient for the calorimeter to attain a steady temperature change.

The calorimeter was wound with double silk covered No. 40 (B. & S. gage) copper wire which served for energy input and for the temperature estimation. The winding was baked on with Bakelite lacquer and the whole was seasoned thoroughly by cooling with liquid air about twenty times. The resistance at 273°K. was about 220 ohms.

The resistance of the calorimeter winding was determined at the ice point,[3] the sublimation point of carbon dioxide, and liquid oxygen. The calorimeter was placed in a thin copper container with a lid and a small-bore copper outlet tube for lead wires soldered in position on the top. A platinum resistance thermometer certified by the Bureau of Standards was fastened to the outside of the copper container in good thermal contact. Since the temperature reference baths could be maintained at a constant value for several hours, it was assumed that both thermometers had acquired the same temperature. The Callendar equation with the corrections recommended by Henning[4] was employed for the correct temperatures. A smooth curve was drawn through the three points so determined. A subsequent determination of the resistance of the calorimeter thermometer immersed in liquid nitrogen without the use of the platinum thermometer produced a value which was in agreement with the curve drawn from the other three reference points.

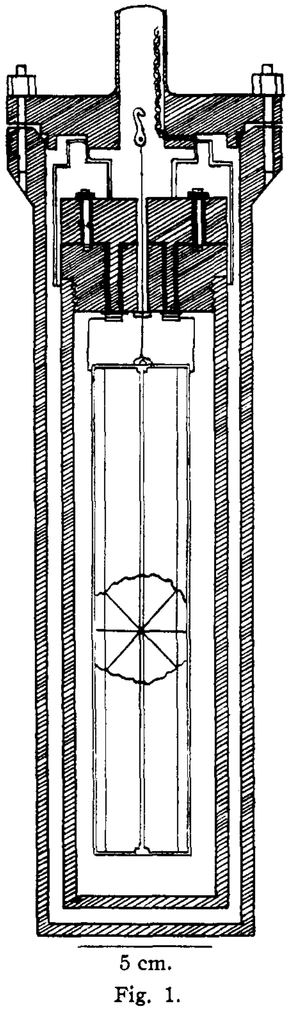

Fig. 1.

The shield was constructed entirely of copper and weighed about three kilograms. It was made in two sections which could be screwed together. The details of its construction will be obvious from the diagram. Its temperature was ascertained by a winding of copper wire similar to that used for the calorimeter.

All measurements were made with a White double potentiometer and standardized resistances. A special switch box was constructed with a number of double throw copper switches immersed in transformer oil. The

---

[1] From a portion of the thesis submitted by E. G. Haas to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements of the degree of Doctor of Philosophy.

[2] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

[3] The ice point was assumed to be 273.16°K.

[4] Henning, *Ann. Physik*, **40**, 647 (1913).

necessary circuit changes could be made in minimum time so that one operator was able to collect all the required data. All time measurements were made with an electric stopclock. Its deviation was less than one-fifth of a second per hour when checked with radio signals.

The sensitivity of the galvanometer used was sufficient to permit an estimate of the temperature of the calorimeter to 0.001°. The determination of the temperature of the calorimeter during energy input was facilitated by the use of lead in wires whose resistance change with the temperature was negligible.

Lead Sulfate

The sulfate used was prepared by the addition of dilute sulfuric acid to a dilute solution of lead nitrate. The precipitate was stirred for many hours in the solution which was gradually replaced with distilled water. The solid was pure white and was dried in an oven at about 150°. On analysis it was found to contain 99.80% of the theoretical quantity of lead.

Procedure

The procedure followed was similar to that recommended by Gibson and Giauque.[3] No attempt was made to provide a constant temperature bath for the outside container as it was found that the addition of small quantities of liquid air to the enclosing Dewar container provided any desired temperature.

Discussion of Results

The results of the investigation are contained in the table.[5] About 80% of the values found in the table deviate from the best curve drawn through the points by about 0.3 of one per cent. for the lower temperature values. At higher temperatures the extent of the deviation increases somewhat, rising in some cases to as much as 2%. The temperature region from 238 to 254°K. produced a deviation from the expected values far beyond the experimental error. About thirty measurements were made in this range without finding satisfactory values. The deviation was most pronounced when the region was approached from lower temperatures, but the deviations could not be duplicated. This made it appear unlikely that a change in state was being experienced by the crystalline solid. It was thought that possibly a small amount of sulfuric acid might have resisted the washing process. Such a contamination would make the complete removal of water difficult and the combination of the two impurities might account for values higher than those expected if a melting process were to take place in this temperature range.

TABLE OF SPECIFIC HEAT VALUES

C_p in calories per mole

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
83.00	14.17	154.74	18.22	226.40	22.53
84.66	14.37	157.39	18.37	227.75	22.68
86.12	14.50	160.57	18.60	231.14	22.80
88.05	14.55	163.20	18.74	233.37	22.97
91.85	14.66	166.54	18.94	235.14	23.02
93.71	14.71	168.96	19.13	238.59	23.28
96.95	14.76	171.01	19.20	242.09	23.48
100.83	14.93	173.22	19.27	247.66	23.08
102.91	15.01	175.46	19.41	249.63	23.67
105.00	15.14	179.94	19.63	249.98	23.75
107.38	15.24	182.39	19.83	250.33	23.67
108.83	15.35	184.74	19.99	252.44	23.75
110.65	15.47	188.28	20.24	254.76	23.81
112.04	15.58	190.38	20.39	258.86	24.03
114.36	15.63	194.26	20.59	264.95	24.19
116.82	15.87	197.35	20.77	275.20	24.52
124.46	16.17	199.10	20.90	278.31	24.58
128.54	16.48	201.10	21.11	281.87	24.91
131.91	16.79	204.65	21.23	283.69	24.98
134.70	16.85	211.48	21.60	286.42	25.17
137.32	17.09	214.63	21.75	289.03	25.47
142.50	17.40	218.41	21.99	294.98	25.96
147.61	17.75	222.36	22.20	295.21	26.03
151.89	18.05	224.84	22.47	297.09	26.18

On plotting the molecular specific heat against the temperature a distinct inflection in the curve is noted which begins in the neighborhood of 100°K. An attempt was made to find a combination of Debye and Einstein functions which would make possible an extrapolation of the specific heat to absolute zero. However, such combinations of these functions as appeared to satisfy the lower range of measured values deviated from the others so extensively that the calculation of the entropy of the compound was abandoned. It appears to be necessary to extend the measurements to still lower temperatures before the uncertainty in such a calculation will be reduced to an acceptable figure. Unfortunately, facilities for reaching temperatures below the boiling point of liquid nitrogen were not available in this investigation.

The authors express their appreciation to Dr. C. T. Anderson of the United States Bureau of Mines for the use of data obtained in his investigation and for other valued suggestions.

Summary

1. A low temperature calorimeter has been constructed and its characteristics described.

2. The heat capacity of lead sulfate has been measured over the temperature range of 83 to 298°K.

PITTSBURGH, PENNA. RECEIVED MARCH 7, 1936

---

(5) The factor 0.23895 has been used for converting joules to calories.