

activation free energy necessary to dehydrate partially the negative ions, or both.

Similar calculations for Mn⁺⁺, Cu⁺⁺, Co⁺⁺, and Ni⁺⁺ for the solutions of Table I yield lower limits for first-order rate constants analogous to Eq. (1) of 1×10^7 , 6×10^6 , 2×10^6 , and 4×10^4 sec⁻¹, respectively. The order of efficiency in producing relaxation of O¹⁷ in H₂O is similar although not identical, to that found

by Wertz for Cl⁻. A parallelism would be expected although there is no necessity of exact agreement.

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Heat Capacities and Thermodynamic Properties of the Iron Tellurides Fe_{1.11}Te and FeTe₂ from 5 to 350°K*

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Heat capacities of the two iron telluride phases, Fe_{1.11}Te and FeTe₂, were measured in the range 5 to 350°K. In Fe_{1.11}Te a cooperative type of transformation was observed at about 63°K involving an entropy increment of 0.57 cal/mole °K. The thermodynamic functions were evaluated and the values of C_p , $S^\circ - S_0^\circ$, and $(H^\circ - H_0^\circ)/T$ at 298.15°K are 13.15, 21.272, and 9.575 cal/mole °K, respectively, for Fe_{1.11}Te, and the values of C_p , $S^\circ - S_0^\circ$, $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ for FeTe₂ are 17.60 and 23.940 cal/mole °K, 3567.4 cal/mole, and 11.975 cal/mole °K, respectively.

INTRODUCTION

NO HEAT-CAPACITY data exist on iron tellurides. As part of a thermodynamic study of the transition metal chalcogenides, low-temperature heat capacities of the iron tellurides have been determined.

In the iron-tellurium system¹ only two intermediate phases exist below 488°C: the β -phase, Fe_{1.11}Te or Fe₉Te₈, with a narrow range of homogeneity, and the ϵ phase with composition ranging from FeTe_{1.95} to FeTe_{2.10}. Later work by Chiba² on the magnetic properties and phase diagram of the iron-tellurium system confirms the existence of these two phases. She shows the composition limits at Fe_{1.18}Te and Fe_{1.05}Te for the β phase and at FeTe_{1.97} and FeTe_{2.10} for the ϵ phase. In a study of some electrical characteristics of iron-monotelluride single crystals it was noted³ that an ingot with the composition Fe_{1.072}Te contained some ϵ phase, indicating that the β phase contains more iron than indi-

cated by the formula. The resistance of the β phase showed an unusual variation with temperature as it increased by a factor of 50 between room temperature and 40°K, indicating the possibility of a transition taking place. Magnetic measurements on FeTe gave evidence⁴ of an antiferromagnetic transition around 500°C, but no further discontinuities in the temperature dependence of the magnetic susceptibility were observed down to 79°K. More recently the thermal expansion of the ϵ phase of the iron-tellurium system has been measured⁵ and the relation between the volume-expansion coefficient and heat capacity studies, making use of the data presented here.

The pure β phase was judged to be best represented by a sample with composition Fe_{1.11}Te and the ϵ phase by a sample with the composition FeTe₂. These samples were therefore made up in sufficient quantities from high purity materials, and their heat capacities determined in the range 5 to 350°K.

EXPERIMENTAL

Preparation of the Samples

The iron used for making the alloys was prepared from "Ferrum reductum," Merck, by reduction with dry, purified hydrogen gas at 400 to 600°C and then

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¹ Grønvold, Haraldsen, and Vihovde, *Acta Chem. Scand.* **8**, 1927 (1954).

² S. Chiba, *J. Phys. Soc. Japan* **10**, 837 (1955).

³ Finlayson, Greig, Llewellyn, and Smith, *Proc. Phys. Soc. (London)* **B69**, 860 (1956).

⁴ E. Uchida and H. Kondoh, *J. Phys. Soc. Japan* **10**, 357 (1955).

⁵ J. P. Llewellyn and T. Smith, *Proc. Phys. Soc. (London)* **B70**, 1113 (1957).

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

$T, ^\circ\text{K}$	C_p	$T, ^\circ\text{K}$	C_p	$T, ^\circ\text{K}$	C_p
β phase ($\text{Fe}_{1.11}\text{Te}$; mole wt=189.66 g)					
Series I		Series III		65.41	12.40
121.50	10.20	4.87	0.0395	67.30	7.794
126.46	10.37	5.70	0.0624	69.32	7.380
134.37	10.65	6.56	0.0703	71.87	7.434
143.21	10.93	7.37	0.0984	75.08	7.698
152.48	11.79	8.38	0.152	Series V	
162.00	11.40	9.43	0.198	52.06	5.326
171.70	11.60	10.64	0.269	57.35	6.066
181.40	11.79	11.89	0.350	60.49	6.720
191.11	11.96	30.08	2.491	61.60	8.948
200.75	12.10	33.11	2.894	62.44	14.66
210.35	12.23	36.41	3.324	63.08	17.76
219.86	12.35	40.39	3.833	63.67	17.54
229.35	12.47	45.06	4.422	64.25	16.97
Series II		49.92	5.048	64.77	15.82
6.09	0.0418	54.98	5.718	65.28	13.10
6.89	0.0559	55.26	5.754	66.24	9.085
7.60	0.103	60.56	9.020	67.49	7.663
8.41	0.152	65.62	12.10	68.60	7.411
8.97	0.177	71.92	7.488	70.58	7.387
9.65	0.210	79.24	7.972	226.85	12.43
10.93	0.287	85.93	8.438	236.34	12.55
12.33	0.384	92.70	8.843	245.87	12.67
13.62	0.491	100.20	9.252	242.07	12.57
14.84	0.609	108.36	9.647	250.49	12.67
16.15	0.735	116.65	10.01	260.03	12.78
17.66	0.903	124.93	10.34	269.74	12.88
19.45	1.113	Series IV		279.49	12.97
21.54	1.373	51.66	5.275	289.33	13.06
23.93	1.681	56.78	5.974	299.46	13.14
26.61	2.018	60.08	6.582	309.83	13.28
29.55	2.421	61.85	10.97	320.23	13.37
		63.61	17.54	330.82	13.46
				341.65	13.55
ϵ phase ($\text{FeTe}_{2.000}$; mole wt=311.07 g)					
Series I		13.86	0.140	94.02	10.72
100.24	11.30	15.15	0.188	168.89	15.13
105.54	11.73	16.61	0.253	174.75	15.33
113.73	12.35	18.20	0.342	181.90	15.55
122.79	12.99	19.90	0.458	191.57	15.81
131.28	13.50	21.77	0.610	201.28	16.04
139.58	13.95	23.83	0.803	210.72	16.24
148.20	14.36	26.09	1.054	219.96	16.42
157.46	14.75	28.52	1.358	229.40	16.61
166.97	15.10	31.22	1.734	238.90	16.78
Series II		34.32	2.192	248.62	16.93
6.83	0.0144	37.73	2.726	251.27	16.95
7.71	0.0197	39.60	3.046	261.34	17.11
8.67	0.0293	43.43	3.683	271.24	17.24
9.52	0.0472	47.81	4.419	281.38	17.36
10.24	0.0488	52.96	5.271	291.66	17.53
11.45	0.0768	58.71	6.204	302.20	17.66
12.65	0.104	64.89	7.218	312.84	17.78
		71.66	8.199	323.49	17.90
		79.28	9.079	334.18	18.06
		86.65	9.957	344.88	18.16

at 1000°C until constant weight was attained. A spectrographic analysis showed only the presence of about 0.01% Ni, 0.001% Mn, and 0.01% Si as impurities in the metal. The tellurium metal was supplied by The British Drug Houses, Ltd. It was purified by repeated

vacuum distillations in a vitreous silica apparatus. According to spectrographic analysis, the distilled product contained less than 0.01% Fe and only traces of Al, Mg, and Pb.

Accurately weighed quantities of the elements corresponding to the compositions $\text{Fe}_{1.11}\text{Te}$ and FeTe_2 were sealed in evacuated silica tubes of about 25 cm length and 2.5 cm internal diameter. After being heated at 700°C for one week in an electric muffle furnace, the samples were cooled, fragmented in an agate mortar in dry nitrogen gas, and transferred to new tubes. They were then heated at 400°C for two weeks and cooled to room temperature at a rate of 50°C per day. X-ray powder photographs confirmed the homogeneity 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 9 to 46% 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

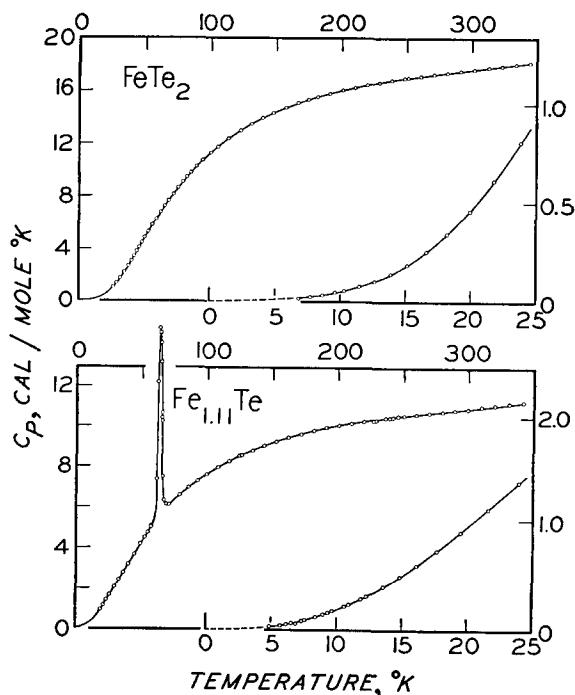


FIG. 1. Heat capacity of iron tellurides.

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

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.

The calorimeter was loaded with sample and evacuated, and helium was added at 2 cm Hg pressure at about 25°C to provide thermal contact between sample and calorimeter. It was then sealed, placed in the cryostat, and cooled. The mass of sample used was 120.567 g Fe_{1.11}Te and 154.505 g FeTe₂.

TABLE II. Thermodynamic properties of the β phase, Fe_{1.11}Te.

T, °K	C_p	$S^0 - S_0^0$	$\frac{H^0 - H_0^0}{T}$
	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$
5	(0.040)	(0.013)	(0.010)
10	0.230	0.0767	0.0575
15	0.619	0.236	0.174
20	1.179	0.488	0.353
25	1.813	0.819	0.581
30	2.479	1.208	0.841
35	3.143	1.640	1.123
40	3.782	2.102	1.416
45	4.416	2.583	1.714
50	5.060	3.082	2.016
60	6.558	4.126	2.637
70	7.367	5.790	3.797
80	8.046	6.814	4.282
90	8.684	7.800	4.737
100	9.241	8.744	5.160
110	9.721	9.649	5.553
120	10.137	10.513	5.918
130	10.500	11.339	6.257
140	10.832	12.129	6.572
150	11.12	12.887	6.866
160	11.36	13.612	7.139
170	11.58	14.308	7.394
180	11.77	14.976	7.632
190	11.94	15.617	7.854
200	12.09	16.232	8.062
210	12.23	16.826	8.257
220	12.35	17.397	8.441
230	12.47	17.949	8.613
240	12.58	18.481	8.776
250	12.69	18.998	8.931
260	12.78	19.497	9.077
270	12.88	19.981	9.216
280	12.98	20.452	9.349
290	13.08	20.909	9.476
300	13.17	21.353	9.597
350	13.63	23.420	10.141
273.15	12.91	20.131	9.259
298.15	13.15	21.272	9.575

TABLE III. Thermodynamic properties of the ϵ phase, FeTe_{2.000}.

T, °K	C_p	$S^0 - S_0^0$	$H^0 - H_0^0$	$-\frac{(F_0 - H_0^0)}{T}$
	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$	$\frac{\text{cal}}{\text{mole}}$	$\frac{\text{cal}}{\text{mole } ^\circ\text{K}}$
5	(0.007)	(0.0023)	(0.009)	(0.0005)
10	0.0450	0.0150	0.112	0.0038
15	0.182	0.0550	0.635	0.0127
20	0.465	0.142	2.18	0.033
25	0.929	0.293	5.60	0.069
30	1.559	0.516	11.76	0.124
35	2.294	0.811	21.37	0.200
40	3.113	1.169	34.85	0.298
45	3.943	1.584	52.49	0.417
50	4.785	2.043	74.32	0.557
60	6.408	3.060	130.33	0.888
70	7.889	4.161	201.98	1.276
80	9.173	5.300	287.39	1.708
90	10.32	6.448	385.01	2.170
100	11.27	7.586	493.1	2.656
110	12.08	8.699	609.9	3.155
120	12.80	9.781	734.3	3.662
130	13.43	10.831	865.5	4.173
140	13.97	11.847	1002.6	4.686
150	14.43	12.827	1144.7	5.196
160	14.83	13.772	1291.0	5.703
170	15.18	14.681	1441.1	6.204
180	15.50	15.559	1594.5	6.701
190	15.77	16.404	1750.9	7.189
200	16.01	17.219	1909.8	7.670
210	16.23	18.005	2071.0	8.143
220	16.43	18.765	2234.3	8.609
230	16.62	19.499	2399.6	9.066
240	16.79	20.210	2566.6	9.516
250	16.94	20.899	2735.2	9.958
260	17.09	21.565	2905.4	10.391
270	17.22	22.213	3076.9	10.817
280	17.36	22.842	3249.9	11.235
290	17.50	23.454	3424.2	11.647
300	17.62	25.049	3599.8	12.050
350	18.21	26.812	4496.1	13.966
273.15	17.27	22.414	3131.4	10.950
298.15	17.60	23.940	3567.4	11.975

RESULTS

The heat-capacity determinations are listed in Table I in chronological order, expressed in terms of the thermochemical calorie, defined as 4.1840 abs joules. The ice point is taken to be 273.15°K, and the atomic weights of iron and tellurium as 55.85 and 127.61, respectively. The data are expressed in terms of one mole of substance, i.e., 189.66 g Fe_{1.11}Te and 311.07 g FeTe₂. 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. The most interesting feature is the

λ -type transition encountered in $\text{Fe}_{1.11}\text{Te}$ at about 63°K. Achievement of equilibrium in this region required only slightly more time than usual. For FeTe_2 the heat-capacity curve has the normal sigmoid shape predicted by the Debye theory.

Values of C_p , $S^\circ - S_0^\circ$, and $(H^\circ - H_0^\circ)/T$ for $\text{Fe}_{1.11}\text{Te}$ at selected temperatures are listed in Table II; the reason for not giving the reduced free-energy function is the uncertainty about complete ordering of the excess iron atoms. For FeTe_2 no such complication is likely to be present, and values of C_p , $S^\circ - S_0^\circ$, $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ are given in Table III. The enthalpy and entropy increments were computed by numerical 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. Values below 6°K were extrapolated with a T^3 function. The effect of nuclear spin is not included in the entropy and free-energy functions. The estimated probable error in the entropy, enthalpy, and free-energy functions is 0.1% above 100°K, but in order to make the tables internally consistent, some of the values are given to an additional digit.

DISCUSSION

The entropy involved in the steep λ -type transition in $\text{Fe}_{1.11}\text{Te}$ is 0.57 cal/mole °K. There is at present no factual information about its origin, but it seems reasonable to relate it to a structural or magnetic ordering of the iron atoms.

The structure of $\text{Fe}_{1.11}\text{Te}$ is considered¹ to be of a type intermediate between that of tetragonal PbO (the

B10 structure type of the *Strukturbericht*) and that of Fe_2As (the *C38* type). The arrangement in the *B10* structure can be described as a quadratic net of iron atoms, which, together with the tellurium atoms, form square pyramids sharing edges, and with apex alternately above and below the net of iron atoms. Each iron atom from the 11% excess beyond stoichiometry probably converts a pyramid into an octahedron without appreciably disturbing the original grouping. X-ray work carried out so far has failed to indicate an ordering of the excess iron atoms at room temperature, and the transition at 63°K therefore might possibly be related to an ordering of the iron atoms. It seems more probable, however, that the transition is connected with a change in the population of the magnetic energy levels, and the compound might be anticipated to be ferrimagnetic below 63°K because of the crystallographic inequality of the iron atoms. For the idealized situation of a simple cubic lattice the spin-wave theory⁷ predicts an electronic heat capacity proportional to $T^{3/2}$ over a limited temperature range. For $\text{Fe}_{1.11}\text{Te}$ the heat capacity over the range 5 to 20°K can be well fit by the function

$$C_p = 0.000141T^3 + 0.00163T^{3/2}.$$

If the first term may be identified as a Debye T cubed lattice vibrational contribution, the second term has a coefficient of the magnitude to be expected from spin-wave theory.⁶ For the purpose of testing this further, it would be desirable to extend the heat-capacity measurements to lower temperatures.

⁷ J. S. Kouvel and H. Brooks, Office of Naval Research, Tech. Rept. No. 198 (Harvard University, May 20, 1954).