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Heat Capacity and Thermodynamic Functions of $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$

J. E. MOORE* AND R. A. BUTERA

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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The heat capacities of $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$ have been experimentally determined from 10 to 300 K. The smoothed heat capacity and the thermodynamic functions $(H_T^\circ - H_0^\circ)$ and S_T° are reported for the two compounds over the temperature range 10 to 300 K. The error in these data is thought to be less than 1%. A subtle heat capacity anomaly was observed in $MnCl_2 \cdot 4H_2O$ over the temperature range 52 to 90 K. The entropy associated with the anomaly is of the order 0.4 J/mole K.

Introduction

The interest in $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$ has been principally due to the antiferromagnetic ordering which occurs in these compounds at low temperatures. The Néel temperatures are 2.12 and 1.62 K, respectively, and therefore, most of the thermodynamic data reported for these compounds have been limited to temperatures below 20 K.

These two compounds are the first in a series of manganese halide hydrates and their corresponding deuterates that we have investigated. These results are the first in an ongoing study of the hydrogen bonding in these materials. We have experimentally determined the heat capacity of these compounds from 10 to 300 K. Most members in this family of compounds show a heat capacity anomaly in the temperature range 40 to 100 K. We were unable to detect such an anomaly in $MnBr_2 \cdot 4H_2O$, and the anomaly in $MnCl_2 \cdot 4H_2O$ is very subtle.

These anomalies as a general feature of the manganese halide hydrates and deuterates will be presented and discussed in a forthcoming paper.[1] Presently it is our purpose to report the smoothed heat capacity and the thermodynamic functions $(H_T - H_0)$ and S_T over the temperature range 10 to 300 K for $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$.

Sample Preparation

Manganese bromide and manganese chloride solutions were prepared by reacting manganese metal[2] with aqueous hydro-

* Chemistry Building #62, University of Pittsburgh, Pittsburgh, PA 15260.

[1] In preparation for publication.

[2] Puratronic grade 1 manganese flake, from Johnson Matthey Chemicals Ltd., Orachard Rd. Royston, Herts, SG85HE, England; distributed by Alpha Products, Danvers, Mass. 01923.

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bromic and hydrochloric acids,[3] respectively. The tetrahydrates were formed by controlled evaporation of the solutions at room temperature.

The calorimeter samples were approximately 50 g of 2- to 3-mm crystals, which were isopiestically equilibrated with their respective saturate solutions. Both the $MnBr_2 \cdot 4H_2O$ and the $MnCl_2 \cdot 4H_2O$ samples displayed crystal morphology characteristic of the stable α-phase (*1, 2*).

Apparatus

The adiabatic calorimeter used in this study has been described elsewhere (*3*), however, a few comments are in order.

The calorimeter normally operates with a temperature step size (hereafter referred to as ΔT) of 1 to 5 K, however, we have successfully operated the calorimeter with a ΔT as small as 0.2 K. The small ΔT is necessary to resolve the shape of heat capacity features which are narrow in temperature. The scatter in the heat capacity data obtained with the small ΔT is, however, greater by about a factor of 2. The precision with which the temperature difference can be measured and the relative contribution of the heat leaks appear to be primarily responsible for the enhanced scatter.

The specific heat of the eimer was determined by measuring the heat capacity of NBS copper with a nominal ΔT of $T/10$ to 50 and 5 K above 50 K. With the smoothed eimer blank removed, the copper heat capacity data contained scatter of less than 1% for temperatures above 15 K, and increased to about 2% at 10 K. This increase in scatter can be attributed to the decreased sensitivity of the platinum resistance thermometer below 15 K. Based on these results, we expect the data obtained from this calorimeter to be accurate to better than 1%.

[3] ACS Reagent grade, from Fisher Scientific Co., Fairlawn, N.J. 07410.

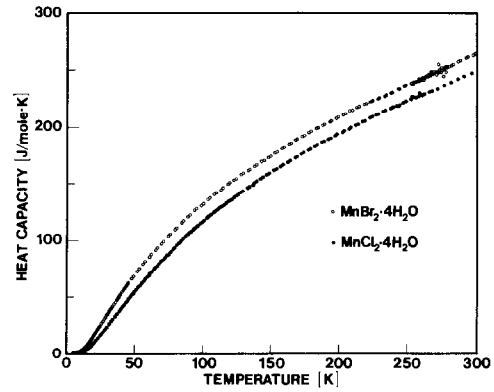

FIG. 1. Experimental heat capacity data for $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$.

Results and Discussion

The heat capacity data are shown in Fig. 1[4] for the two compounds. The smoothed heat capacity and the thermodynamic functions $(H_T^\circ - H_0^\circ)$ and S_T° are given in Tables I and II for $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$, respectively.

Our method of smoothing the experimental data involves the use of a draftman's spline and 3-foot wide roles of K&E millimeter graph paper. The data are plotted in such a manner that the resolution of the graph paper is much greater than the experimental scatter. The final smooth curve is a sequence of overlapping splined sections. From the smooth curve, smooth heat capacity data are obtained at intervals sufficiently close such that quadratic interpolation between neighboring points yields insignificant error. The smoothness of the

[4] **See NAPS document No. 04272 for 25 pages of** supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE I

SMOOTH THERMODYNAMIC FUNCTIONS FOR $MnBr_2 \cdot 4H_2O$

T (K)	Cp (J/mole K)	$H_T^\circ - H_0^\circ$ (J/mole)	S_T° (J/mole K)
10.00	2.35	31.48	15.62
15.00	7.42	54.04	17.39
20.00	15.60	110.70	20.59
25.00	24.83	211.51	25.05
30.00	34.21	359.19	30.41
35.00	43.35	553.19	36.38
40.00	52.07	791.86	42.74
45.00	60.57	1073.75	49.37
50.00	68.79	1397.55	56.18
55.00	76.29	1760.50	63.10
60.00	83.45	2160.00	70.04
65.00	90.19	2594.22	76.99
70.00	96.71	3061.55	83.92
75.00	103.12	3561.04	90.81
80.00	109.40	4092.14	97.66
85.00	115.35	4653.89	104.47
90.00	121.00	5245.05	111.22
95.00	126.33	5863.49	117.91
100.00	131.20	6507.40	124.51
110.00	140.82	7868.10	137.48
120.00	149.89	9322.01	150.12
130.00	158.35	10863.55	162.46
140.00	166.29	12487.04	174.48
150.00	174.01	14188.80	186.22
160.00	181.46	15966.33	197.69
170.00	188.64	17817.24	208.91
180.00	195.48	19737.86	219.89
190.00	202.06	21725.75	230.63
200.00	208.44	23778.61	241.16
210.00	214.23	25892.32	251.47
220.00	219.74	28062.35	261.57
230.00	225.13	30286.71	271.45
240.00	230.50	32564.84	281.15
250.00	235.95	34897.09	290.67
260.00	241.29	37283.31	300.03
270.00	246.71	39723.22	309.23
273.15	248.37	40502.95	312.10
280.00	252.02	42216.86	318.30
290.00	257.49	44764.64	327.24
298.15	261.94	46881.34	334.44
300.00	262.96	47366.87	336.06

splined curve, particularly in the regions of overlap, is checked by numerically evaluating the derivative of the smooth heat capacity data.

Figures 2 and 3 show the percentage de-

TABLE II

SMOOTH THERMODYNAMIC FUNCTIONS FOR $MnCl_2 \cdot 4H_2O$

T (K)	Cp (J/mole K)	$H_T^\circ - H_0^\circ$ (J/mole)	S_T° (J/mole K)
10.00	1.37	22.69	15.93
15.00	4.73	37.00	17.05
20.00	9.96	73.05	19.09
25.00	16.63	139.16	22.01
30.00	23.88	240.22	25.67
35.00	31.57	378.80	29.93
40.00	39.35	556.14	34.65
45.00	46.99	772.01	39.73
47.50	50.57	893.98	42.37
50.00	54.08	1024.88	45.05
52.50	57.55	1164.39	47.78
55.00	61.19	1312.76	50.54
57.50	64.99	1470.49	53.34
60.00	68.65	1637.58	56.18
62.50	72.11	1813.55	59.06
65.00	75.55	1998.14	61.95
67.50	78.86	2191.16	64.87
70.00	82.12	2392.43	67.79
75.00	88.27	2818.50	73.67
80.00	94.18	3274.72	79.56
85.00	99.89	3759.98	85.44
90.00	105.38	4273.23	91.30
95.00	110.66	4813.39	97.14
100.00	115.75	5379.46	102.95
110.00	125.50	6585.82	114.44
120.00	134.65	7887.25	125.76
130.00	143.26	9277.21	136.88
140.00	151.55	10751.78	147.80
150.00	159.14	12305.18	158.52
160.00	166.67	13934.40	169.03
170.00	173.79	15637.05	179.35
180.00	180.51	17408.76	189.47
190.00	187.14	19247.06	199.41
200.00	193.41	21149.92	209.17
210.00	199.38	23113.96	218.75
220.00	205.15	25136.98	228.16
230.00	210.95	27217.69	237.41
240.00	216.34	29354.30	246.50
250.00	221.63	31544.21	255.44
260.00	226.86	33786.55	264.24
270.00	232.14	36081.53	272.90
273.15	233.78	36815.37	275.60
280.00	237.30	38428.81	281.43
290.00	242.45	40827.50	289.85
298.15	246.69	42820.68	296.63
300.00	247.66	43277.95	298.16

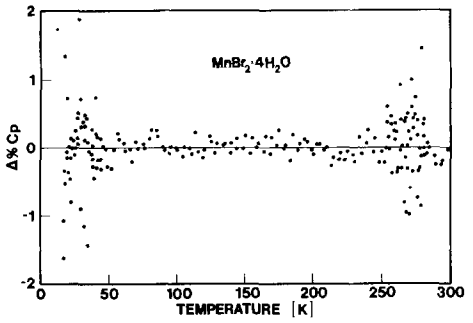

FIG. 2. Percentage deviation between smoothed and experimental heat capacity data for $MnBr_2 \cdot 4H_2O$.

viation between the experimental data and the smoothed curves for the two compounds. For these plots, the percentage deviation is given by

$$\Delta\%Cp = \frac{\text{Smooth } Cp - \text{Experimental } Cp}{\text{Smooth } Cp} \cdot 100\%.$$

The larger scatter at low temperatures, as previously mentioned, can be attributed to the platinum resistance thermometer. The other regions of enhanced scatterd are due to the use of a small ΔT in the heat capacity measurement.

The reported thermodynamic functions were obtained numerically from the smooth heat capacity data. The heat capacity data density used in these evaluations was much higher than reported here. The error introduced due to the numerical techniques of evaluation is insignificant.

In order to reference the enthalpy and entropy to absolute zero, previously reported heat capacity data were used (*4–12*). These data span the liquid-helium and liquid-hydrogen temperature ranges, and the present work extends the data to 300 K. Where overlap exists between the present work and the previously reported heat capacity data, good agreement is found for the $MnCl_2 \cdot 4H_2O$ (*6*). In the case of $MnBr_2 \cdot 4H_2O$, our measured heat capacity agrees well with the work of Schelleng and Friedberg (*8*), but is low with respect to the results reported by Kapadnis and Hartmans (*4*). We believe this discrepancy can be attributed to a small miscalibration of the phosphor bronze resistance thermometer used by Kapadnis and Hartmans over the temperature range 11 to 20 K (*13*). Our thermometry is based on a platinum resistance thermometer, the calibration of which is traceable to NBS.

From the lowest temperatures reported (*7*), our smooth heat capacity curve was splined to zero with zero slope at absolute zero. In doing this extrapolation from 0.3 to 0.0 K, we have ignored the small heat capacity contribution from the hyperfine splitting since the experimental data reported by Miedema *et al.* (*7*) are insufficient to accurately determine the Schottky anomaly. We expect this omission to produce a negligible error in the tabulated thermodynamic functions.

The previously reported data were smoothed in the same manner as our own experimental data. Based on the quantity and quality of the data below 10 K, the error in the thermodynamic functions at 10 K should be within 1%.

The heat capacity anomaly in $MnCl_2 \cdot 4H_2O$ is shown in Fig. 4. The solid line corresponds to the smoothed heat capacity and the dashed line is our estimated blank heat capacity. These lines and the experimental

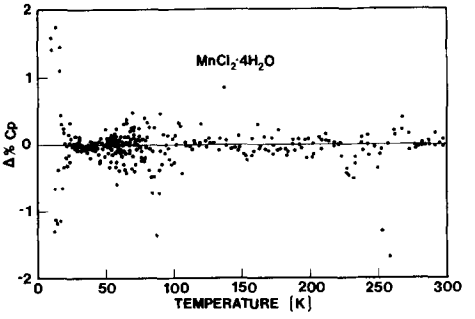

FIG. 3. Percentage deviation between smoothed and experimental heat capacity data for $MnCl_2 \cdot 4H_2O$.

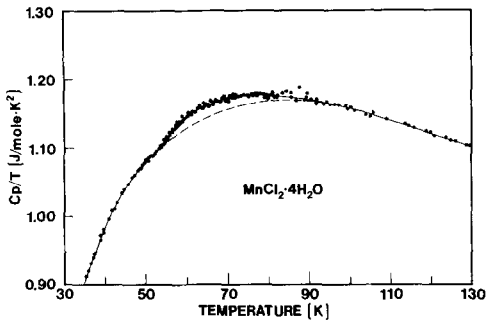

FIG. 4. Heat capacity anomaly in $MnCl_2 \cdot 4H_2O$.

data are plotted as Cp/T versus T to improve the visibility of the feature.

Our estimated blank heat capacity is based on a sequence of 6th-order polynomial least-squares fits to the smoothed data adjacent to the anomaly region. Since the temperature at which the anomaly ends is by no means clear from the data, a sequence of blank curves was generated by changing the end temperature from a minimum of 85 K to a maximum of 125 K. Based on this sequence of blanks, we estimate the entropy of the anomaly to be of the order 0.4 J/mole K.

Although the entropy involved is very small, the precision of the raw data as depicted in Fig. 4 allows one to clearly discern an inflection point in the Cp/T versus T curve around 55 K. Such an inflection point cannot be accounted for on the basis of a simple Debye-like lattice heat capacity, and is indicative of a transformation.

Recent experimental work in this laboratory on $MnCl_2 \cdot 4D_2O$ further supports the existence of a transition around 50 K.[1] In what could be viewed as an unusual isotope effect, the deuterated analog displays a more prominent λ-shaped anomaly at 48 K with an entropy of approximately 1.2 J/mole K.

We are fairly certain these processes involve the rearrangement or ordering of some of the hydrogen bonds. It has been established that at room temperature $MnCl_2 \cdot 4H_2O$ possesses some weak bifurcated hydrogen bonds (*14*). Low-temperature ordering of some or all of these bonds could account for the observed anomaly. We are currently working to develop a more quantitative picture of the possible processes in this and similar compounds.

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