[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of Manganese Carbide and Manganese Dioxide[1]

BY K. K. KELLEY[2] AND G. E. MOORE[3]

The low-temperature specific heats of manganese-containing substances have been the subject of several previously reported investigations of the Pacific Experiment Station of the Bureau of Mines.[4] The present paper deals with measurements of specific heat in the temperature range 51 to 298°K. of manganese carbide (Mn_3C), for which no previous data are available, and of manganese dioxide, for which the previous data now are known to be unreliable, as will be discussed later. The need for such data has been enhanced in recent times by the strategic position occupied by manganese in the present emergency.

Materials[5]

To prepare manganese carbide, an intimate mixture of pure powdered electrolytic manganese and high-purity carbon was placed in an alundum thimble inside a silica tube. The mixture was evacuated with a mercury diffusion pump and heated in vacuum to 850°K., where it was held for seventy-two hours. Analysis gave 6.71 per cent. total carbon and 93.15 per cent. total manganese, as compared with the theoretical figures 6.79 and 93.21 per cent. In addition, 0.015 per cent. inorganic residue from the carbon was present and possibly a trace, <0.02 per cent., of hydrogen. The product was nearly completely soluble in hydrochloric acid solution, some carbon residue always being obtained, the amount varying with the dissolution procedure and acid concentration, and having its source at least mainly in the decomposition of hydrocarbons formed by the reaction with the acid. The minimum amount of such carbon obtained, 0.043 per cent., could be considered the maximum free-carbon content of the preparation; but it is our opinion that no free carbon was present. It may be estimated from these results that the material was essentially 98.8 per cent. manganese carbide (Mn_3C) and 1.2 per cent. manganese, but it is not implied that the latter was present as a separate phase. Correction in the specific-heat results was made for the excess manganese. A 322.61-gram sample was employed in the measurements.

Manganese dioxide was prepared from pure electrolytic manganese and reagent-quality nitric acid. The manganese was dissolved in the concentrated acid, followed by evaporation and slow decomposition at 200° over a number of days. This process gave a product that was unusually dense and of steel-gray color. This was pulverized and heated at 500° in a stream of pure oxygen until removal of water was complete, oxygen being used to prevent decomposition of the dioxide. Previous to the last treatment the product contained appreciable water, which is in accord with the findings of Wright and Menke,[6] who reported that 0.62 per cent. water remained after heating in dry air at 210°K. for four hours. Our final product was analyzed by reduction to manganous oxide with hydrogen and by reaction with excess sodium oxalate, followed by back titration with permanganate. The results obtained corresponded to a purity of 99.88 and 100.21 per cent., respectively. The measurements were made on a 351.77-g. sample.

Specific Heats

The method and apparatus previously described[7] again were employed. The specific-heat results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. The formula masses used and recorded in Table I are in accordance with the 1941 International Atomic Weights.

The results for manganese carbide have been corrected for 1.2% excess manganese, as mentioned previously. This correction varied from -0.30 to $+0.13\%$, depending on the temperature. The manganese carbide specific-heat curve is regular and requires no discussion. There are no previous measurements for this substance at low temperatures, but Southard and Moore[8] recently have reported high temperature–heat content measurements extending to 1500°K. on the same material used in the present work. The two sets of data, because of the difference in experimental methods, do not overlap but one extrapolates into the other satisfactorily.

Manganese dioxide exhibits a marked "hump" in its specific heat curve, the maximum being at 92.12 ± 0.05°K. This made necessary a more elaborate study than if the curve had been regular. Two complete sets of data, labeled "a" and "b" in Table I, were made in the temperature range 79 to 253°K. The excellent agreement obtained shows the specific heat to be reproducible throughout the region of the maximum. The results

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(4) (a) Millar, THIS JOURNAL, **50**, 1875 (1928); (b) Anderson, *ibid.*, **53**, 476 (1931); (c) Anderson, *ibid.*, **56**, 849 (1934); (d) Kelley, *ibid.*, **61**, 203 (1939); (e) Kelley, *ibid.*, **63**, 2750 (1941); (f) Kelley and Moore, *ibid.*, in press; (g) Moore and Kelley, *ibid.*, **64**, 2949 (1943).

(5) The authors gratefully acknowledge their indebtedness to F. S. Boericke for the preparation of the manganese carbide, and to Drs. E. H. Huffman and C. H. Shomate for analyses.

(6) Wright and Menke, *J. Chem. Soc.*, **37**, 22 (1880).

(7) Kelley, THIS JOURNAL, **63**, 1137 (1941).

(8) Southard and Moore, *ibid.*, **64**, 1769 (1942).

TABLE I

SPECIFIC HEAT OF Mn_3C (MOL. WT. = 176.80)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
52.6	3.393	114.2	11.71	215.7	19.17
56.0	3.846	124.7	12.82	225.7	19.68
60.3	4.452	134.4	13.69	235.5	20.06
64.8	5.144	144.8	14.63	245.3	20.52
69.2	5.829	155.2	15.46	255.5	20.92
74.1	6.569	165.1	16.20	265.5	21.31
80.6	7.514	175.4	16.88	275.6	21.67
85.1	8.159	188.6	17.73	285.3	21.94
94.7	9.507	195.8	18.15	295.2	22.25
104.3	10.63	205.5	18.67		

SPECIFIC HEAT OF MnO_2 (MOL. WT. = 86.93)

53.5 c	1.754	99.2 b	5.196	183.9 a	8.985
57.3 c	2.042	100.4 a	5.178	184.5 b	9.013
61.1 c	2.360	102.0 b	5.185	194.4 a	9.465
65.5 c	2.781	103.3 a	5.199	195.0 b	9.499
69.8 c	3.220	105.4 b	5.243	204.6 a	9.886
73.9 c	3.701	106.7 a	5.278	205.2 b	9.916
79.8 b	4.483	111.1 a	5.437	214.7 a	10.29
80.4 a	4.595	112.5 b	5.492	215.3 b	10.32
83.3 b	5.121	120.7 a	5.865	224.8 a	10.67
84.3 a	5.367	122.2 b	5.940	225.4 b	10.71
86.7 b	6.088	132.0 a	6.432	235.9 b	11.08
87.6 a	6.494	132.9 b	6.474	241.1 a	11.27
89.4 b	7.848	142.6 a	6.972	245.7 b	11.44
90.1 a	8.819	143.4 b	7.021	252.5 a	11.66
91.4 b	11.41	152.5 a	7.480	256.4 b	11.77
92.1 a	10.92	153.4 b	7.522	266.3 b	12.09
93.5 b	7.117	163.3 a	8.014	276.1 b	12.37
94.4 a	5.935	164.1 b	8.058	285.8 b	12.61
96.2 b	5.371	173.6 a	8.501	294.7 b	12.86
97.4 a	5.266	174.3 b	8.540		

marked "c" were obtained after a very different cooling history and also indicate complete reproducibility, as will be seen more markedly when the measurements of the total heat absorbed between 85 and 100°K. are discussed. In this connection it also should be noted that the time interval necessary for reaching equilibrium in the calorimeter after energy input was normal in the region of the "hump" and not prolonged as has been observed with some substances.

The present results do not agree with the values obtained by Millar[4a] fourteen years ago, being lower by several per cent. This deviation was very distracting until we critically investigated Millar's notebooks which fortunately are still available. By far the larger part of the disagreement has to do with two corrections for the effect of the temperature of the surrounding "block" on the measured temperature rise of the calorimeter.

The first correction is for heat interchange with the "block" according to the method of Giauque and Wiebe.[9] The procedure is first to correct on the assumption of linear (with time) heating of the calorimeter, and then to take account of the temperature rise of the outside of the calorimeter above the temperature calculated for linear heating. The latter correction involves calculating the temperature of the surface of the calorimeter from the energy current and potential measured during energy input. When these readings are taken, a volt-box is in parallel with the calorimeter, and Millar did not take into account the portion of the current, amounting to about 0.25% of the whole, that passed through the volt-box leg of the circuit when computing the temperature of the surface of the calorimeter above the temperature calculated for linear heating, although he did take account of this factor in calculating energy input. As a result, in his determinations at room temperature his calculated difference between these temperatures was as low as one-fourth of the true difference, and his correction correspondingly low. The second correction is for the effect of the temperature of the "block" on the readings

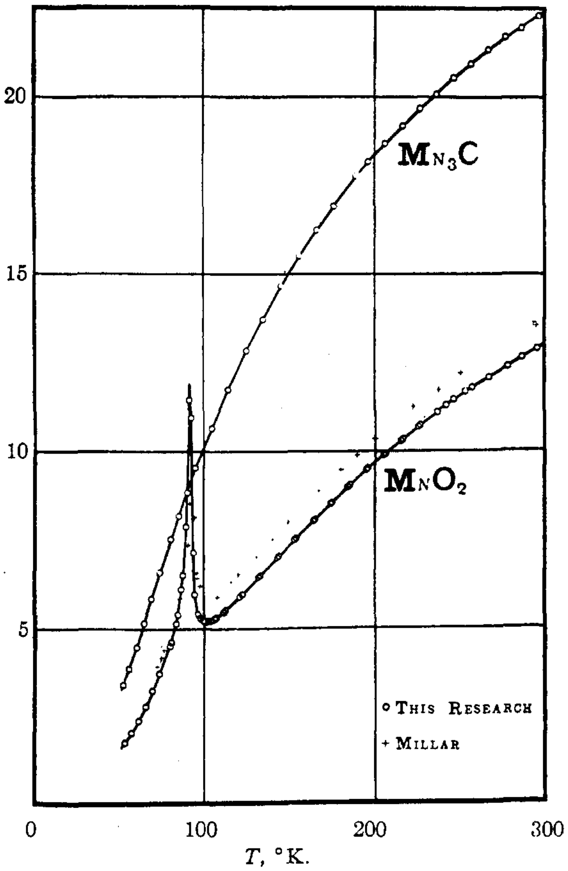

Fig. 1.—The specific heats of Mn_3C and MnO_2.

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[9] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

of the resistance thermometer at the start and end of a determination, which is of the same sign and approximate magnitude as the correction for nonlinear heating of the surface of the calorimeter. This effect presumably had not been analyzed and evaluated at the time of Millar's work and so of course he did not make correction for it.

The net effect is that his heat capacities are too high by a few per cent. at room temperature, and too high by decreasing amounts at lower temperatures. Recalculation of a few of the determinations in his notebooks gives heat capacities in substantial agreement with our own.

It should be added that, because of a defect discovered in the potentiometer used in establishing the temperature scale that Millar employed, a correction of 0.115% must be applied to his thermocouple readings in order to use the published scale for Standard Couple No. 17 of Giauque, Buffington, and Schulze.[10] No record appears in Millar's notebooks indicating that he was informed of this and such correction was not made. This is reflected in the upward temperature displacement of his lower temperature specific heats of about 0.5° which, however, is not particularly noticeable except in the region of the specific heat maximum.

The present measurements on manganese dioxide were made just prior to determinations of the specific heat of pure iron,[11] for which the results are in accord with the more recent and better of the older data. The specific heat of manganese dioxide at elevated temperatures is available to us from unpublished work of Moore. His data cover the temperature range 341 to 778°K. and extrapolate to 12.97 calories per mole at 298.16°K., while the value for this temperature read from a smooth curve through the present results is 12.91 calories per mole. Thus, the present data are checked by independent means in the region where the calorie per mole deviation from Millar's results is the greatest.

Total Heat Absorbed between 85 and 100°K.

Two separate measurements of the total heat absorption of manganese dioxide in the temperature range 85 to 100°K. were made. The value labeled "A" in Table II was obtained after cooling to 51°K. and making the specific heat measurements marked "c" in Table I. The result "B" was obtained after cooling to only 80°. The close agreement between these results indicates the extent of the before-mentioned reproducibility in the region of the specific heat maximum. Table II also contains two other results, "C" and "D." These were obtained by summing, $\sum_i C_{pi} \Delta T_i$, the specific heat values in the "a" and "b" series, respectively. As the determinations in each series in this range were made consecutively without skipping any gaps, so that the final temperature of each measurement was never more than 0.004° different from the initial temperature of the next, the corrections involved in making these summations are of a minor nature. These calculations also make possible the assigning of the correct average temperature, $T_{av.}$, for the entropy calculation to follow, as $\frac{\Delta H}{T_{av.}} = \sum_i \frac{C_{pi}\,\Delta T_i}{T_i}$. This average temperature is 91.95°K., as compared with the peak temperature, 92.12°, previously mentioned.

TABLE II

TOTAL HEAT ABSORBED BETWEEN 85 AND 100°K.

Run	$H_{100} - H_{85}$ (cal./mole)
A	102.51
B	102.53
C	102.52
D	102.41
Mean	102.5

Entropies at 298.16°K.

The entropies were calculated in the usual manner, the portion above 50.12°K. being obtained graphically from a plot of C_p *vs.* log T, and the portion below 50.12° being obtained by extrapolation. For the latter purpose it was found that the specific heat results for manganese carbide are represented within 0.5% up to 160°K. by the function sum $D(233/T) + 2E(338/T) + E(599/T)$. The manganese dioxide results cannot be so represented over any wide range of temperature because of the "hump." The lower temperature results appear just on the verge of coincidence with $D(308/T)$, and this function was used for the extrapolation. The results are in Table III.

TABLE III

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

Mn_3C		MnO_2
1.24	0–50.12°K. (extrap.)	0.60
	102.5/91.95	1.11
22.38	50.12–85.00°K. (graph.)	1.56
	85.00–298.16°K. (graph)	9.41
23.6 ± 0.3	$S_{298.16}$	12.7 ± 0.1

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[10] Giauque, Buffington, and Schulze, THIS JOURNAL, **49**, 2343 (1927). See also Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

[11] Kelley, *J. Chem. Phys.*, **11**, 16 (1943).

The value for manganese dioxide is 1.2 units lower than that given by Millar.[4a] Part of this difference is the result of his less certain extrapolation from about 72°K. (because of the effect of the specific heat "hump"), and the remainder is attributable to the previously discussed defects in his data. The manganese carbide value fortuitously is nearly identical with a previously assumed quantity, 23.7.[12]

Related Thermal Data

A redetermination of the heat of formation of manganese dioxide, nearing completion in this Laboratory, probably will enable the calculation of a more precise free energy value than is possible at present. Bichowsky and Rossini[13] adopt $-123,000$ calories per mole as the heat of formation of this substance. The entropy of the dioxide and the entropies of the elements[14] involved lead to $\Delta S_{298.16} = -43.9$. Combination of these values yields $\Delta F^0_{298.16} = -109,900$ calories per mole as the free energy of formation of manganese dioxide from the elements.

Bichowsky and Rossini give $-23,000$ calories per mole as the heat of formation of manganese carbide. The same value also has been listed by Roth.[15] From the entropies there is obtained $\Delta S_{298.16} = -0.6$. The free energy of formation from the elements, therefore, is $\Delta F^0_{298.16} = -22,800$ calories per mole. The error in this result may be taken as of the same order of magnitude as is attributed to the heat of formation, namely, ±2000 calories.

Summary

The specific heats of manganese carbide and manganese dioxide have been measured in the temperature range 51 to 298°K.

Manganese dioxide has a marked anomaly in its specific heat curve with the peak at 92.12 ± 0.05°K. The total heat absorbed between 85 and 100°K. was measured as 102.5 calories per mole.

The following entropy values were computed—$S_{298.16} = 23.6 \pm 0.3$ calories per mole per degree for manganese carbide and $S_{298.16} = 12.7 \pm 0.1$ for manganese dioxide.

The calculated free energies of formation from the elements are $\Delta F^0_{298.16} = -22,800$ calories per mole and $\Delta F^0_{298.16} = -109,900$ calories per mole, respectively, for the carbide and dioxide.

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[12] Kelley, Bureau of Mines Bulletin 407, 1935, 66 pp.

[13] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[14] Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.

[15] Roth, *Z. angew. Chem.*, **42**, 981 (1929).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Manganomanganic Oxide and Manganese Dioxide[1]

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The determination of the heats of formation of substances of metallurgical importance is one of the fields of study of the Pacific Experiment Station of the Bureau of Mines. In a previous paper[3] measurements of the heats of formation of manganous oxide and manganous sulfate were reported. The present paper presents similar data for manganomanganic oxide and manganese dioxide.

Previous values of the heats of formation of manganomanganic oxide and manganese dioxide depend almost entirely upon combustion experiments.[4] Combustion of manganese metal or of its oxides always produces a mixture of oxides and large errors in the heats of formation so obtained may result from rather minor errors in the analysis of the resulting mixture. In addition, most of the combustion reactions require a promotor such as charcoal or paraffin oil and in some instances the heat evolved in burning the promoter has been several times the magnitude of the heat of reaction under investigation. It is not surprising, therefore, that values in the literature for the heat of formation of manganomanganic oxide vary from $-318,000$ to $-345,000$ cal. per mole and for manganese dioxide from $-119,600$ to $-126,000$ cal. per mole. In view of these wide variations it appeared desirable to redetermine these quantities

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[3] Southard and Shomate, THIS JOURNAL, **64**, 1770 (1942).

[4] (a) Le Chatelier, *Compt. rend.*, **122**, 80 (1896); (b) Mixter, *Am. J. Sci.*, [4] **30**, 193 (1910); (c) Ruff and Gersten, *Ber.*, **46**, 394 (1913); (d) Roth and Müller, *Z. angew. Chem.*, **42**, 981 (1929); (e) Simon and Fehér, *Z. Elektrochem.*, **38**, 137 (1932); (f) Siemonsen, *ibid.*, **45**, 637 (1939).