[Contribution from the Pacific Experiment Station, Bureau of Mines, United States Department of the Interior]

Low Temperature Heat Capacities and Entropies at 298.16°K. of Ferrous Oxide, Manganous Oxide and Vanadium Monoxide[1]

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The heat capacities of ferrous oxide, manganous oxide and vanadium monoxide were measured throughout the temperature range from 52 to 298°K. The first two substances have heat capacity maxima at 188.5 and 117.8°K., respectively. The molal entropies at 298.16°K. were obtained as 14.2 ± 0.2, 14.27 ± 0.10, and 9.3 ± 0.2 cal./deg., respectively.

Introduction

Thermodynamic calculations for ferrous oxide and manganous oxide have been hampered by uncertainties in their entropy values, and a value for vanadium monoxide has not been available. This paper reports the results of low temperature heat capacity measurements and the corresponding entropy values at 298.16° K. for these three substances. Ferrous and manganous oxides were similarly studied some twenty years ago by Millar.[2,3] No previous data exist for vanadium monoxide.

Materials

The ferrous oxide used in this work was the same as that described by Coughlin, King and Bonnickson[4] and employed in their high temperature heat content measurements. Details of the method of preparation and the results of identification tests were given by them and need not be repeated here. The substance analyzed 76.60% iron, 23.18% oxygen and 0.17% silica. The iron:oxygen ratio corresponds to $Fe_{0.947}O$, which has nearly the maximum iron content possible for thermodynamically stable, single-phase material.[5,6]

Manganous oxide was prepared from electrolytic manganese. The latter was dissolved in concentrated nitric acid, and the solution was evaporated and decomposed to produce manganese dioxide, which, in turn, was reduced to manganous oxide by action of hydrogen at 1100°. The product gave 99.99% of the theoretical calculated value for conversion to sulfate. Available oxygen was 0.032% by the oxalic acid–permanganate method, equivalent to 0.14% dioxide. The sulfur content was 0.005%. Based upon these results, the purity was estimated to be 99.85%.

Vanadium monoxide was prepared by prolonged heating in an atmosphere of hydrogen at 1350° of a mixture of vanadium sesquioxide and vanadium metal, with intermittent grindings to −325 mesh, analyses, and adjustments of composition. The final product contained 74.72% vanadium, 0.92% silicon, 0.10% iron and aluminum oxides, and 0.23% sodium oxide. Upon this basis alone, the purity was estimated as 98.2%. However, evidence of some disproportionation was found during the measurements as discussed later. The X-ray diffraction pattern agreed with the findings of Mathewson, Spire and Samans.[7]

Measurements and Results

Previously described apparatus was used.[8] The measured heat capacities, expressed in defined cal./deg./mole, are listed in Table I and plotted in Fig. 1. Molecular weights accord with the 1949 International Atomic Weights. The masses of the substances used in the measurements were 312.89 g. of ferrous oxide, 313.09 g. of manganous oxide and 220.42 g. of vanadium monoxide.

Table I

Heat Capacities

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
$Fe_{0.947}O$ (mol. wt. 68.89)					
54.37	1.931	155.93	10.15	197.97	11.08 (a)
58.24	2.213	165.84	11.13	202.87	10.90 (a)
62.44	2.544	167.52	11.34 (a)	206.65	10.87
66.91	2.900	172.56	11.96 (a)	216.52	10.91
71.42	3.255	175.89	12.40	226.21	10.99
75.91	3.615	177.03	12.52 (a)	236.06	11.06
80.22	3.968	180.58	12.93 (a)	245.84	11.12
84.96	4.355	183.33	13.20 (a)	257.20	11.19
94.95	5.174	185.54	13.39 (a)	266.08	11.29
104.72	5.963	185.92	13.51	276.05	11.35
114.66	6.802	187.67	13.91 (a)	286.29	11.43
124.81	7.606	190.10	13.66 (a)	296.46	11.47
135.97	8.507	193.50	11.74 (a)	298.16	(11.50)
146.31	9.329	196.32	11.25		
MnO (mol. wt. 70.93)					
54.69	2.708	113.32	10.82 (b)	185.99	8.824
58.42	3.064	114.94	12.32	196.02	9.042
62.45	3.478	116.25	13.52 (b)	206.26	9.237
66.80	3.925	117.78	76.70 (b)	216.20	9.443
71.27	4.379	119.19	7.760 (b)	226.16	9.620
75.73	4.833	120.69	7.516	236.00	9.775
80.55	5.347	121.41	7.469 (b)	245.69	9.929
85.21	5.852	124.63	7.407	256.05	10.06
94.71	6.974	135.74	7.551	265.94	10.19
102.10	7.986 (b)	145.90	7.818	276.07	10.33
103.99	8.314	155.66	8.054	286.28	10.44
106.04	8.689 (b)	165.74	8.328	296.40	10.53
109.76	9.547 (b)	175.92	8.579	298.16	(10.54)
VO (mol. wt. 66.95)					
54.97	1.061	104.53	3.564	226.13	9.054
58.61	1.217	114.72	4.122	237.24	9.390
63.11	1.429	124.62	4.654	245.79	9.636
68.07	1.671	135.96	5.262	256.10	9.903
72.87	1.904	146.22	5.811	266.20	10.17
77.61	2.141	155.95	6.306	275.58	10.39
80.49	2.298	160.46	6.553	286.34	10.64
85.40	2.548	206.39	8.373	296.36	10.84
94.98	3.055	216.23	8.725	298.16	(10.86)

The heat capacity of ferrous oxide passes through a pronounced maximum at 188.5° K. The anomalous behavior extends over a wide temperature range but is most marked in the region from 165 to 205°K. The increase to the maximum from the low-temperature side is much less abrupt than the

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(1) Article not copyrighted.

(2) R. W. Millar, This Journal, **50**, 1875 (1928).

(3) R. W. Millar, *ibid.*, **51**, 215 (1929).

(4) J. P. Coughlin, E. G. King and K. R. Bonnickson, *ibid.*, **73**, 3891 (1951).

(5) E. R. Jette and F. Foote, *Trans. Am. Inst. Mining and Met. Engrs.*, **105**, 276 (1933).

(6) L. S. Darken and R. W. Gurry, This Journal, **67**, 1398 (1945); **68**, 798 (1946).

(7) C. H. Mathewson, E. Spire and C. H. Samans, *Trans. Am. Soc. Metals*, **20**, 357 (1932).

(8) K. K. Kelley, B. F. Naylor and C. H. Shomate, *U. S. Bur. Mines, Tech. Paper* **686** (1946).

decrease on the high-temperature side, as is usual for this general type of transformation. The determinations labeled (a) in Table I are a continuous set, made without skipping any temperature gaps. Those near the peak were made with temperature rises of about 2°. In addition to the heat capacity measurements in Table I, two determinations were made of the total heat absorbed in warming from 165.00 to 205.00°K. The results are 479.8 and 481.0 cal./mole, in substantial agreement. The earlier data of Millar[3] show poor agreement with the present results. To a large extent, this may be attributed to the impurity content and lack of definition of his sample.

The heat capacity of manganous oxide also passes through a high maximum. The peak temperature is 117.8°K., and the general characteristics are the same as for ferrous oxide. The determinations labeled (b) in Table I are a continuous set, without temperature gaps. Smaller than usual temperature rises were involved as the peak was approached, the smallest being 0.583° for the 117.78°-point. Two determinations were made of the total heat absorbed in warming through the region of most anomalous behavior, 100.00 to 122.00°K. The results, 245.9 and 246.0 cal./mole, show excellent agreement. Comparison with the earlier data of Millar[2] shows that his values are high by a few per cent. at the lower end of the common temperature range, in satisfactory agreement at intermediate temperatures, and low by a few per cent. around room temperature.

The heat capacity results for vanadium monoxide showed a residuum of the maximum found by Anderson[9] for vanadium sesquioxide. There was about 20 cal./mole heat absorption in excess of the "normal" smooth curve in the region from 168.04 to 191.30°K., as determined from summation of seven consecutive heat capacity runs (not listed in Table I) in this interval. This is taken as evidence of either lack of complete reaction in preparing the sample or subsequent disproportionation of vanadium monoxide, the latter being the more probable. Consequently, values are not reported in Table I for temperatures between 160.5 and 206.3°K. No correction was applied to the listed values; however, it should be noted that, except in the omitted interval, the net correction for equivalent amounts of vanadium sesquioxide and vanadium would be relatively small. The trend in the heat capacity curve as reported appears normal, being very similar to that for nickel oxide.[10]

Entropies at 298.16° K.

In extrapolating to absolute zero, the heat capacity curve for ferrous oxide was merged into Debye function $D(300/T)$. The corresponding entropy increment below 52°K. was computed to be 0.70. To this was added 0.41, the amount calculated for completely random distribution of the vacant iron spaces in the $Fe_{0.947}O$ lattice, making a total entropy at 52°K. of 1.11. The entropy increments for the intervals from 52 to 165°K. and 205 to 298.16°K. were obtained by Simpson rule integrations of C_p *vs.* log T plots. For the interval from 165 to 205°K., the average total heat absorption, 480.4 cal./mole, was used, together with the calculated effective mean temperature, 184.1°K., giving $\Delta S = 2.61$ for this interval. The effective mean temperature was obtained from the continuous set of determinations labeled (a) in Table I.

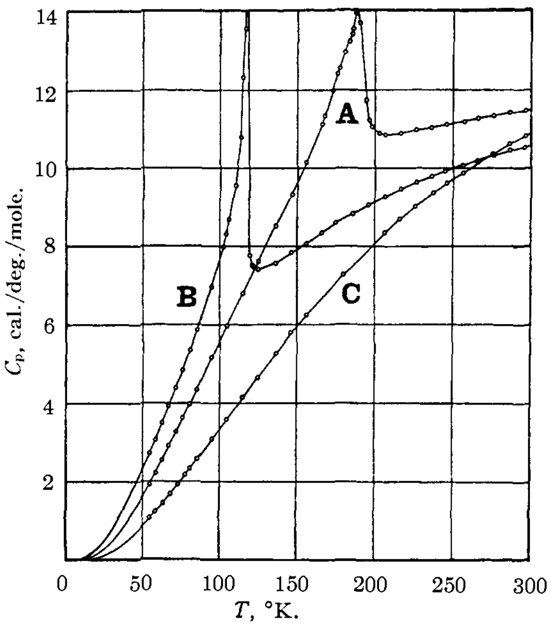

Fig. 1.—Heat capacities: A, $Fe_{0.947}O$; B, MnO; C, VO.

Similarly, the heat capacity curve for manganous oxide was merged into Debye function $D(249/T)$, for extrapolation to absolute zero. Upon this basis, the entropy at 52°K. is 1.08. The other calculations were made in a manner analogous to that for ferrous oxide. For the interval from 100 to 122°K., the average total heat absorption, 245.95 cal./mole, and the calculated effective mean temperature, 112.04°K., were used.

The entropy calculation for vanadium monoxide has no unusual features. The heat capacity data up to 78°K. are well-represented by $D(398/T)$, which was used to obtain the extrapolated portion of the entropy. The increment between 52 and 298.16°K. was obtained by Simpson rule integration. The entropy values appear in Table II.

TABLE II

MOLAL ENTROPIES (CAL./DEG.)

	$Fe_{0.947}O$	MnO	VO
0–52°K., (extrap.)	1.11	1.08	0.33
52–298.16°K. (meas.)	13.04	13.19	8.98
$S^0_{298.16}$	14.2 ± 0.2	14.27 ± 0.10	9.3 ± 0.2

The results for ferrous and manganous oxides considerably reduce the uncertainties inherent in previously adopted values,[11] 13.4 ± 1.0 for ferrous oxide and 14.4 ± 0.6 for manganous oxide. No entropy value for vanadium monoxide has been reported previously. It should be noted that an extra uncertainty allowance has been assigned to the vanadium monoxide result because of the impurity content.

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[9] C. T. Anderson, THIS JOURNAL, **58**, 564 (1936).

[10] H. Seltz, B. J. DeWitt and H. J. McDonald, *ibid.*, **62**, 88 (1940).

[11] K. K. Kelley, *U. S. Bur. Mines Bull.* **477** (1950).