[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF THE SULFIDES OF COPPER AND LEAD[1]

BY C. TRAVIS ANDERSON[2]

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As a part of the general program of the study of the thermodynamic properties of metals, oxides and sulfides which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has determined the heat capacities and calculated the entropies of the sulfides of copper and lead. A previous report has been presented on the sulfides of manganese, iron and calcium.[3] As in the case of the latter sulfides, the heat capacities of the oxides of copper and lead had been previously determined.[4]

Since the last report an entirely new wiring system, switchboard and vacuum line have been installed. All wires from the calorimeter to the switchboard, located behind the potentiometer, have been placed in a flexible metal conduit, which has improved the shielding of the electrical circuits and has proved to be a much more satisfactory arrangement than the previous method of stringing single wires. The wires collect no dust nor do they swing in the earth's magnetic field and cause variations in the potentiometer readings. The volt box correction was redetermined after the new wiring was installed by the same method as described previously.[5] The thermocouple was again compared with a standard between sets of measurements and the standard cell checked as usual. Otherwise the method and accuracy are practically the same as have been described previously.

Materials

The sample of cuprous sulfide was made by the carbon dioxide–carbon disulfide method used for the preparation of the sulfides of manganese, iron and calcium. Analysis of the material after preparation showed it to contain considerable cupric sulfide. To remove this excess sulfur the sample, in a silica flask, was placed in a furnace, evacuated and heated to about 860°. Cupric sulfide is dissociated under these conditions, and excess sulfur distilled off. The resulting sulfide was crystalline, and analyzed 99.8% Cu_2S. It had a density of 5.76 at 22.4°. The calorimeter was filled with 315.5 g.

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[2] Assistant physical chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

[3] Anderson, THIS JOURNAL, **53**, 476 (1931).

[4] Millar, *ibid.*, **51**, 215 (1929); Nernst and Schwers, *Sitz. preuss. Akad. Wiss.*, 355 (1914).

[5] Anderson, THIS JOURNAL, **52**, 2296 (1930).

The sample of cupric sulfide used was the natural mineral covellite. It was kindly furnished by Mr. R. E. Head, Microscopist of the United States Bureau of Mines at the Intermountain Experiment Station, Salt Lake City, Utah. It had been obtained by him from the Tacoma smelter of the American Smelting and Refining Company. This specimen was very carefully cleaned on an emery wheel. All small spots of silica were removed, as well as any spots which indicated the presence of chalcocite. After cleaning, the sample was crushed and screened. The fines were discarded. The electrolytic deposit from this sample was within 0.02% theoretical for CuS. No measurable impurities could be found. It had a density of 4.64 at 21.2°. A 263.6-g. sample was studied.

Two samples of lead sulfide were studied, (1) a sample of galena which was also obtained through Mr. Head from the Joplin district, and (2) a lead sulfide prepared by the carbon dioxide–carbon disulfide method. The most satisfactory method found for analyzing the lead sulfides was by precipitating the lead as the molybdate. Considerable effort was expended to prepare the sample as pure as possible. After preparation of the sample and repeatedly heating the evacuated sample, the analysis did not improve. On the last heating the furnace was at a higher temperature than previously and permitted the sulfide to distil from the bottom. It condensed in the neck and upper part of the flask. While cooling, the flask cracked, oxidizing a small part of the material. On breaking the flask a grayish powder was found in the bottom. Qualitative tests on this powder showed it to contain iron as well as copper. It was necessary to re-treat the sample with the carbon dioxide–carbon disulfide mixture. After treatment, small portions were placed in a heavy-walled silica tube about 20–25 cm. long, with a constriction about 7–10 cm. from the bottom. A silica tube was attached to the upper part leading through the furnace for evacuating. The galena distilled from the bottom to the upper part, leaving a small amount of residue. The tube was broken after cooling and the distillate removed. The residue in the lower part, as well as the small amount of distillate above the main portion, was discarded. This procedure was repeated several times on the entire sample. The resulting sulfide had a galena structure and the composition PbS, within the accuracy of analysis (0.1%). The calorimeter contained 431.0 g. of the lead sulfide. Its density was found to be 7.57 at 22.4°.

Analysis of the galena indicated that it was pure to within the limits of analytical error (0.1%). The calorimeter was filled with 468.2 g. Its density was also measured at 22.4° and found to be 7.57.

Screen tests using Tyler standard screens were made on these materials and are shown in Table I. Coarser material was used in these measurements than previously. All the samples were −14 mesh.

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

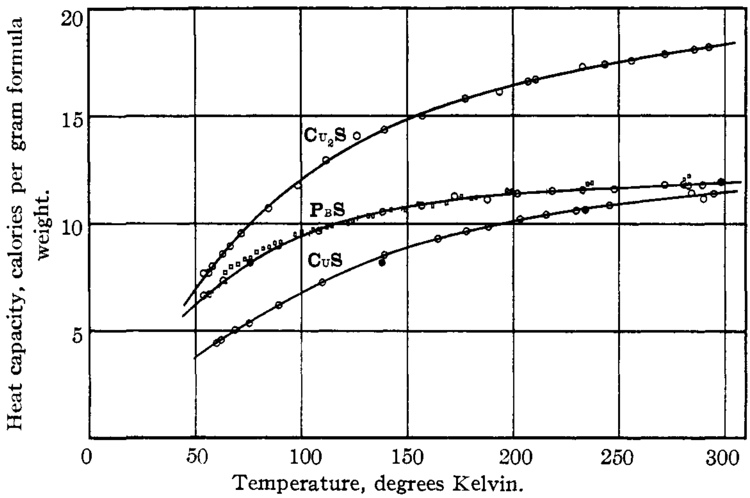
Screen size	Cu_2S, %	Covellite, %	Galena, %	PbS, %
+35	51.4	59.5	52.0	49.1
+48	24.0	16.5	17.7	21.2
+65	14.8	12.5	14.5	16.1
+100	8.8	10.5	13.3	13.0
−100	1.0	1.0	2.5	0.6

The Specific Heats

No previous low temperature measurements have been made on cuprous sulfide. Russell[6] has determined the mean specific heat of cupric sulfide

[6] Russell, *Physik. Z.*, **13**, 59 (1912).

at three points, and Eastman and Rodebush[7] have determined the specific heat of a sample of galena. The results of these investigators, together with those obtained in this Laboratory on the heat capacities of cuprous sulfide, covellite, galena and lead sulfide, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1. The experimental determinations of the heat capacities are shown in Tables II to V. In converting joules to calories, the factor 1/4.184 was used. The calculations were made on the basis of Cu = 63.57, Pb = 207.20 and S = 32.06.



○, Anderson; +, Anderson, PbS; □, Eastman and Rodebush, galena; ●, Russell, CuS.

Fig. 1.—The heat capacities of cuprous sulfide, covellite, galena and lead sulfide in calories per gram formula weight.

It is to be noted that the determinations on the heat capacity of the prepared lead sulfide coincide with the smooth curve of galena, and also that this curve is below that of Eastman and Rodebush at both the lowest

Table II

Heat Capacity per Gram Formula Weight of Cuprous Sulfide

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
58.0	7.988	97.6	11.71	210.4	16.68
53.7	7.674	111.6	12.91	232.5	17.27
56.1	7.677	126.0	14.05	243.0	17.39
62.6	8.567	139.0	14.33	255.6	17.56
66.1	8.931	157.0	14.99	271.4	17.86
71.3	9.524	177.2	15.80	285.4	18.08
84.4	10.68	193.3	16.13	292.2	18.18
		206.8	16.59		

[7] Eastman and Rodebush, This Journal, **40**, 489 (1918).

Table III

Heat Capacity per Gram Formula Weight of Covellite (CuS)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
59.8	4.413	139.0	8.509	229.7	10.56
61.9	4.548	164.4	9.279	245.4	10.81
68.6	5.041	177.6	9.618	284.1	11 37
75.1	5.344	188.0	9.822	289.9	11.10
89.0	6.179	203.2	10.16	294.6	11.34
109.9	7.241	215.4	10.39		

Table IV

Heat Capacity per Gram Formula Weight of Galena (PbS)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.7	6.626	138.2	10.51	247.5	11.55
56.5	6.700	156.5	10.82	271.3	11.76
63.0	7.338	172.1	11.24	280.4	11.78
75.6	8.167	201.9	11.36	282.6	11.74
89.2	8.950	218.3	11.48	289.4	11.75
108.1	9.634	232.7	11.53		

Table V

Heat Capacity per Gram Formula Weight of Lead Sulfide (Synthetic Sample)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.0	6.530	76.2	8.206	215.7	11.47
57.3	6.762	103.8	9.511	233.7	11.50
61.1	7.078	126.4	10.24	281.7	11.87
64.2	7.483	147.4	10.68		

and highest temperatures. From the galena, lead sulfide results we may assume that the specific heat of natural chalcocite would be the same as that of the prepared sample. Several samples of supposedly pure chalcocite were analyzed, but all were found to contain from 5 to 30% covellite.

Calculation of Entropies.—The usual graphical method was employed in calculating the entropies. The experimental heat capacity curves were extended and coincided with Debye functions having the following parameters (Θ): for Cu_2S, 92; covellite, 166; and galena and PbS, 107. In Table VI are given the results of the entropy calculations.

Table VI

Entropy Data

	Cu_2S	Covellite	Galena and PbS
Extrap. (0–56.2) °K.	6.06	2.64	5.30
Graph. (56.2–298.1) °K.	22.80	13.29	16.56
$S°_{298}$	28.9 ± 0.5	15.9 ± 0.3	21.9 ± 0.4

Debye and Einstein functions of the following combinations were found to fit the specific heat curves per formula weight of these sulfides.

$$C_{Cu_2S} = D\,\frac{(92)}{T} + D\,\frac{(379)}{T}$$

$$C_{CuS} = D\,\frac{(166)}{T} + E\,\frac{(428)}{T}$$

$$C_{PbS} = D\,\frac{(107)}{T} + 2D\,\frac{(320)}{T}$$

The Cu_2S combination fits the experimental heat capacity curves up to 115°K., that for CuS to 130°K., and PbS to 80°K. By use of the function sums the entropies at 298°K. are 28.8, 15.8 and 21.8 units, respectively, a difference of only 0.1 unit in each from the experimental values.

Related Thermal Data.—The heats of formation of cuprous and cupric sulfides have been determined by v. Wartenberg[8] by direct combination of copper with sulfur. For cuprous sulfide he gives −19,000 cal., and for cupric sulfide −11,600 cal. Using the entropy values given above and the values 7.92 for copper and 7.6 for sulfur, the free energy of cuprous and cupric sulfides may be calculated from the thermodynamic equation $\Delta F = \Delta H - T\Delta S$, as −20,640 and −11,720 cal., respectively. Günther[9] has recalculated Thomsen's[10] value for the heat of formation of lead sulfide as −20,900 cal. Berthelot[11] gives −20,300 as the heat of formation. Taking the average value of −20,600 cal. as the heat of formation of lead sulfide, the value of 15.63 as the entropy of lead, 7.6 as that of sulfur and the entropy obtained for lead sulfide, the free energy was calculated as −20,200 cal.

Summary

The heat capacities of cuprous sulfide, covellite, galena and lead sulfide from about 55 to 300°K. have been determined, and their corresponding entropies and the free energies calculated. The following table contains the summarized results.

	$S°_{298}$	$\Delta F°_{298}$	$\Delta H°_{298}$
Cu_2S	28.9	−20,640	−19,000
CuS	15.9	−11,720	−11,600
PbS	21.9	−20,200	−20,600

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[8] V. Wartenberg, *Z. physik. Chem.*, **67**, 446 (1909).

[9] Günther, *Z. Elektrochem.*, **23**, 197 (1917).

[10] Thomsen, "Thermochemistry," Longmans, Green and Co., London, **1908**, p. 309.

[11] Berthelot, "Thermochemie," Vol. II, **1897**, p. 341.