

Heat Capacities and Thermodynamic Properties of the Pyrrhotites FeS and Fe_{0.877}S from 5 to 350°K*

F. GRØNVOLD, *Chemical Institute A, University of Oslo, Blindern, Norway,*

AND

E. F. WESTRUM, JR., AND CHIEN CHOU,† *Department of Chemistry, University of Michigan, Ann Arbor, Michigan*

(Received September 29, 1958)

Heat capacities were measured from 5 to 350°K for two pyrrhotites at the iron-rich limit (Fe_{1.000}S) and the sulfur-rich limit (Fe_{0.877}S) of the homogeneity range. The heat-capacity curves follow the normal sigmoid shape with the exception of an upward trend for Fe_{1.000}S above 300°K, and two small, broad humps for Fe_{0.877}S near 8 and 30°K. From these data the entropy and enthalpy functions were calculated. At 298.15°K the values of C_p , $S^\circ - S_0^\circ$, and $(H^\circ - H_0^\circ)/T$ are 12.08, 14.415, and 7.496 cal/mole °K, respectively, for Fe_{1.000}S, and 11.92, 14.529, and 7.396 cal/mole °K for Fe_{0.877}S. The values on FeS are lower by approximately 10% over the range 58 to 296°K than those previously reported in the literature.

INTRODUCTION

THE relationships between structural and thermodynamic properties of the solid solutions occurring in the transition metal chalcogenides have not been extensively studied. In these systems two different aspects of the order-disorder process are involved, one due to changes in temperatures and the other due to changes in composition. One of the systems for which the structural data are most complete is the iron-sulfur system, and the particularly interesting phase is the pyrrhotite phase Fe_{1-x}S with a composition range $0 \leq x \leq 0.123$ at 360°C.¹ At this temperature the phase has a hexagonal NiAs-like structure with a varying number of vacant iron positions and the tendency of ordering is apparently slight. As the temperature is lowered, discrete phases occur due to the decrease in free energy by the ordering process, and at least three phases with slightly different compositions exist: β_1 at the composition Fe_{1.000}S, β_2 in the composition range between Fe_{0.936}S and Fe_{0.900}S, and β_3 with a composition close to Fe_{0.877}S. The crystal structure of both the first and the last of these has been studied by Bertaut^{2,3} and the ordering principles leading to the formation of the superstructures explained.

The low-temperature heat capacity of pyrrhotite has been studied by Anderson⁴ in the range from 57.9 to 296.0°K on a synthetic sample. In view of the rather large variations in composition of pyrrhotite, it is necessary to have samples with accurately known composition and a high degree of purity and ho-

mogeneity. For this purpose two pyrrhotites were made up, one representing the iron-rich limit and the other the sulfur-rich limit for pyrrhotite, and as the first step in evaluating the thermodynamic functions their heat capacities were determined in the temperature range 5 to 350°K.

EXPERIMENTAL

Preparation of the Samples

The iron used for making the samples was prepared from Fe₂O₃, Merck "Ferrum oxydatum sec. L. Brandt," by reduction with dry, purified hydrogen gas at 400 to 600°C and then at 1000°C until constant weight was attained. A spectrographic analysis showed the presence of the following impurities: Ni~0.01%, Mn~0.001%, Si~0.01%. Sulfur from Schering-Kahlbaum A. G., "Sulfur cryst. puriss.," was purified by double distillation in a silica apparatus and only the middle fractions were used.

The two pyrrhotites with composition Fe_{1.000}S and Fe_{0.877}S were prepared by heating appropriate proportions of the elements in a silica apparatus. Because of the large amounts of sulfide to be prepared, the elements were kept in separate vitreous silica tubes about 25 cm long and 2.5 cm internal diameter with a connecting tube 10 cm long and 0.8 cm i.d. having a side arm for evacuating and sealing the system. The tube containing the iron was heated in an electric furnace to about 800°C and the sulfur slowly distilled into it. After the reaction had gone almost to completion, the tube then containing the iron sulfide was kept cool and the other tube put into the furnace to transfer the remaining trace of unreacted sulfur before sealing off. The samples were then heated 7 days at 800°C, cooled down 100°C per day to room temperature, and fragmented in an agate mortar in a dry box filled with nitrogen gas. The homogenization treatment was carried out at 290°C and after 30 days the pyrrhotites were cooled down to room temperature over a period of 6 days. X-ray powder photographs confirmed the ho-

* This work was supported by the Division of Research of the U. S. Atomic Energy Commission and by the Nansen Foundation (F. G.). It was presented in part at the Conférence de Physique des Basses Températures, Paris, September, 1955.

† Present address: Institute of Applied Physics, Academia Sinica, Peking, China.

¹ F. Grønvold and H. Haraldsen, *Acta Chem. Scand.* **6**, 1452 (1952).

² F. Bertaut, *Compt. rend.* **234**, 1295 (1952); *Acta Cryst.* **6**, 557 (1953); *J. phys. radium* **16**, 42S (1955).

³ F. Bertaut, *J. phys. radium* **15**, 77S (1954); *Bull. soc. franç. minéral. et crist.* **79**, 276 (1956).

⁴ C. T. Anderson, *J. Am. Chem. Soc.* **53**, 476 (1931).

mogeneity of the samples and their identical nature to those obtained earlier.¹

Cryostat and Calorimeter

The Mark I cryostat and technique employed for low-temperature calorimetry are described elsewhere.⁶ The copper calorimeter (laboratory designation W-7) has a capacity of 40.33 cc; it is gold-plated inside and out and has only four vanes. The heat capacity of the empty calorimeter was determined separately, using the same thermometer and heater; it represented from 15 to 68% of the total heat capacity observed. A correction for slight differences in the amount of indium-tin solder used for sealing and Apiezon-T grease for thermal contact with the thermometer and heater was applied. The platinum resistance thermometer (laboratory designation A-3) has been calibrated by the National Bureau of Standards, and the temperatures are judged to correspond with the thermodynamic temperature scale within 0.03°K from 10 to 90°K and within 0.04°K from 90 to 350°K. Precision is considerably better, and the temperature increments are probably correct to a millidegree after corrections for quasi-adiabatic drift.

Procedure and Results

The calorimeter was loaded with sample, evacuated, and filled with helium at 2 cm Hg pressure to provide thermal contact between sample and calorimeter. It was then sealed, placed in the cryostat, and cooled down. The mass of sample used was 79.257 g Fe_{1.000}S and 90.509 g Fe_{0.877}S. The heat capacity determinations are listed in Table I in chronological order, expressed in terms of the thermochemical calorie, defined as 4.1840 abs j. The ice point is taken to be 273.15°K, and the atomic weights of iron and sulfur as 55.85 and 32.066, respectively. The data are expressed in terms of one mole of substance, i.e., 87.92 g Fe_{1.000}S and 81.05 g Fe_{0.877}S. An analytically determined curvature correction for the finite temperature increments was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments can usually be inferred from the adjacent mean temperatures in Table I.

The heat-capacity *versus* temperature curves are shown in Fig. 1. For Fe_{1.000}S it has the usual sigmoid shape, predicted by the Debye theory, up to about 300°K. From there on a definite upward trend is noted. In the case of Fe_{0.877}S the heat-capacity curve is normal at the higher temperatures, but small, relatively broad humps appear near 8 and 30°K.

Values of C_p , $S^\circ - S_0^\circ$, and $(H^\circ - H_0^\circ)/T$ at selected temperatures are listed in Table II. The enthalpy and entropy increments were computed by numerical

TABLE I. Heat capacity of pyrrhotites, cal/mole °K.

T, °K	C _p	T, °K	C _p	T, °K	C _p
Iron-rich pyrrhotite (Fe _{1.000} S; mol. wt=87.92)					
Series I					
		17.42	0.1655	69.89	4.202
		18.90	0.2177	76.19	4.696
88.72	5.637	20.63	0.2904	83.16	5.233
95.96	6.111	22.63	0.3871	90.82	5.778
104.18	6.618	24.85	0.5122	159.12	9.141
112.76	7.113	27.29	0.6702	168.14	9.434
121.00	7.555	30.16	0.8758	177.57	9.712
129.31	7.966	33.46	1.128	187.20	9.970
137.68	8.331	37.06	1.424	196.73	10.21
146.16	8.676	41.11	1.766	206.16	10.42
154.88	8.999	45.71	2.160	215.88	10.62
163.96	9.307	50.67	2.594	225.75	10.82
				235.53	11.01
				245.35	11.18
				255.25	11.35
Series II					
6.97	0.0086	Series III			
8.32	0.0160	7.05	0.0089	265.27	11.52
9.05	0.0198	7.80	0.0113	275.34	11.69
9.86	0.0261	8.48	0.0159	285.33	11.86
10.56	0.0316	9.11	0.0204	294.91	12.01
11.42	0.0392	9.75	0.0251	304.92	12.22
12.39	0.0518	47.93	2.356	314.90	12.45
13.32	0.0657	52.81	2.776	324.74	12.68
14.38	0.0852	58.03	3.223	334.71	13.07
15.84	0.1201	63.80	3.714	344.70	13.44
Sulfur-rich pyrrhotite (Fe _{0.877} S; mol. wt=81.05)					
Series I					
		169.95	9.277	18.96	0.4199
		194.10	9.949	20.90	0.5332
82.50	5.052	223.47	10.61	23.19	0.6851
85.92	5.297	240.61	10.95	25.72	0.8820
91.76	5.686	252.46	11.17	28.34	1.134
98.77	6.109	262.52	11.35	30.88	1.479
106.21	6.546	272.68	11.52	33.70	1.543
114.28	6.986	282.83	11.68	37.26	1.705
123.44	7.456	293.09	11.85	41.41	1.993
132.83	7.891	303.38	12.00	45.69	2.308
141.63	8.271	313.63	12.15	50.18	2.649
150.19	8.603	323.84	12.30	55.22	3.030
158.69	8.912	334.05	12.45	60.62	3.443
164.39	9.100	344.27	12.59		
173.39	9.375			Series V	
182.49	9.641	Series III		5.82	0.0022
190.68	9.883	246.87	11.07	6.52	0.0075
200.89	10.11	256.33	11.24	7.20	0.0194
210.12	10.33	266.32	11.41	8.48	0.0569
219.45	10.52	276.40	11.59		
228.87	10.72	286.51	11.74	Series VI	
238.50	10.91	296.68	11.90	5.97	0.0029
248.25	11.09	306.86	12.05	6.36	0.0059
		317.01	12.21	7.88	0.0518
		327.12	12.35	10.17	0.0855
		337.27	12.50		
		347.48	12.65	Series VII	
Series II					
53.65	2.917	Series IV		6.07	0.0035
57.16	3.178	7.55	0.0357	7.90	0.0511
62.08	3.558	8.88	0.0588	7.92	0.0521
67.34	3.956	10.21	0.0870	9.79	0.0760
73.04	4.369	11.22	0.1115	29.06	1.214
79.29	4.825	12.18	0.1367	30.57	1.445
86.06	5.307	13.16	0.1657	32.21	1.494
93.74	5.803	14.30	0.2054	33.97	1.540
101.84	6.293	15.67	0.2604	35.87	1.620
108.69	6.687	17.23	0.3308		
117.20	7.141				
126.00	7.574				
134.89	7.982				
149.76	8.590				

⁶ E. F. Westrum, Jr., and A. F. Beale, Jr., J. Am. Chem. Soc. (to be published).

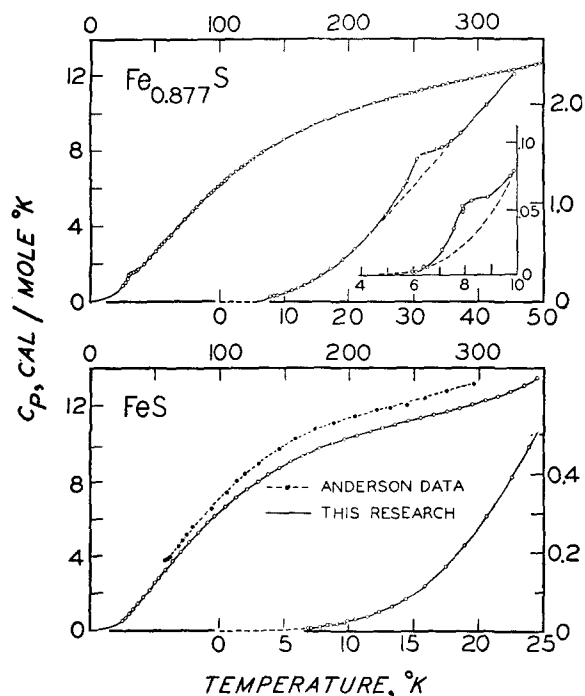


FIG. 1. Heat capacity of iron sulfides. The open circles represent data from this research; the solid circles are the data of Anderson.⁴

integration, using graphically interpolated values of heat capacity. The heat-capacity values are considered to have a probable error of 0.1% above 25°K, 1% at 10°K, and about 5% at 5°K. The values of entropy are considered to be accurate to ± 0.01 cal/mole °K, even at the higher temperatures, and the enthalpy values have an estimated probable error of 0.1%, except at the lowest temperatures. Some of the tabular data are given to an additional digit because of their significance when entropies or enthalpies at different temperatures or compositions are compared.

DISCUSSION

The heat capacity of the iron-rich pyrrhotite $\text{Fe}_{1.000}\text{S}$ shows normal behavior, except for a trend to higher values with increasing rapidity as 350°K is approached, probably as a prelude to the structomagnetic α transformation at 411°K.^{6,7} There is, however, a striking discrepancy between the present results and those previously reported by Anderson⁴ for FeS. His heat capacity values run 8.2 to 15.9% higher, and the resulting entropy value at 298.1°K is 16.1 ± 0.3 eu, which disagrees considerably with the value 14.415 eu found here. The most probable reason for the deviation is that Anderson's sample did not have the composition FeS, but was somewhat richer in sulfur because it was

prepared by passing a mixture of carbon disulfide and carbon dioxide over iron at 850°C. Another indication of the excess sulfur content is the low observed density, 4.65 g/cc. According to the x-ray data¹ the density of FeS should be 4.83 g/cc and that of $\text{Fe}_{0.877}\text{S}$, 4.63 g/cc.

Enthalpy data on FeS in the range up to 100°C are listed in Table III. There is a fair agreement between the literature values and those obtained in this research, the results by Regnault⁸ being lower and those by Bornemann and Hengstenberg⁹ considerably higher, while those by De la Rive and Marcet,¹⁰ measured over a 10°C interval, are remarkably close. Because of excess sulfur in Bornemann and Hengstenberg's⁹ and Coughlin's¹¹ samples, pretransition effects might account for the high values.

Although the literature data discussed so far refer to synthetic samples, some data have also been ob-

TABLE II. Thermodynamic properties of pyrrhotites, cal/mole °K.

$T, ^\circ\text{K}$	C_p	$S^\circ - S_0^\circ$	$\frac{H^\circ - H_0^\circ}{T}$	C_p	$S^\circ - S_0^\circ$	$\frac{H^\circ - H_0^\circ}{T}$
	Iron-rich pyrrhotite ($\text{Fe}_{1.000}\text{S}$)			Sulfur-rich pyrrhotite ($\text{Fe}_{0.877}\text{S}$)		
10	0.0269	0.0090	0.0067	0.0812	0.0207	0.0173
20	0.262	0.0795	0.0608	0.479	0.178	0.133
30	0.863	0.289	0.219	1.395	0.511	0.372
40	1.670	0.645	0.479	1.893	0.973	0.683
50	2.535	1.110	0.803	2.633	1.474	0.998
60	3.393	1.648	1.163	3.397	2.021	1.334
70	4.212	2.233	1.541	4.143	2.601	1.682
80	4.996	2.847	1.924	4.875	3.202	2.036
90	5.718	3.478	2.306	5.569	3.818	2.391
100	6.365	4.115	2.680	6.191	4.437	2.740
110	6.955	4.750	3.042	6.758	5.054	3.080
120	7.504	5.379	3.392	7.281	5.665	3.408
130	7.998	5.999	3.727	7.763	6.267	3.725
140	8.429	6.608	4.048	8.202	6.858	4.029
150	8.823	7.203	4.353	8.597	7.438	4.321
160	9.173	7.784	4.644	8.957	8.005	4.600
170	9.491	8.350	4.920	9.277	8.557	4.865
180	9.779	8.901	5.182	9.570	9.096	5.119
190	10.04	9.436	5.431	9.843	9.621	5.360
200	10.28	9.958	5.667	10.09	10.132	5.590
210	10.51	10.465	5.892	10.32	10.630	5.810
220	10.71	10.958	6.107	10.53	11.115	6.020
230	10.90	11.438	6.311	10.74	11.588	6.221
240	11.08	11.906	6.506	10.94	12.049	6.413
250	11.26	12.362	6.693	11.12	12.499	6.598
260	11.43	12.807	6.872	11.30	12.939	6.775
270	11.60	13.242	7.044	11.47	13.369	6.946
280	11.76	13.667	7.209	11.64	13.789	7.111
290	11.93	14.082	7.369	11.80	14.200	7.270
300	12.11	14.490	7.524	11.95	14.603	7.423
350	13.68	16.459	8.277	12.68	16.501	8.123
273.15	11.65	13.377	7.097	11.53	13.503	6.999
298.15	12.08	14.415	7.496	11.92	14.529	7.396

⁸ V. Regnault, *Ann. chim. phys.* [3], **1**, 129 (1841).

⁹ K. Bornemann and O. Hengstenberg, *Metall u. Erz* **17**, 339 (1920).

¹⁰ De la Rive and Marcet, *Ann. Physik* **52**, 120 (1841).

¹¹ J. P. Coughlin, *J. Am. Chem. Soc.* **72**, 5445 (1950).

⁶ H. Haraldsen, *Z. anorg. u. allgem. Chem.* **231**, 78 (1937); **246**, 169 and 195 (1941).

⁷ Hirone, Maeda, and Tsuya, *J. Phys. Soc. Japan* **9**, 503 (1954).

TABLE III. Comparison with earlier enthalpy measurements. Values in the upper half of the table are compared with those for Fe_{1.000}S, the rest with those for Fe_{0.877}S.

Author	Sample	T ₁ , °K	T ₂ , °K	H _{T₁} - H _{T₂} , cal/mole	
				Literature value	This research
Regnault ^a	FeS	371	290	970	1060
De la Rive and Marcet ^b	FeS	288	278	123	118
Bornemann and Hengstenberg ^c	Fe _{0.97} S	373	273	1460	1290
Coughlin ^d	Fe _{0.98} S	355.8	298.16	790	745
Coughlin ^d	Fe _{0.98} S	366.6	298.16	950	895
Neumann ^e	pyrrhotite	373	273?	1240	1226
Regnault ^a	pyrrhotite	371	283	1140	1086
Abt ^f	Fe _{0.87} S	368	286	1020	1011
Lindner ^g	pyrrhotite	373	273	1180	1226
Bornemann and Hengstenberg ^c	Fe _{0.87} S	373	273	1240	1226

^a See reference 8.

^b See reference 10.

^c See reference 9.

^d See reference 11.

^e See reference 13.

^f See reference 12.

^g See reference 14.

tained on natural pyrrhotites. Only Abt¹² and Bornemann and Hengstenberg⁹ analyzed their samples and found compositions corresponding approximately to that of the sample studied here. It is assumed that the samples studied by Neumann,¹³ Regnault,⁸ and Lindner¹⁴ had the same composition, and the molar enthalpy

values listed in Table III are calculated for the composition Fe_{0.877}S. As can be seen from the table, the literature values are in good agreement with the results of the present research.

As noted earlier, two small, relatively broad humps appear at low temperatures for the Fe_{0.877}S sample. The one around 8°K involves an entropy increment of 0.003 cal/mole °K and the one around 30°K an entropy increment of 0.03 cal/mole °K. There is at present no obvious explanation of these anomalies.

¹² A. Abt, Ann. Physik **62**, 474 (1897); Z. Kryst. **30**, 184 (1898).

¹³ F. E. Neumann, Ann. Physik **23**, 1 (1831).

¹⁴ G. Lindner, dissertation, Erlangen (1903).