Magnetism and the Third Law of Thermodynamics. The Heat Capacity of Manganous Fluoride from 13 to 320°K.

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The multiple electronic states present in paramagnetic compounds cause at sufficiently low temperatures a contribution to the heat capacity due to the changing population of the magnetic ions among the various states. Calorimetric investigation yields information about the number and separation in energy of the electronic states in the solid. For example, from low temperature heat capacity measurements on $NiSO_4 \cdot 7H_2O^1$ it has been possible to infer the magnetic energy spectrum in the solid. At high temperatures the random distribution of the magnetic ions among the various states gives rise to a magnetic contribution to the entropy. In order to apply the third law of thermodynamics to the calculation of entropies from low temperature heat capacity measurements, it is necessary to correct for any magnetic entropy remaining at the lowest temperature of measurement. The investigation of the thermal behavior of typical paramagnetic salts contributes to our knowledge of and ability to allow for such magnetic entropy.

The measurements of Bizette and Belling[2] and of de Haas, Schultz and Koolhaas[3] show that the magnetic susceptibility of anhydrous manganous fluoride exhibits a sharp maximum at 72°K. At the temperatures of liquid hydrogen the susceptibility varies with the field strength and there is a small remanent magnetization when the field is removed. We have measured the low temperature heat capacity of manganous fluoride in order to investigate the calorimetric phenomena associated with the behavior of the susceptibility curve as well as to obtain, through the application of the third law of thermodynamics, the entropy at 298°K. for use in thermodynamic calculations.

Apparatus.—The calorimeter consisted of a cylindrical copper can 5.1 cm. in diameter and 10.2 cm. long. An open copper tube, 1.27 cm. i. d., extended axially along the center of the calorimeter. The resistance thermometer made a snug fit inside this tube. A chamber of volume 11 cc. in the top of the calorimeter was connected to a reflux tube in thermal contact with the shield and the liquid hydrogen and nitrogen reservoirs. The portion of the reflux tube between the calorimeter and the surrounding shield consisted of a nickel–silver tube, 6.5 cm. long, 0.32 cm. o. d. and 0.010 cm. in wall thickness. The reflux tube and chamber were used to cool the calorimeter before the start of measurements. The volume of the sample chamber in the calorimeter was 169.5 cc. The sample was introduced through a nickel–silver tube, 0.63 cm. i. d., opening into the bottom of the sample chamber. After the introduction of the sample a copper cap with a small pinhole was soldered on the filling tube. The air was removed from the sample chamber and helium gas at one atmosphere pressure introduced through the pinhole which was then closed with solder. The outside of the calorimeter was gold plated in order to reduce the radiation loss and to prevent tarnishing. The weight of the empty calorimeter was 126.8 g. and of the resistance thermometer 46.6 g.

The calorimeter was mounted in the cryostat which has been described by Blue and Hicks.[4] The inside of the shield surrounding the calorimeter was covered with aluminum foil to decrease the heat radiated to the calorimeter and the lead wires were heat stationed at the top of the shield. A copper–constantan difference thermocouple read the temperature difference between the shield and the calorimeter and another couple measured the difference between the top and bottom of the shield. The current in the shield heaters was manually controlled so as to keep the shield always at the same temperature as the calorimeter. The readings of the difference couples were recorded and corrections have been applied when necessary for the small heat interchange between the shield and calorimeter when the conditions were not completely adiabatic. The maximum correction for non-adiabaticity between 25 and 310°K. was 0.2% of the measured heat capacity. Below 25°K. the shield was not kept at exactly the same temperature as the calorimeter and the corrections for heat interchange were made as in the Nernst-type apparatus. Above 200°K., where radiation is important, the adiabatic apparatus permits a more accurate determination of heat capacities than does the Nernst-type apparatus since the heat interchange can be made very small and corrected for accurately. Furthermore, the temperature difference between the outside radiating surface of the calorimeter and the surrounding shield is measured directly and no assumptions as to the temperature distribution throughout the calorimeter during energy input are necessary. This is particularly important when the thermometer-heater is on the inside of the calorimeter, as in the present case.

Energy was introduced and the temperatures measured by means of the platinum–rhodium resistance thermometer of laboratory designation R222. The calibration of the thermometer has been described by Blue and Hicks.[4] During the present measurements the thermometer was

(1) Stout and Giauque, THIS JOURNAL, **63**, 714 (1941).
(2) Bizette and Belling, *Compt. rend.*, **209**, 205 (1939).
(3) de Haas, Schultz and Koolhaas, *Physica*, **7**, 57 (1940).
(4) Blue and Hicks, THIS JOURNAL, **59**, 1962 (1937).

checked at the ice point and at the triple point of hydrogen and found to agree with the original calibration to within 0.01°. The leads to the resistance thermometer (No. 30 B. and S. gage D. S. C. copper) were wrapped once around the calorimeter. Each of the four lead wires was connected to a corresponding lead from the heat station on the shield by one inch of No. 40 B. and S. gage copper wire so as to minimize the heat conduction. Electrical measurements were made with a Leeds and Northrup Wenner potentiometer.

The method of measurement and the corrections applied to the heat capacities, other than those discussed above, followed the standard practice[5] in low temperature calorimetry. The ice point was taken as 273.16°K. The temperatures calculated from the resistance thermometer calibration of Blue and Hicks[4] were corrected for the change in the choice of the ice point. The defined calorie, 4.1833 international joules, was used throughout.

Material.—The manganous fluoride used for the heat capacity measurements was prepared by the method described by Kurtenacker, Finger and Hey.[6] Manganous carbonate was precipitated from a solution of analytical reagent manganous sulfate by means of a solution of sodium carbonate containing sufficient sodium bicarbonate to prevent the formation of basic carbonates. Only about 90% of the available manganese was precipitated as the carbonate in order to avoid precipitating any magnesium which was a probable impurity in the original manganous sulfate. The manganous carbonate, after being washed free of soluble impurities, was added to a 50% solution of hydrofluoric acid contained in a platinum dish. A fine precipitate of pink manganous fluoride was obtained. In order to remove all the volatile impurities from the precipitated manganous fluoride it was necessary to heat the sample at 250° for five hours. During the heating the manganous fluoride was kept in an atmosphere of carbon dioxide in order to prevent reaction with the oxygen of the air. When the resulting material was examined under a microscope individual crystals could not be distinguished but from the extinction of polarized light it was estimated that the crystals were between 10^{-5} and 10^{-6} cm. in size. A sample of the manganous fluoride was analysed for manganese by Professor G. G. Marvin of this Laboratory. He obtained 58.9% Mn; calcd. for MnF_2 59.11%. Two of the heat capacity points just below the ice-point are about 0.3% high. If this is due to the fusion of ice it would correspond to 0.01% by weight of water in the sample. The presence of this amount of water would produce a negligible effect upon the observed heat capacities so no correction has been made for it.

The Heat Capacity of Manganous Fluoride.—The calorimeter contained 1.7604 moles (163.593 g. in vacuo) of manganous fluoride. The heat capacity measurements are presented in Table I and represented graphically in Fig. 1. In Table I Series I and II are exploratory runs. The measurements of Series III extend from 13°K. to above the maximum in the heat capacity curve. In the neighborhood of the maximum the temperature increments were made small in order to determine the shape of the curve.

(5) (a) Giauque and Wiebe, This Journal, 50, 101 (1928) Giauque and Johnston, ibid., 51, 2300 (1929); (c) Hicks, ibid., 60,: 1000 (1938).

(6) Kurtenacker, Finger and Hey, Z. anorg. Chem., 211, 83 (1933).

Series IV consists of measurements with small temperature increments extending through the region of the maximum. Immediately before the start of Series IV the calorimeter was cooled from above 80°K. to 65.86°K. The good agreement with the points of Series III shows that there was no supercooling of the heat effect associated with the maximum in the curve. At no time during the measurements was there evidence of thermal hysteresis or slowness in the attainment of equilibrium. Series V and VI extend the measurements to room temperatures. The point in Series VII was measured after the completion of

TABLE I

THE HEAT CAPACITY OF MANGANOUS FLUORIDE
0°C. = 273.16°K. Molecular weight 92.93

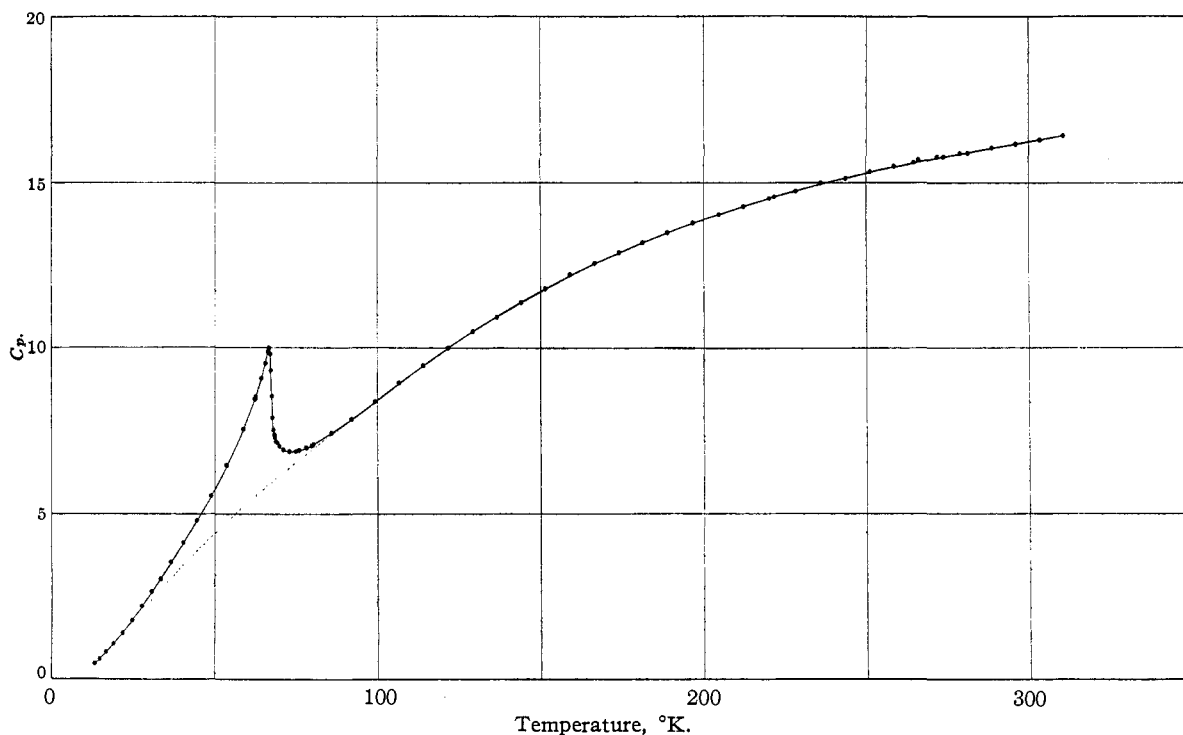| T, °K.	Approx. ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	Approx. ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}
Series I			67.25	0.48	8.532
264.62	7.12	15.61	67.74	.52	7.520
271.67	6.98	15.78	68.27	.52	7.309
278.61	6.88	15.87	68.79	.53	7.164
Series II			Series V		
61.94	2.99	8.419	80.12	5.05	7.091
65.53	4.17	9.333	85.60	5.90	7.426
70.04	4.84	7.053	91.85	6.61	7.865
74.81	4.70	6.902	98.98	7.44	8.388
79.40	4.47	7.057	106.35	7.29	8.939
Series III			113.78	7.57	9.474
13.18	0.53	0.458	121.47	7.80	10.01
14.68	1.39	.622	129.06	7.38	10.50
16.60	1.59	.802	136.29	7.23	10.94
18.82	2.40	1.050	143.72	7.66	11.37
21.56	2.93	1.384	151.23	7.33	11.79
24.49	3.15	1.762	158.77	7.73	12.20
27.49	2.84	2.182	166.35	7.45	12.56
30.36	2.90	2.605	173.67	7.20	12.89
33.16	2.91	3.024	181.11	7.77	13.19
36.44	3.63	3.514	188.77	7.54	13.48
40.32	4.14	4.121	196.56	8.04	13.78
44.33	3.90	4.780	204.57	7.82	14.03
48.68	4.67	5.551	212.28	7.62	14.29
53.47	4.91	6.460	220.14	8.10	14.53
58.51	5.19	7.536	Series VI		
62.29	2.36	8.520	221.52	5.31	14.59
64.08	1.26	9.076	228.09	7.85	14.75
65.23	1.05	9.550	235.84	7.65	14.99
66.05	0.58	9.892	243.44	7.54	15.14
66.55	.43	9.987	250.96	7.37	15.35
66.99	.45	9.332	258.26	7.22	15.55
67.47	.50	7.903	265.77	7.80	15.71
67.98	.52	7.385	273.38	7.67	15.80
68.59	.71	7.194	280.98	7.54	15.93
69.48	1.06	7.036	288.46	7.41	16.07
70.72	1.42	6.926	295.60	7.28	16.20
72.67	2.48	6.875	303.11	7.17	16.32
75.77	3.73	6.925	310.22	7.05	16.45
Series IV			Series VII		
66.11	0.49	9.932	78.02	3.52	6.999
66.50	.29	9.996			
66.83	.36	9.802			

Fig. 1.—Heat capacity in calories per degree per mole of manganous fluoride.

Integral Heat No. 2 mentioned below. During each series of measurements the calorimeter was under continuous observation.

Values of the heat capacity read from a smooth curve through the observations are given in Table II. These values are believed accurate to 0.2% above 35°K., to 1% at 20°K. and to 5% at 15°K.

TABLE II

THE HEAT CAPACITY OF MANGANOUS FLUORIDE. VALUES FROM A SMOOTH CURVE THROUGH THE OBSERVATIONS

0°C. = 273.16°K.   Molecular weight, 92.93

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.638	140	11.16
20	1.189	150	11.73
25	1.830	160	12.25
30	2.551	170	12.73
35	3.297	180	13.14
40	4.067	190	13.52
45	4.895	200	13.88
50	5.791	210	14.22
55	6.769	220	14.53
60	7.896	230	14.82
66.5	10.0 (max.)	240	15.08
70	6.978	250	15.32
75	6.900	260	15.54
80	7.086	270	15.73
90	7.733	280	15.91
100	8.471	290	16.10
110	9.207	300	16.27
120	9.908	310	16.44
130	10.56	320	16.60

The heat capacity measurements listed in Table I are values of $\Delta H/\Delta T$ and when ΔT and the curvature of the heat capacity–temperature curve are large, as is the case with some of the measurements in Series II, may differ appreciably from the differential heat capacity. The values in Table II represent the true differential heat capacity.

The heat capacity curve of manganous fluoride rises smoothly to a maximum of about 10.0 cal. deg.$^{-1}$ mole^{-1} at 66.5°K. and then falls rapidly, but not discontinuously, on the high temperature side of the maximum. The measurements indicate that the maximum is rounded at the top, that is, there is no discontinuity in the slope of the heat capacity curve. Measurements of the rate of warming under a small temperature head qualitatively confirmed the shape of the curve given by the short heat capacity measurements. The maximum in the magnetic susceptibility curve[2,3] is at 72°K.

Two measurements were made of the total energy necessary to heat the sample from 61.00 to 76.50°K. In Table III these values are compared with those obtained from the heat capacity measurements. Corrections have been applied in order to convert the different measurements to a common temperature interval for comparison.

TABLE III

CHANGE OF HEAT CONTENT OF MANGANOUS FLUORIDE BETWEEN 61.00° AND 76.50°K.

Measurement	Temp. interval, °K.	H (76.50) − H (61.00), cal. mole^{-1}
Integral heat no. 1	61.34–76.67	121.76
Integral heat no. 2	60.97–76.26	121.79
$\Sigma C_p \Delta T$, Series II	60.46–77.17	121.72
$\Sigma C_p \Delta T$, Series III	61.12–77.64	121.61
	Accepted value	121.8

The entropy was evaluated by graphical integration of $\int C_p \, d \ln T$. The calculation is summarized in Table IV. In making the entropy extrapolation to the absolute zero the function 3/4 D (119.6°K.) per mole of manganous fluoride, which gave the best representation of the lowest temperature heat capacity data, was used. D is the Debye function.

TABLE IV

THE ENTROPY OF MANGANOUS FLUORIDE

0–15°K., Debye extrapolation	0.22
15–298.16°K., graphical integration	22.03
S at 298.16°K.	22.25 ± 0.10 cal. deg.$^{-1}$ mole^{-1}

Discussion.—The ground state of the free Mn^{++} ion is, according to Hund,[7] a ^6S. The magnetic susceptibility measurements as well as theoretical considerations[8] show that in solid manganous salts at high temperatures the magnetic ions are randomly distributed among the six states per ion. As the temperature is lowered the distribution of the magnetic ions among the states changes until at the absolute zero they are all in a completely ordered arrangement of zero entropy. The maximum in the heat capacity curve of manganous fluoride as well as the anomalous behavior of the magnetic susceptibility[2,3] of this substance is associated with the loss of the magnetic entropy. The dotted line in Fig. 1 is an estimate of the "normal" heat capacity curve due to the crystalline vibrations. The entropy contributed by that portion of the measured heat capacity lying above this curve is 1.2 cal. deg.$^{-1}$ mole^{-1}. This is to be compared with $R \ln 6 = 3.56$ cal. deg.$^{-1}$ mole^{-1} which is the total amount of magnetic entropy present at high temperatures which must be acquired as the temperature increases from the absolute zero. It is apparent that a large portion of the magnetic entropy must be acquired in regions of temperature other than that in which there is the evident anomaly in the heat capacity curve. It seems most probable that there is a gradual increase in the magnetic entropy at temperatures above the region of the

maximum so that the magnetic contribution to the heat capacity cannot be distinguished from that due to the crystalline vibrations. A similar conclusion was drawn in the case of anhydrous copper sulfate[9] which also exhibits a maximum in its heat capacity curve. Another possibility, which we believe to be very unlikely, is that even at 13°K. there remains a large amount of magnetic entropy which would be lost at lower temperatures.

The maximum in the heat capacity curve is much sharper and narrower than would be the case if the energy states available to each magnetic ion were independent of the situation of its neighbors as is the case in NiSO$_4$·7H$_2$O.[1] The name antiferromagnetism has been given to such a cooperative phenomenon which occurs frequently at low temperatures in concentrated paramagnetic salts. Van Vleck[10] has proposed a theory of antiferromagnetism which is formally similar to the Weiss theory of ferromagnetism. The theory predicts that the magnetic heat capacity would rise gradually to a maximum and then drop discontinuously to zero. At the temperature of the maximum the complete magnetic entropy of $R \ln 6$ would have been acquired. These predictions are not in agreement with our results.

Summary

The heat capacity of manganous fluoride has been measured from 13 to 320°K. There is a maximum in the heat capacity curve, due to the changing distribution of the magnetic manganous ions among the available energy states, at 66.5°K. Short heat capacity measurements were taken in the region of the maximum in order to define accurately the shape of the curve. Measurements were also made of the total heat absorbed between 61.00 and 76.50°K.

The entropy of manganous fluoride calculated from the heat capacity measurements is 22.25 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

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(7) Hund, "Linienspektren," Berlin, 1927, p. 161.

(8) Van Vleck, "Electric and Magnetic Susceptibilities," 1932, p. 301.

(9) Stout, J. Chem. Phys., 9, 285 (1941).

(10) Van Vleck, ibid., 9, 85 (1941).