The data in Table II were obtained after the procedure was altered to provide for the seeding of the melt and a slow, orderly solidification of the crucible contents. The details of the necessary modifications are contained in the earlier description (*1*) of experiments with the element tellurium, where a similar problem was encountered.

The data obtained clearly indicate that the melting points of Sb_2Te_3 and PbTe must initially increase as the pressure rises above one atmosphere. In contrast, above 15,000 atmospheres the melting points of both these compounds were observed (*2*) to decrease with increasing pressure. Thus, in each case, a maximum melting point must be encountered at some intermediate pressure. A direct measurement of these values was not possible since the high pressure equipment used (a tetrahedral anvil apparatus) does not provide sustained, reliable pressure below about 15,000 atmospheres.

LITERATURE CITED

(1) Ball, D.L., J. Chem. Eng. Data 8, 61 (1963).
(2) Ball, D.L., "Liquids - Structure, Properties, and Solid Interaction," Proceedings of General Motors Research Laboratories Symposium, Sept. 5–6, 1963, Warren, Mich., Elsevier, in press.
(3) Fritts, R.W., "Thermoelectric Materials and Devices," p. 146, Reinhold, New York, 1960.
(4) Testardi, L.R., Wiese, J.R., *Trans. AIME* **221**, 647 (1961).
(5) West, T.D., "West's Molders' Text-Book," pp. 4–7, Wiley, New York, 1885.

RECEIVED for review June 8, 1964. Accepted September 8, 1964.

Heat Capacity of β-Manganese

R. A. BUTERA and R. S. CRAIG
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

The molar heat capacity of β-Mn has been measured from 14° to 300° K. in an adiabatic calorimeter. Both measured and smooth values of the data are presented.

THE ELEMENT MANGANESE has in recent years been a subject of considerable interest. In 1958, Weiss and Tauer published a paper (*6*) on the thermodynamics and magnetic structure of the allotropic modifications of this element. Additional thermal data on some of the allotropic forms were needed. More recently Arrott, Zimmerman, and coworkers have been engaged in a comprehensive study of the thermodynamics of α-, β-, and γ-manganese (*2*). As a contribution to this effort, the authors have undertaken to measure the specific heat of β-Mn between 14° and 300° K.

Previous thermal measurements on β-Mn have been made at low temperatures by Booth, Hoare, and Murphy (*3*) (12° to 20° K.) and Zimmerman (*2*) (1.6° to 19° K.). Heat capacity measurements were also made in the high temperature region (1000° to 1050° K.) by Armstrong and Grayson-Smith (*1*).

EXPERIMENTAL

The adiabatic calorimeter used in the investigation has been described (*4*). The sample container employed is one which had been used in heat capacity measurements on Cd and Mg. It consisted of a thin-walled copper can into which the sample could be sealed with a few cm. of He gas to promote heat exchange. It was designed to receive a sample machined to cylindrical form with a tapered hole along the axis. The tapered hole was intended to fit over a tapered pin, an integral part of the sample container, which contained the heater and Pt resistance thermometer so that good thermal contact could be established. The β-Mn sample, however, was in the form of small chunks and not readily adaptable to the customary method of loading. The β-Mn (262.401 grams) was simply sealed into the sample container, and reliance was placed upon the He exchange gas to maintain thermal equilibrium. The atomic weight of manganese was taken as 54.94 grams per mole.

The starting material was electrolytic α-Mn which was arc melted under argon and quenched to convert it to the β-allotrope. The principle impurities, shown by spectrographic analysis, and their approximate concentrations in per cent were Fe(0.2), Ni(0.04), Pb(0.05), and Si(0.05). X-ray diffraction patterns, obtained both before and after the heat capacity measurements, showed no α-Mn lines. The x-ray patterns did show evidence for the presence of MnO, however, and it was estimated that this substance might be present in the sample to the extent of about 2 mole % (*7*).

RESULTS AND DISCUSSION

The raw data are shown in Table I. As an index of the precision, the averages of the absolute values of the percentage deviations of the measured points from the smooth curve have been computed. Between 13° and 40° K. the average deviation is about 2.5%, between 40° and 100° K. the average deviation is about 0.3%, between 100° and 273° K. it is less than 0.1%, while between 273° and 300° K. the average deviation is about 0.2%. The precision obtained in these measurements is not as good as has been obtained in measurements on other metals in the calorimeter. The fact that the sample was in the form of pellets rather than a single solid piece may account for the difference in behavior.

A large scale plot of the raw data shows a slight deviation in the curve of C_p *vs.* T at about 125° K. The magnitude of the deviation is such that a smooth curve interpolated

Table I. Heat Capacity of β-Manganese, Measured Values[a]

T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$
72.33	2.514	191.39	5.564	277.33	6.305
77.14	2.745	197.39	5.634	283.67	6.323
81.60	2.950	203.44	5.691	289.99	6.342
85.79	3.139	209.45	5.762	296.26	6.406
89.76	3.300	215.41	5.819		
		221.32	5.868	284.64	6.335
		227.18	5.926	290.94	6.351
94.05	3.464	233.03	5.977	297.21	6.384
98.73	3.634	238.88	6.016	303.44	6.435
103.36	3.798	244.67	6.066		
108.04	3.950	250.43	6.117	13.76	0.178
112.63	4.090	256.16	6.141	15.59	0.212
117.36	4.242	261.84	6.190	18.62	0.270
122.22	4.393	267.65	6.226	22.65	0.356
126.95	4.524	273.65	6.254	26.49	0.406
131.73	4.590	279.76	6.296	30.23	0.605
				34.45	0.722
		276.41	6.269	38.63	0.855
		282.72	6.342	42.69	1.068
		289.02	6.362	43.55	1.119
133.47	4.643	295.31	6.397		
138.27	4.737	301.56	6.418	42.80	1.070
143.22	4.831	307.78	6.465	48.98	1.350
148.29	4.931	313.98	6.503	54.42	1.652
153.46	5.020			59.02	1.868
158.96	5.106			63.44	2.094
164.57	5.203	108.04	3.952	67.77	2.303
170.19	5.288	110.21	4.025	71.73	2.489
175.79	5.365	112.55	4.102		
181.46	5.441	115.06	4.183	17.85	0.254
187.42	5.515	117.81	4.262	23.34	0.376
193.54	5.584	120.79	4.353	28.94	0.536
199.82	5.657	123.77	4.450	33.00	0.672
118.97	4.295	126.76	4.517	36.96	0.821
123.83	4.440	129.77	4.572	40.93	0.990

[a] Values are presented in the chronological order in which measurements were made. A gap in the table indicates that one or more days elapsed between different series of measurements.

between about 115° and 135° K. passes about 0.7% below the measured points in the neighborhood of 125° K. As MnO has a magnetic transition which is known to lead to a very sharp maximum in the heat capacity at 117° K. (*5*), the deviation in the present data may be explained by the presence of a small amount of MnO impurity, whose transition is smeared out and displaced to higher temperatures. The smoothing process, which was used to obtain the data in Table II, was not carried out in such a way as to eliminate the anomaly. This appears on the smooth curve as a more rapidly changing slope in the neighborhood of 125° K.

Table II. Heat Capacity of β-Manganese, Smoothed Values

T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} Deg.$^{-1}$
14	0.188	95	3.498	200	5.658
16	0.222	100	3.677	205	5.712
18	0.258	105	3.848	210	5.764
20	0.297	110	4.012	215	5.812
22	0.341	115	4.172	220	5.860
24	0.391	120	4.326	225	5.904
26	0.444	125	4.476	230	5.947
28	0.503	130	4.578	235	5.989
30	0.565	135	4.672	240	6.028
35	0.741	140	4.768	245	6.066
40	0.942	145	4.862	250	6.104
45	1.165	150	4.954	255	6.139
50	1.406	155	5.042	260	6.176
55	1.663	160	5.126	265	6.208
60	1.918	165	5.206	270	6.240
65	2.167	170	5.283	275	6.272
70	2.407	175	5.352	280	6.304
75	2.643	180	5.420	285	6.333
80	2.877	185	5.483	290	6.360
85	3.102	190	5.544	295	6.387
90	3.296	195	5.602	300	6.401

ACKNOWLEDGMENT

The sample used in this investigation was furnished by R.J. Weiss and was prepared under his direction in the laboratories of the Watertown Arsenal. X-ray measurements were carried out by C.P. Gazzara of the Watertown Arsenal. The assistance of the U. S. Atomic Energy Commission in this work is acknowledged.

LITERATURE CITED

(1) Armstrong, L.D., Grayson-Smith, H., *Can. J. Res.* **A28**, 51 (1949).
(2) Arrott, A., Zimmerman, J.E., Scientific Laboratory, Ford Motor Co., Dearborn, Mich., private communication, 1963.
(3) Booth, G.L., Hoare, F.E., Murphy, B.T., *Proc. Phys. Soc.* **B68**, 830 (1955).
(4) Craig, R.S., Krier, C.A., Coffer, L.W., Bates, E.A., Wallace, W.E., *J. Am. Chem. Soc.* **76**, 238 (1954).
(5) Todd, S.S., Bonnickson, K.R., *Ibid.*, **73**, 3894 (1951).
(6) Weiss, R.J., Tauer, K.J., *J. Phys. Chem. Solids* **4**, 135 (1958).
(7) Weiss, R.J., Watertown Arsenal, Watertown, Mass., private communication, 1964.

RECEIVED for review May 12, 1964. Accepted December 1, 1964.