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High-temperature Heat Content of Mn_3O_4, $MnSiO_3$ and Mn_3C[1]

BY J. C. SOUTHARD[2] AND G. E. MOORE[3]

This paper is a report of part of a program of study of the thermodynamic properties of manganese compounds that is being conducted at the Pacific Experiment Station of the Bureau of Mines, U. S. Department of the Interior. Entropies of Mn_3O_4,[4] $MnSiO_3$[5] and Mn_3C[6] have been determined previously. Heats of formation of these substances are given in standard reference tables, so that high-temperature heat contents are the only additional quantities required for the calculation of their free energies at high temperatures. These calculations will not be presented here, however, because present values of the heats of formation are not considered satisfactorily accurate and a redetermination of them is in progress.

Apparatus and Materials

The high-temperature heat contents were determined in an apparatus previously described.[7] The apparatus was calibrated electrically, using the relation 1 calorie = 4.1833 Int. Joules. During the measurements Mn_3O_4 was contained in an unsealed platinum-alloy capsule, $MnSiO_3$ in a sealed platinum-alloy capsule, and Mn_3C in an evacuated and sealed silica-glass capsule.

Mn_3O_4 was prepared by roasting a high-purity sample of $MnSO_4$ in air at about 1000°. Analysis for active oxygen by titration with ferrous sulfate and potassium permangate gave 7.01 and 7.03% before the measurements and 6.96% afterward (calcd. 6.99%). Manganese was determined to be 71.89 and 71.92% (calcd. 72.02%). The sample was sintered at 1200° before use. Description of the preparation and analysis of the $MnSiO_3$ sample has been given by Kelley.[5] Mn_3C was prepared by F. S. Boericke from ground electrolytic manganese and high-purity, degassed carbon black by heating three days at 850°. Analysis showed that the sample contained about 98.8% Mn_3C and 1.2% free manganese. No correction will be made for this impurity, since it would be of the order of 0.1%.

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(4) R. W. Millar, THIS JOURNAL, **50**, 1875 (1928).

(5) K. K. Kelley, *ibid.*, **63**, 2750 (1941).

(6) K. K. Kelley and G. E. Moore, unpublished.

(7) J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

Results

The experimentally determined heat contents above 298.1° K. of Mn_3O_4, $MnSiO_3$ and Mn_3C are given in Tables I, II, and III in the order in which they were taken. Graphs of the data show transitions in Mn_3O_4 at 1445 ± 40° K. amounting to 4500 cal./g. f. w., and in Mn_3C at 1310 ± 2° K. amounting to 3140 cal./g. f. w. The heat-content curve of $MnSiO_3$ shows no discontinuities. No previous high-temperature heat-content data for these substances appear in the literature.

TABLE I

HIGH-TEMPERATURE HEAT CONTENT OF Mn_3O_4 (g. f. w. = 228.79)

Temp., °K.	$H_T - H_{298.1}$ cal./g. f. w.
1290.9	42,180
1429.9	49,680
1421.1	49,050
985.6	28,020
984.3	27,890
1510.2	57,840
1476.0	56,520
1547.5	60,040
1448.6	55,110
1431.4	49,870
1441.4	50,370
763.0	18,480
760.2	18,340
498.9	7,560
498.3	7,520
1188.6	37,110
1768.8	71,200
1761.1	70,830

TABLE II

HIGH-TEMPERATURE HEAT CONTENT OF $MnSiO_3$ (g. f. w. = 130.99)

Temp., °K.	$H_T - H_{298.1}$ cal./g. f. w.
1058.0	20,670
1060.1	20,640
845.6	14,400
844.4	14,320
666.1	9,290
664.9	9,240
1245.0	26,190
1245.7	26,270
488.5	4,470
502.5	4,880
1365.6	30,050
1451.8	32,710
1508.7	34,550

TABLE III

HIGH-TEMPERATURE HEAT CONTENT OF Mn_3C (g. f. w. = 176.80)

Temp., °K.	$H_T - H_{298.1}$ cal./g. f. w.
871.0	15,370
872.3	15,390
668.3	9,640
670.8	9,660
470.7	4,250
1071.6	21,500
1069.9	21,420
1176.3	24,840
1321.0	33,050
1252.8	27,410
1292.0	28,810
1371.1	34,940
2d series	
1268.5	28,070
1393.3	35,690
1309.1	30,360
1307.9	29,950
1295.3	29,350
1420.4	36,830

Table IV is a summary at even 100° intervals of their heat contents and entropies above 298.1° K.

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.1° K. IN CAL./G. F. W. AT 100° INTERVALS

Temp., °K.	Mn_3O_4 $H_T - H_{298.1}$	Mn_3O_4 $S_T - S_{298.1}$	Mn_3C $H_T - H_{298.1}$	Mn_3C $S_T - S_{298.1}$	$MnSiO_3$ $H_T - H_{298.1}$	$MnSiO_3$ $S_T - S_{298.1}$
400	3,700	10.60	2,450	7.07	2,320	6.66
500	7,590	19.26	5,020	12.79	4,800	12.19
600	11,590	26.54	7,700	17.67	7,430	16.98
700	15,760	32.96	10,490	21.96	10,200	21.24
800	19,980	38.59	13,350	25.78	13,080	25.09
900	24,230	43.59	16,300	29.25	15,980	28.50
1000	28,620	48.22	19,300	32.41	18,890	31.56
1100	33,130	52.52	22,400	35.36	21,830	34.37
1200	37,740	56.53	25,650	38.19	24,900	37.04
1300	42,620	60.43	29,200	41.03	27,950	39.45
1310			α29,550	41.30		
1310			β32,690	43.70		
1400	47,960	64.39	36,040	46.17	31,090	41.77
1445	α50,460	66.15				
1445	β54,960	69.26				
1500	57,700	71.12	39,840	48.79	34,300	43.99
1600	62,700	74.38				
1700	67,740	77.40				
1800	72,820	80.31				

This table, in combination with similar tables for oxygen, carbon, and silicon, permits ready calculation of free energies at these temperatures from whatever values of the heat of formation an investigator may select.

Summary

The heat contents of Mn_3O_4, $MnSiO_3$ and Mn_3C from room temperature to temperatures between 1140 and 1500° have been determined. These determinations have disclosed transitions of Mn_3O_4 at 1172° and Mn_3C at 1037°.

A table summarizing the increments in the heat contents and entropies of these substances above room temperature at 100° intervals has been prepared from these data and others in the literature.

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Heat of Formation and High-temperature Heat Content of Manganous Oxide and Manganous Sulfate. High-temperature Heat Content of Manganese[1]

BY J. C. SOUTHARD[2] AND C. HOWARD SHOMATE[3]

The free energy of formation of manganous oxide at high temperatures has been uncertain because of the lack of satisfactory high-temperature heat content data. Further, the heat of formation of manganous oxide has been based almost entirely on heats of combustion. The combustion of manganese metal with oxygen in the bomb calorimeter does not proceed according to any definite reaction but yields a mixture of oxides assumed to be manganous oxide and manganomanganic oxide.[4,5] The mixture consists of 10 to 50 per cent. manganous oxide. The heat of formation of manganous oxide therefore has depended on the combustion of manganous oxide to manganomanganic oxide. This requires the use of paraffin oil and also yields a product of varying composition. Under these conditions the heat of reaction is only 5 per cent. of the total heat measured.[5] The heat of reaction also seemed to depend on whether the fraction converted to manganomanganic oxide was determined by increase in weight or by actual analysis.[4] Determination of the heat of formation of manganous oxide by a completely independent, more direct, method appears advantageous.

The thermodynamic properties of manganese sulfate have been studied and entropies of the substances involved already have been determined, as well as the high-temperature heat-content data, with the exception of manganous sulfate. The heat of formation of manganous sulfate has not been determined since the days of Thomsen and Berthelot, at which time pure manganese was not available.

Methods and Materials

The high-temperature heat contents were determined in an apparatus previously described.[6] The apparatus was calibrated electrically, using the relation 1 calorie = 4.1833 Int. joules. During the measurements manganous oxide and manganous sulfate were contained in a sealed platinum-alloy capsule and manganese metal in an evacuated and sealed silica-glass capsule. The heats of formation of manganous oxide and manganous sulfate

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