putation for "a" values constitutes a very critical test of the Debye-Hückel theory. The fact that the highly simplified picture employed by Debye and Hückel represents the facts for Pb^+ and Tl^+, which are known to form complexes with chloride ions at higher concentrations, as closely as it does is more remarkable than are the comparatively insignificant deviations just mentioned.

Summary

The solubility of thallous iodate has been measured in ethyl alcohol-water mixtures ranging from zero to 47% ethyl alcohol. The values of the average radii calculated using Born's formula for the electrostatic work of transfer are compared with the values of the parameter "a" computed from the interaction theory for the solubility in salt solutions as extended by Gronwall, La Mer and Sandved.

New York, New York

[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 MANGANESE SULFIDE, FERROUS SULFIDE AND CALCIUM SULFIDE[1]

By C. Travis Anderson[2]

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Pursuing its general program of 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 of the sulfides of manganese, iron and calcium. The thermodynamic properties of these sulfides have both theoretical interest and practical importance. The heat capacities of the oxides corresponding to these sulfides have been determined, which enables an interesting comparison to be made.[3] Knowledge of the entropies of these sulfides was especially desired for use in connection with studies of the desulfurization of iron.

The method, apparatus and accuracy have been described in previous publications,[4] but it may be noted that between the sets of experiments

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[1] This paper presents the results of work done under a coöperative agreement between the U. S. Bureau of Mines and the University of California. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[3] Millar, This Journal, **50,** 1875 (1928); **51,** 215 (1929); Parks and Kelley, *J. Phys. Chem.*, **30,** 47 (1926).

[4] Anderson, This Journal, **52,** 2296, 2712 (1930).

with the different samples the thermocouple was again compared with a standard, and the standard cell checked from time to time with others having Bureau of Standards certificates.

Materials

After considerable preliminary testing of various methods of preparation of pure sulfides, the method of Schöne[5] was modified to give excellent results. Schöne passed carbon dioxide saturated with carbon disulfide vapor over heated carbonates of various metals (especially calcium), obtaining nearly quantitative yields of sulfides. It has been found that the sulfates of metals having very stable oxides are preferable to carbonates, and that control of temperature of heating, and partial vapor pressure of carbon disulfide are essential. When completeness of conversion is desired, it was also found better to prepare a number of small samples than to attempt a single large preparation. The reason for these precautions will be obvious from a consideration of the mechanism of the conversion, which probably involves the reversible formation of carbonyl sulfide from carbon dioxide and carbon disulfide.

The sample of manganese sulfide was prepared from a C. P. grade of manganese sulfate. Small portions of the sulfate were placed in a silica tube which fitted conveniently in a tube furnace. Carbon dioxide was bubbled through gas washing bottles containing carbon disulfide at 25°. The tube furnace was heated to 750°. The resulting manganese sulfide had the theoretical composition of MnS to within the limits of analytical error, in this case about 0.1%. Its density was found to be 3.93 at 21.9°. A 166.3-g. sample was studied.

The ferrous sulfide was prepared from a mixture of iron oxides which were made from strips of pure ingot iron by heating them in air for several days at about 900°. The oxide material so obtained was crushed to −14 mesh and the metallic iron separated mechanically. The iron oxides were placed in the silica tube in the combustion furnace and carbon dioxide saturated with carbon disulfide at 25° was passed over the oxide at about 850°. The resulting sulfide was definitely crystalline and had the theoretical composition of FeS to within the limits of analytical error (0.2%). It had a density of 4.65 at 23.9°. The calorimeter was filled with a 270.4-g. sample.

Calcium sulfide proved to be the most difficult of the materials to prepare. Finely divided calcium sulfate was used and was placed in the silica tube which had been used for the preparation of the two other sulfides. The furnace in this case was heated to about 700° and the carbon dioxide was saturated with carbon disulfide at 27°. It was necessary to re-treat the material several times before the sulfate was completely converted to the sulfide. The resulting sulfide had the theoretical composition of CaS to within the limits of analytical error, in this case about 0.1%. The sulfide was necessarily very finely divided, since coarse material could not be completely converted. The sample was compressed into pellets at pressures of several tons per square inch, so that the calorimeter could be filled with an adequate weight of material. The pellets were broken and the calorimeter finally filled with a sample of 77.1 g. Without compressing, the contents would have been less than 10 g. The density was 2.56 at 23.6°.

Screen tests using Tyler screens were made on these materials and are shown in

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[5] Schöne, *Pogg. Ann.*, **112**, 194 (1861).

Table I. The sizes of the calcium sulfide, of course, do not indicate the crystal size, as the material was all probably finer than 300-mesh before compressing.

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

Screen size	MnS, %	FeS, %	CaS, %
+ 35	22.0	0.5	54.0
+ 48	7.0	4.5	16.5
+ 65	8.5	25.0	19.0
+100	8.0	28.5	7.0
+150	8.0	21.0	2.0
+200	11.5	14.0	1.0
−200	35.0	6.5	0.5

The Specific Heats

No previous low temperature measurements have been made on any of these sulfides. The results obtained in this Laboratory on the heat capacities of manganese sulfide, ferrous sulfide and calcium sulfide, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1. The experimental determinations of heat capacities for ferrous sulfide and calcium sulfide are given in Tables II and III. The values for manganese sulfide, except those between 100° and 170°K. are given in Table IV. The values for the heat capacities for manganese sulfide between 100 and 170°K. with the temperature rise (ΔT) of the determination are given in Table V and are shown graphically in Fig. 2. Except

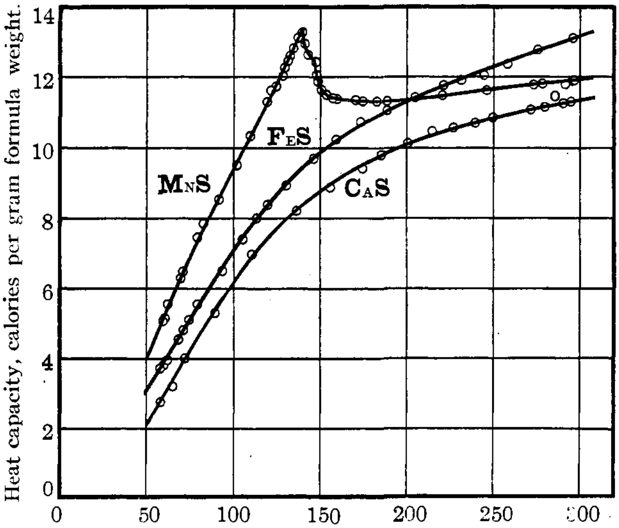

Fig. 1.—The heat capacity of manganese sulfide, ferrous sulfide and calcium sulfide in calories per gram formula weight.

for this range, the temperature rise of the determinations varied from about 3 to 6°. In changing joules to calories the factor $^{1}/_{4.184}$[6] was used. The calculations were made on the basis of Mn = 54.93, Fe = 55.84, Ca = 40.07, and S = 32.06.

Table II

Heat Capacity per Gram Formula Weight of Calcium Sulfide

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
58.1	2.772	155.9	8.894	239.4	10.71
65.1	3.225	174.7	9.418	249.6	10.87
72.0	4.017	185.3	9.795	271.2	11.09
89.5	5.307	200.5	10.14	279.5	11.16
110.8	6.984	214.6	10.42	285.5	11.48
136.4	8.224	226.9	10.56	290.1	11.28
				294.9	11.32

Table III

Heat Capacity per Gram Formula Weight of Ferrous Sulfide

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
57.9	3.729	105.7	7.412	204.6	11.44
60.1	3.818	113.5	8.010	221.2	11.78
62.0	3.963	119.9	8.395	231.6	11.92
68.4	4.555	130.4	8.940	244.6	12.07
71.1	4.816	146.4	9.705	258.0	12.38
74.5	5.118	159.0	10.25	275.8	12.79
79.4	5.562	173.1	10.74	296.0	13.12
93.7	6.512	188.2	11.07		

Table IV

Heat Capacity per Gram Formula Weight of Manganese Sulfide

Run	*T*, °K.	C_p	Run	*T*, °K.	C_p	Run	*T*, °K.	C_p
1	59.8	5.068	76	187.4	11.34	89	246.0	11.64
2	62.3	5.557	77	193.1	11.38	90	257.5	11.77
3	71.0	6.485	78	199.3	11.38	91	262.8	11.79
4	79.1	7.467	79	212.9	11.50	92	268.0	11.78
5	91.8	8.529	80	216.8	11.52	93	273.0	11.80
11	291.4	11.82	81	220.5	11.51	94	278.1	11.83
34	215.3	11.43	82	218.9	11.53	95	283.4	11.88
35	60.7	5.164	83	222.7	11.55	96	289.6	11.92
36	69.9	6.296	84	226.2	11.53	97	295.3	11.92
37	82.8	7.857	85	230.3	11.54	98	175.7	11.33
73	170.1	11.36	86	232.5	11.56	99	195.9	11.39
74	174.3	11.33	87	236.0	11.58	100	204.4	11.43
75	182.4	11.32	88	239.5	11.60	101	296.9	11.93

Previous work on manganese oxide and ferrous oxide at low temperatures had shown a hump in each heat capacity curve. The ferrous oxide curve also showed a tendency at room temperature to be approaching

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[6] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF MANGANESE SULFIDE

Run	T, °K.	ΔT	C_p	Run	T, °K.	ΔT	C_p
6	102.0	2.573	9.513	42	139.4	1.272	13.22
7	109.5	3.308	10.35	43	140.7	1.266	13.05
8	119.1	2.674	11.31	44	143.0	1.245	12.73
9	131.3	3.034	12.55	45	144.2	1.237	12.62
10	145.7	2.590	12.48	46	145.4	1.226	12.54
12	124.6	1.705	11.76	47	146.7	1.213	12.53
13	128.5	1.595	12.05	48	147.9	1.230	12.08
14	131.2	1.501	12.48	49	149.2	1.232	11.85
15	132.8	1.457	12.62	50	150.4	1.260	11.71
16	134.3	1.414	12.84	51	151.7	1.219	11.62
17	135.7	1.379	12.99	52	133.2	1.385	12.73
18	137.1	1.347	13.13	53	138.2	1.266	13.30
19	138.4	1.315	13.26	54	139.4	1.245	13.32
20	139.8	1.295	13.28	55	139.4	1.229	13.23
21	141.1	1.300	12.96	56	147.2	1.192	12.46
22	141.6	1.290	12.82	57	151.5	1.200	11.63
23	142.9	1.285	12.65	58	152.7	1.191	11.58
24	144.2	1.274	12.56	59	153.9	1.183	11.51
25	145.5	1.263	12.49	60	155.1	1.173	11.48
26	146.8	1.247	12.47	61	156.3	1.162	11.46
27	148.8	2.532	11.90	62	157.3	1.143	11.42
28	150.7	1.260	11.66	63	158.4	1.130	11.44
29	151.9	1.245	11.66	64	159.6	1.119	11.44
30	153.2	1.241	11.51	65	160.7	1.113	11.36
31	155.0	2.445	11.46	66	161.8	1.100	11.40
32	157.0	1.202	11.43	67	163.0	1.089	11.41
33	158.2	1.195	11.34	68	165.2	1.071	11.39
38	109.3	3.155	10.39	69	166.3	1.060	11.38
39	121.3	3.507	11.51	70	167.4	1.049	11.40
40	129.3	1.509	12.28	71	168.5	1.037	11.45
41	138.0	1.289	13.23	72	169.2	1.026	11.38

another anomaly. The particular sample of ferrous oxide which had been used analyzed only 83% ferrous oxide, the remaining material being a solution of iron and magnetite in the ferrous oxide.

The sample of manganous oxide was apparently a pure sample. These results would indicate that the corresponding sulfides should show anomalies at a higher temperature than their corresponding oxides. This was observed in the case of the manganese sulfide, but the ferrous sulfide curve was normal in the region where the hump was suspected. This would indicate that the hump observed in the ferrous oxide might be attributed to the solution of the magnetite and iron present in the ferrous oxide. However, the trend of the heat capacity curve for ferrous sulfide at room temperature seems to indicate that a transition is starting to take place, as in the case of the ferrous oxide. The heat capacity of the ferrous sulfide above room temperature will be measured in the near future in this Laboratory. Figure 2 shows the heat capacity curve for manganese sulfide in the vicinity of the hump, between 100 and 170°K. Just previously to Run 35 an attempt was made to supercool the manganese sulfide from room temperature to below 60°K. There was no indication of supercooling, since the points fell on the same smooth curve, independently of the history of the substance. The hump was perfectly reproducible, in fact so much so that no measurements were made on the heat of apparent transition. After reaching a maximum the downward part of the curve flattened to about 147°K., at which point it dropped off suddenly from about 12.5 to 12.0 cal. per gram formula weight. This particular anomaly seems to be more nearly a discontinuity, but was also perfectly reproducible. It was thought that this second anomaly might possibly be ascribed to the temperature scale, but after going over that portion of the scale no discrepancy could be found, indicating that this anomaly actually exists, and since the specific heat here drops almost vertically with the temperature, the correspondence with an actual discontinuity is more marked than at the maximum point. The heat capacity curve on either side of the humps possesses very different slopes, but this does not necessarily indicate a change in crystal structure, because the factors causing the anomaly are obviously active over a considerable temperature range and may well be affecting the normal course of the curve over a wide temperature interval. A study of the magnetic changes in this region would be of great interest.

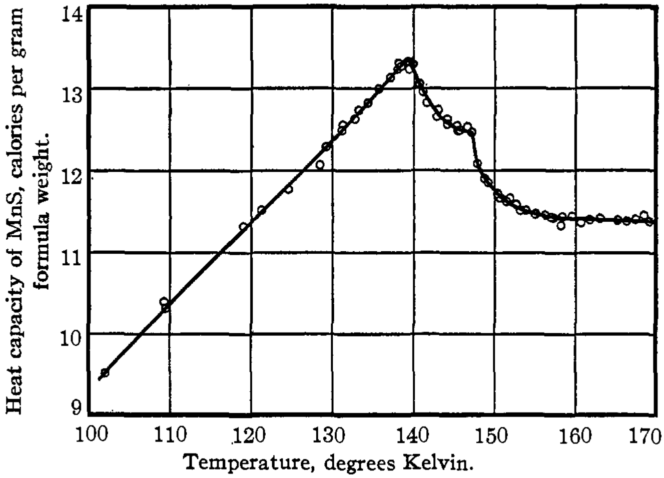

Fig. 2.—The heat capacity of manganese sulfide in calories per gram formula weight.

The experimental data on manganese sulfide do not in themselves give explanation for the double cusped nature of the hump observed. However, it is an obvious hypothesis to suppose that the curve as observed may represent the sum of two simple curves, each of which has a separate hump at temperatures near those of the cusps. This point of view has led Professor E. D. Eastman of the University of California to suggest that there may be some sort of analogy between the factors causing doublet spectral lines and those responsible for the "doublet" hump here observed.

Calculation of Entropies

The entropies were calculated graphically by plotting the heat capacity against the logarithm of the temperature. The heat capacity curves were extrapolated to the absolute zero by means of combinations of Debye and Einstein functions. The Debye functions used had the following parameters (Θ): for MnS, 205; FeS, 205; and CaS, 284. In Table VI are given the results of the entropy calculations.

TABLE VI

ENTROPY DATA

	MnS	FeS	CaS
Extrap. (0–56.2) °K.	2.14	1.43	1.32
Graph. (56.2–298.1) °K.	16.58	14.68	12.21
S°_{298}	18.7 ± 0.3	16.1 ± 0.3	13.5 ± 0.3

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights of the three sulfides.

$$C_{\text{MnS}} = D\,\frac{(205)}{T} + E\,\frac{(263)}{T}$$

$$C_{\text{FeS}} = D\,\frac{(205)}{T} + E\,\frac{(370)}{T}$$

$$C_{\text{CaS}} = D\,\frac{(284)}{T} + E\,\frac{(369)}{T}$$

The MnS combination fits the experimental curve up to 50°K., the FeS combination to 75° and that for the CaS to 133°.

Related Thermal Data

The heat of formation of manganese sulfide has been determined by Wologdine and Penkiewitsch[7] by direct combination of manganese and sulfur. They give $\Delta H^\circ_{298} = -62{,}900$ cal. Using this value in combination with the entropies of manganese and rhombic sulfur, as given by Lewis and Randall,[8] and the entropy of manganese sulfide given above, the free energy of manganese sulfide was calculated as −64,000 cal.

Parravano and P. de Cesaris[9] measured the heat of formation of ferrous sulfide by the combination of iron and rhombic sulfur and give $\Delta H^\circ_{298} = -23{,}070$ cal. Using their value and Lewis and Randall's values for the

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[7] Wologdine and Penkiewitsch, *Compt. rend.*, **158**, 498 (1914).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 464.

[9] Parravano and P. de Cesaris, *Gazz. chim. ital.*, **47**, 144 (1917).

entropies of iron and rhombic sulfur and the measured entropy of ferrous sulfide, the value −23,600 cal. was calculated as the free energy of ferrous sulfide.

Sabatier[10] determined the heat of formation of calcium sulfide by direct union of calcium and rhombic sulfur. He gives the value of $\Delta H^\circ_{298} = -111{,}200$ cal. Using this value and the values of the entropies of calcium and rhombic sulfur as given by Lewis and Randall, and the entropy obtained for calcium sulfide, the free energy of calcium sulfide was calculated as −109,800 cal.

Summary

The heat capacities of manganese sulfide, ferrous sulfide and calcium sulfide from about 60 to 300°*K*. have been determined, and their corresponding entropies and free energies calculated.

The following table contains the summarized results.

	S°_{298}	ΔF°_{298}	ΔH°_{298}
MnS	18.7	−64,000	−62,900
FeS	16.1	−23,600	−23,070
CaS	13.5	−109,800	−111,200

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND THE UNIVERSITY OF OKLAHOMA]

THE DECOMPOSITION OF REFRACTORY SILICATES BY FUSED AMMONIUM FLUORIDE AND ITS APPLICATION TO THE DETERMINATION OF SILICA IN GLASS SANDS

BY A. C. SHEAD[1] AND G. FREDERICK SMITH

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For years the opening of silicates, preparatory to the analysis of the alkali metals, has been a serious problem. The method of J. Lawrence Smith, though satisfactory as to accuracy, is laborious in technique, consequently the hydrofluoric–sulfuric acid process often has been proposed to supplant it but has been unqualifiedly rejected by Hillebrand[2] as unsuitable because of the difficulty of removing fluorides. Lundell[3] proposes to substitute perchloric acid for sulfuric to obviate this difficulty, especially with reference to soda-lime glasses. While working along the same lines, but using crystallized ammonium fluoride, the writers noticed that fusion took place and it occurred to them that possibly a molten reagent might be more ef-

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[10] Sabatier, *Ann. chim. phys.*, [5] **22**, 22 (1881).

[1] Recipient of "The J. T. Baker Fellowship in Analytical Chemistry" at the University of Illinois for the year 1930–31. Assistance is further gratefully acknowledged as a result of a leave of absence granted by the University of Oklahoma.

[2] U. S. Geol. Survey Bull., **700**, 99 (1919).

[3] Lundell and Knowles, *J. Am. Ceramic Soc.*, **10**, 849 (1927).