gated qualitatively over the temperature range 25–100°. No indication was found of a two liquid phase region. A quantitative study at 50° revealed the existence of a simple solubility curve with $KOH \cdot H_2O$ as the stable solid phase in equilibrium with the saturated solution. Data are given in Table II.

TABLE II

SYSTEM HYDRAZINE–WATER–POTASSIUM HYDROXIDE AT 50°

Liquid phase, %		Phases
N_2H_4	KOH	
91.9	1.8	Satd. liq. and $KOH \cdot H_2O$
68.8	12.8	Satd. liq. and $KOH \cdot H_2O$
(23.7	53.8)	Wet residue[12]
59.1	19.1	Satd. liq. and $KOH \cdot H_2O$
42.7	29.3	Satd. liq. and $KOH \cdot H_2O$
38.2	32.2	Satd. liq. and $KOH \cdot H_2O$
19.1	45.6	Satd. liq. and $KOH \cdot H_2O$
13.0	50.2	Satd. liq. and $KOH \cdot H_2O$
4.8	56.0	Satd. liq. and $KOH \cdot H_2O$

The system N_2H_4–H_2O–K_2CO_3 was also investigated qualitatively over the temperature range 25–100° in the search for conjugate liquid phases. Only one liquid phase was found. A quantitative investigation (data for which are given in Table III) was made at 50°. The solid phase in equilibrium with the saturated liquid was found to be $K_2CO_3 \cdot 3/2H_2O$ by Schreinemakers' wet residue method. The solubility of potassium carbonate drops off sharply as the concentration of hydrazine increases.

No indication of two conjugate liquid phases was observed in the temperature interval 25–100° using trisodium phosphate, sodium carbonate, sodium sulfate, potassium carbonate and potassium hydroxide.

TABLE III

SYSTEM HYDRAZINE–WATER–POTASSIUM CARBONATE AT 50°

Liquid phase, %		Phases
N_2H_4	K_2CO_3	
97.0	0.6	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
69.8	2.7	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
(27.7	51.7)	Wet residue[12]
53.4	6.0	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
40.5	14.3	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
28.7	25.0	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
16.2	38.5	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
7.6	47.9	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$

Summary

1. Phase relationships in the ternary system hydrazine–water–sodium hydroxide have been studied quantitatively at 50, 60, 70, 90, 100°. At temperatures above approximately 60° this system separates into two liquid phases within certain concentration ranges. A simple solubility curve is observed at 50° with $NaOH \cdot H_2O$ in equilibrium with saturated solutions of hydrazine, water and sodium hydroxide (including the most concentrated hydrazine solution investigated, 93.1% N_2H_4).

2. No evidence for formation of two liquid phases was observed in a study of ternary systems containing hydrazine, water and any one of the following: potassium hydroxide, potassium carbonate, sodium sulfate, sodium carbonate and trisodium phosphate.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Magnetism and the Third Law of Thermodynamics. Magnetic Properties of Ferrous Sulfate Heptahydrate from 1 to 20°K. Heat Capacity from 1 to 310°K.[1]

BY D. N. LYON AND W. F. GIAUQUE

This paper presents the results of a low temperature magnetic and calorimetric investigation on ferrous sulfate heptahydrate. The work is part of a series of researches on magnetic properties near 1°K. which has been in progress in this Laboratory.

The magnetic susceptibility of ferrous sulfate heptahydrate has been investigated previously by Perrier and Kamerlingh Onnes[1a] at a number of temperatures between 14 and 20°K., and at 64, 77 and 290°K. Their data have been recalculated by Jackson.[2]

Curie's Law, χT = constant, where χ and T represent the magnetic susceptibility and absolute temperature, respectively, is obeyed rather well between 64 and 290°K. However, between 20 and 14°K. the susceptibility is increasing much less rapidly than the high temperature Curie constant would require.

According to Hund's rule the ground configuration of ferrous ion is a $^5D_4$ state. The data of Kamerlingh Onnes and Perrier show that the orbital contribution to the magnetic moment is largely "quenched" in solid ferrous sulfate heptahydrate. Between 64 and 290°K. the Curie constant exceeds the "spin only" value by about 10%. At 14°K. their data are about 2% below the spin only value. This suggested that the heat capacity anomalies arising from depopulation of the upper energy levels might occur at temperatures

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[1a] Perrier and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 122a (1911).

[2] Jackson, *Comm. Phys. Lab. Univ. Leiden*, No. 163 (1923).

below those at which heat capacity due to normal crystalline vibrations is important, but at or above temperatures at which thermometry is still a relatively simple matter. This expectation was not fully realized, for the heat effects associated with the electronic transitions appear to persist to the region of 60°K.

Measurements have been made of the heat capacity of ferrous sulfate heptahydrate between 0.9 and 307°K., the initial magnetic susceptibility between 0.9 and 20°K., the temperature change upon adiabatic magnetization and differential adiabatic susceptibilities in various magnetic fields up to 8500 oersteds between 0.9 and 11°K.

Materials.—The ferrous sulfate heptahydrate used in these measurements was obtained by recrystallizing commercial "Low Manganese" analytical reagent grade $FeSO_4 \cdot 7H_2O$. Ferric ion was minimized by bubbling hydrogen over platinum gauze immersed in the solutions. The crystallizations were made at room temperature *in vacuo*. The final crop of crystals was broken and those passing through a no. 20 but retained by a no. 48 mesh sieve were selected. These were allowed to stand in contact with a saturated solution for forty-eight hours in order to minimize surface area. All handling operations were carried out in an atmosphere of humidified nitrogen. Analysis by chemical methods indicated the following impurities:

Mn	0.01 mole %
Cu	.003
Ni	.005
Co	.004
Alkali and alkaline earths	.05

The Heat Capacity of Ferrous Sulfate Heptahydrate between 13 and 307°K.—The heat capacity between 13 and 307°K. was measured in the copper calorimeter described by Giauque and Archibald[3] and subsequently used by Barieau and Giauque[4] in measurements of the heat capacities of zinc sulfate heptahydrate. The general method of measurement and the calculation of heat capacity from the experimental observations has been described by Giauque and Wiebe[5] and by Giauque and Johnston.[6]

Prior to the measurements on ferrous sulfate heptahydrate, the heat capacity of the empty calorimeter was measured between 64 and 139°K., and, after a correction of about 0.1% for a slight increase in weight due to solder, the heat capacities were found to agree with the results of Barieau over this temperature region with an average deviation of +0.03%, and a root mean square deviation of 0.18%. The values of Barieau for the heat capacity of the empty calorimeter were used after applying the above correction. The ice point was taken as 273.16°K. The calorimeter represented only about 20% of the total heat capacity.

Thermocouple W-26, originally calibrated by Giauque and Egan[7] was used to continuously calibrate the resistance thermometer during the course of the heat capacity measurements. After completion of the heat capacity measurements, the thermocouple was compared with hydrogen at its triple point and boiling temperatures, and with nitrogen at its transition point, triple point and boiling temperatures by condensing these materials in the space around the calorimeter and protective block. At all temperatures except the transition point of nitrogen, the observed thermocouple e. m. f. agreed with previous calibration data to within 0.02°K. At the transition temperature of nitrogen, the observed thermocouple e. m. f., when based upon previous calibration data, corresponded to a temperature 0.06°K. lower than the mean value recorded by Giauque and Clayton.[8] However, since there was a spread of 0.05°K. in the observations of these experimenters on this temperature, and since the limits of error of the original thermocouple calibrations were 0.05°K., the temperature scale was unaltered at this point. The earlier work in this Laboratory was done in terms of 273.10°K. instead of the more recent value 273.16°K. as the ice point. All previous data were corrected to this latter value in making the present comparisons.

The weight of sample transferred to the calorimeter was 168.645 g. *in vacuo*. Anomalous absorption of energy in the immediate region of the ferrous sulfate heptahydrate–ice eutectic temperature indicated excess water to be present in the sample. The amount of excess ice present below the eutectic temperature can be calculated from the magnitude of the excess energy absorption at the eutectic temperature and ΔH for the reaction

$$\frac{1}{A-7}\,FeSO_4 \cdot 7H_2O(s) + H_2O(s) = \left(\frac{1}{A-7}\right) FeSO_4 \cdot AH_2O$$

(saturated solution)

where A is the number of moles of water per mole of ferrous sulfate heptahydrate in a saturated solution at the eutectic temperature. The data of J. Perreu[9] for the heats of solution and dilution of ferrous sulfate heptahydrate at 18° and the heat capacities of aqueous solutions of various composition were used to calculate the heat of formation of a saturated solution at the eutectic temperature. This value, combined with the calculated value for the heat of fusion of ice at this temperature, gives ΔH for the above reaction to be 1523 calories per mole of excess ice. Two determinations of the excess energy absorbed in the eutectic region gave the values 38.27 and 39.37, average 38.8 ± 0.5 cal., for the amount of material in the calorimeter. This corresponds to the presence of 0.0254 mole of excess water. The above heat

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[3] Giauque and Archibald, THIS JOURNAL, **59**, 561 (1937).

[4] Barieau and Giauque, in preparation for publication.

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

[6] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[7] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[8] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

[9] Perreu, *Compt. rend.*, **213**, 286 (1941).

was not absorbed sharply at the eutectic temperature, −1.821°, reported by Fraenckel[10] but covered a range of some 5 or 6° below the eutectic temperature before the heat capacity became normal. This is not surprising since such a small amount of eutectic mixture would be dispersed throughout the solid under conditions which would be expected to produce alterations in the melting points of various portions. Analysis of a portion of the sample gave the contents of the total sample as 0.6049 ± 0.0003 g. atoms iron, corresponding to 168.18 g. of ferrous sulfate heptahydrate—in good agreement with the total weight of the sample and the calorimetric value for the amount of excess water. Ferric iron was determined colorimetrically with thiocyanate to be 0.02 mole %.

The heat capacities of ferrous sulfate heptahydrate are summarized in Table I. For the calculation of energy, one calorie was taken to be equal to 4.1833 international joules. Below the eutectic temperature, the heat capacity of 0.042 mole of ice per mole of ferrous sulfate heptahydrate has been subtracted from the experimental values, using the data of Giauque and Stout[11] for the heat capacity of ice. Above the eutectic temperature, the experimental values have been corrected for the heat effect due to the increasing solubility of ferrous sulfate heptahydrate, using the solubility data given in Gmelin's Handbuch[10b] together with the thermal data of Perreu.[9] These corrections amounted to approximately 0.5% of the heat capacities below the eutectic temperature and approximately 1% above. The results in series A were obtained in preliminary measurements made to check upon the proper functioning of the apparatus. The results in series B were then obtained in a continuous series of measurements. Those of series C were measured after calibration of the thermocouple at hydrogen temperatures.

TABLE I

THE HEAT CAPACITY OF $FeSO_4 \cdot 7H_2O$

Mol. wt. = 278.03, 0°C. = 273.16°K.

Cal. deg.$^{-1}$ mole^{-1}

T, °K.	$\Delta T_{\text{approx.}}$	C_p	T, °K.	$\Delta T_{\text{approx.}}$	C_p
		Series A			
92.94	7.02	34.67	284.11	6.66	90.50
99.54	6.26	36.99	292.53	8.43	92.55
277.55	6.36	88.83			
		Series B			
13.14	0.57	2.00	110.98	7.39	40.92
14.21	1.45	2.34	121.50	11.60	44.40
15.82	1.61	2.75	131.67	8.79	47.72
17.75	2.13	3.28	139.99	7.94	50.67
20.32	3.06	4.06	147.92	8.45	53.35
23.64	3.11	5.27	156.33	7.89	55.39
26.45	2.45	6.31	164.30	7.96	57.79
29.16	2.57	7.37	172.46	8.60	60.25
31.99	2.90	8.62	180.67	7.87	62.92
34.72	2.56	9.92	188.94	8.83	65.07
37.47	2.58	11.14	197.97	8.22	67.43
40.02	2.49	12.38	206.22	8.96	69.94
42.72	2.90	13.63	215.43	8.68	72.39
45.64	2.93	14.98	224.12	8.83	74.83
48.54	2.93	16.35	232.81	9.12	77.25
51.71	3.14	17.88	242.74	9.25	79.76
54.87	3.15	19.43	252.01	9.36	82.40
58.50	4.14	21.04	260.80	8.82	84.49
63.40	5.70	23.14	269.80	8.94	87.00
69.59	6.67	25.76	279.79	10.12	89.88
76.90	7.72	28.69	289.99	8.45	92.61
85.07	8.63	31.81	299.37	7.97	94.65
93.53	8.29	34.59	307.67	5.70	96.64
102.38	9.44	38.02			
		Series C			
140.13	6.52	50.27			
147.64	8.39	52.72			

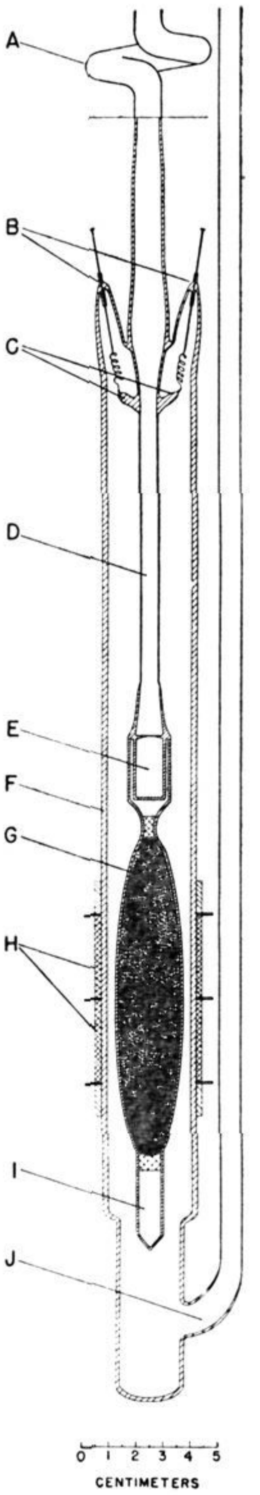

Fig. 1.—Apparatus used for measurements of heat capacity and magnetic properties of ferrous sulfate heptahydrate below 20°K.

Apparatus for the Measurement of Heat Capacity and Magnetic Properties of Ferrous Sulfate Heptahydrate between 0.9 and 20°K.—Figure 1 shows the apparatus used for the measurements between 0.9 and 20°K. The apparatus shown is suspended with the sample at the midpoint of the iron free solenoid magnet described by Giauque and MacDougall.[12] It is surrounded by a Dewar vessel which can be filled with liquid helium or liquid hydrogen so as to completely immerse those parts shown in the diagram.

The sample is contained in an ellipsoidal shell, G, Fig. 1, made from Pyrex glass with room temperature major and minor semi-axes of 6.00 and 1.25 cm. for the inner surface. The measured volume at room temperature was 39.13 cc., compared with a calculated volume of 39.27 cc. Small wads of Pyrex glass wool at the ends of the ellipsoidal shell confined the sample material to the ellipsoidal section. The weight *in vacuo* of the empty container and its supporting tube was 36.09 g., of which 34.1 g.

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[10] (a) Fraenckel, *Z. anorg. Chem.*, **55**, 225 (1907); (b) Gmelin, "Handb. der anorg. Chem.," 58B, Verlag Chemie, G. m. b. H., 1932, p. 401.

[11] Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[12] Giauque and MacDougall, *ibid.*, **57**, 1175 (1935).

was estimated to be in thermal equilibrium with the sample.

There was no apparent tendency toward orientation of the crystal fragments of the sample; consequently, the values obtained for the magnetic properties should represent the average of values for all crystallographic directions.

The total sample weighed 50.967 g. *in vacuo* and consisted of 50.05 g. of ferrous sulfate heptahydrate and 0.915 g. of excess water. Colorimetric analysis gave the ferric iron content of the sample as 0.037 mole %. The free volume of the sample tube was filled with a mixture of nitrogen and helium. The tube was cooled to low temperatures before filling so that it could be evacuated without loss of water. The apparatus was allowed to warm to room temperature before sealing off the filling tube, I. The nitrogen prevented dehydration of the crystals by distillation of water to the wall during subsequent cooling, and the helium provided heat conductivity at low temperatures. The amount of helium added was determined on the basis of the adsorption measurements and low temperature calorimetry of Stout and Giauque.[13]

The sample container was suspended within the insulating vacuum space by means of the thin-walled glass tube D.

In order to cool the sample to temperatures below those obtainable by pumping on the main bath of helium, a cylindrical chamber, E, was sealed to the top of the ellipsoidal sample tube. This chamber could be filled with approximately 1.5 cc. of liquid helium by condensing the required amount of gas in those parts of the tube above the insulating jacket which are in contact with the liquid of the bath. The liquid in this chamber could then be evaporated at considerably reduced pressures by connecting it to vacuum pumping apparatus through tubes A and D. Blaisse, Cooke and Hull[14] and Lassarew and Esselson[15] succeeded in producing temperatures between 0.8 and 1°K. when pumping on liquid helium contained in vessels designed so as to minimize the egress of helium by means of the Rollin helium II film. Consequently, the aperture of the chamber E was restricted to a hole 0.3 mm. in diameter by a diaphragm at the top of the chamber. Great difficulty was encountered in cooling the sample tube from the temperatures of liquid hydrogen to temperatures near 1°K. with this arrangement. This was due in part to an inadequate pump for removing the helium gas. In a later apparatus, used in another investigation in this Laboratory, the diameter of the hole was about doubled; however, the pumping speed was greatly increased at the same time and this may have been the principal reason for a much greater rate of cooling. Also the evaporation chamber in the later apparatus was brought into closer contact with the sample tube.

A carbon thermometer-heater, of the type developed and described by Giauque, Stout and Clark,[16] covered the surface of the sample container. Electrical connections to the thermometer-heater were provided by two platinum–iridium strips, extending from the platinum wire contacts at C down opposite sides of the glass support tube D and the auxiliary helium chamber E to the upper end of the sample tube proper where they terminated in six branching fingers which provided area of contact with the carbon thermometer proper. The strips were deposited in 15 coats of a dilute ether solution of platinic chloride and iridium sesquichloride. After each coat, the strip was heated to a dull red heat. The process was continued until the leads had resistances of 68.5 and 67 ohms, respectively, at room temperature. There is little temperature coefficient of resistance of such leads. The same solution was used to make a comparable strip, and this had resistances of 88 ohms at 293°K., 71 ohms at 77°K., and 69 ohms at 20°K. No. 40 Pt wires fused into the surface of the glass knobs at C prior to the platinizing operation, made contact with no. 30 Pt lead wires welded to tungsten sealed through the wall of the insulating jacket at B. Copper lead wires to the external measuring circuits extended to the bottom of the helium dewar before rising to the tungsten seals in order to minimize the effect of heat leaking down the copper wires themselves and, through their conductivity, heat leaking down the glass support tube A. Thermometer resistance and energy input were measured potentiometrically with a 100,000 microvolt White double potentiometer, using suitable auxiliary standard resistances.

A pair of nearly identical coils, H, were used to measure the magnetic susceptibility of the ferrous sulfate heptahydrate sample. Precise values of the zero field susceptibility were obtained using a fluxmeter arrangement such as that described by Giauque and Stout.[17] Differential susceptibilities in various field up to 8500 oersteds were obtained from measurements of the inductance of the coils with an Anderson bridge.[12] The coils, symmetrically placed with respect to the sample, were wound directly on the wall of the glass tube forming the insulating jacket F. They were separated by Bakelite spacer disks and supported by end rings of Pyrex glass which were held in place with Bakelite lacquer and adhesive tape. The upper and lower coils consisted of 2651 and 2653 turns, respectively, of no. 36 double enamel covered copper wire wound in 14 layers. After completion of the helium temperature experiments, these coils were compared at room temperature with two other sets of coils of accurately known turn area. This comparison indicated that coils H were strained beyond the elastic limit of the wire

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(13) Stout and Giauque, This Journal, (a) **60**, 393 (1938); (b) **63**, 714 (1941).

(14) Blaisse, Cooke and Hull, *Physica*, **6**, 231 (1939).

(15) Lassarew and Esselson, *J. Physics U. S. S. R.*, **5**, 151 (1941).

(16) Giauque, Stout and Clark, This Journal, **60**, 1053 (1938).

(17) Giauque and Stout, *ibid.*, **61**, 1384 (1939).

upon cooling to 4°K. due to the difference in thermal expansion of the Pyrex core and the copper wire. Consequently, the constants for use in the expressions for the susceptibility of the sample in terms of the magnetic flux through the coils were calculated on the assumption that the diameter of the inner layer was equal to that of the glass core at 4°K., and succeeding layers correspondingly larger. The data of Latimer and Buffington[18] were used to obtain the change in dimensions of the glass apparatus between 298 and 4°K. The turn area of the coils at room temperature, when calculated from the dimensions of the glass core at 4°K. and the data of Keesom and van Agt[19] for the thermal expansion of copper, agreed with that indicated by comparison with the reference coils to within 0.1%.

Sequence of Measurements.—The calculation of the susceptibility of the sample requires the value of the inductance of the coils or the flux through the coils when in a medium of unit permeability; this value was calculated from observations made with the coils immersed in liquid helium to eliminate effects due to change in their dimensions with temperature, but with the sample at a known and relatively high temperature at which its susceptibility is known from the previous measurements of Perrier and Onnes and at which its effect upon the coils is small.

Because of the tremendous adsorptive capacity of the carbon of the thermometer, it was not possible to cool the sample with helium in the insulating vacuum space to any temperature above which it was desired subsequently to measure heat capacities, since helium desorbing from the thermometer during energy input would contribute heat leak and apparent heat capacity which could not be correctly evaluated from observations of the heat leak before and after energy input. Therefore, the sample was cooled to some temperature in the region between 20 and 60°K. by means of a stream of cold helium gas, with the insulating vacuum broken with helium. This helium was then pumped from the insulating vacuum space, liquid helium transferred to the dewar so that the measuring coils were completely immersed, and the inductances and flux meter values of the coils measured. A measured quantity of helium was then condensed in the auxiliary helium chamber and the sample allowed to cool by a process of refluxing helium from the chamber E to those parts of the connecting tube which were in contact with liquid of the bath. After the sample had approached the temperature of the bath, the full magnetic field of 8200–8500 oersteds was applied and cooling continued until the cooling rate became impracticably slow, at which time the auxiliary chamber was connected to the vacuum pumps and cooling continued until helium was exhausted from the chamber. The magnetic field was then turned off. Susceptibility and thermometer resistance in zero field were measured; a known magnetic field was then applied and coil inductances and sample temperature (thermometer resistance) measured; the field strength was increased and measurements repeated at intervals of 2500–3000 oersteds until full field was reached. The magnetic field was then removed and the zero field susceptibilities and sample temperature again measured.

Such a series of measurements of differential susceptibility and temperature change upon adiabatic magnetization was followed by one or more determinations of the heat capacity in the absence of a magnetic field. The sequence of measurements was repeated at successively higher temperatures until the decreasing sensitivity of the thermometer made further measurements impractical.

The sample was then heated to about 45°K., the dewar refilled with liquid helium, and the inductances and fluxmeter values of the coils redetermined to check upon the constancy of their dimensions. The insulating vacuum was broken with helium gas and the resistance of the thermometer calibrated at a series of bath temperatures, which were calculated from the observed bath pressures and the values of Schmidt and Keesom[20] for the vapor pressure of liquid helium between 4.4 and 1.6°K., and the equations given by Bleaney and Simon[21] for the vapor pressure of liquid helium between 0.9 and 1.6°K. Measurements of the initial susceptibility of the sample and of the isothermal change in resistance of the thermometer upon application of a magnetic field were also made at the various calibration temperatures. The calibrations were carried to a low temperature of approximately 1.1°K.

Following completion of calibrations with helium, the sample was warmed to about 20°K., and the various calibration measurements carried out at temperatures obtainable with liquid and solid hydrogen. The equations of Martinez and Onnes[22] for the vapor pressure of liquid hydrogen, and those of Giauque, Johnston and Kelley[23] for solid hydrogen were used to calculate the bath temperatures from the observed bath pressures.

Calibration of the Carbon Thermometer.—Approximate thermometer resistances were 23,420 ohms at 20.3°K., 25,295 ohms at 4.2°K. and 28,430 ohms at 1.12°K.

A smoothed table of resistance and $\Delta R/\Delta T$ *versus* temperature was prepared from the calibration data and used to interpolate temperatures corresponding to an observed thermometer resistance. The resistance was extrapolated to 0.8°K. by comparison with the thermometer of Giauque, Stout and Clark.[16]

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[18] Latimer and Buffington, THIS JOURNAL, **48**, 2305 (1926).

[19] Keesom and van Agt, *Comm. Phys. Lab. Univ. Leiden*, No. 182a (1926).

[20] Schmidt and Keesom, *ibid.*, No. 250 (1937).

[21] Bleaney and Simon, *Trans. Faraday Soc.*, **35**, 1205 (1939).

[22] Martinez and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 156b (1922).

[23] Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927).

Within the accuracy of the data the isothermal change in resistance of the thermometer with magnetic field is proportional to the square of the applied field. A smooth curve for $k = \Delta R/R\mathbf{H}^2$ was drawn through the data and used in determining temperature from an observed thermometer resistance in a given magnetic field.

Table II

Heat Capacity of $FeSO_4 \cdot 7H_2O$ between 0.9 and 20°K.

Cal. deg.$^{-1}$ mole^{-1}

$T_{av.}$, °K.	$\Delta T_{approx.}$	C_p
0.98	0.210	0.365
1.19	.198	.387
1.43	.230	.444
1.68	.276	.492
1.99	.346	.523
2.39	.436	.518
2.83	.450	.499
3.25	.446	.502
2.60	.550	.509
3.15	.556	.502
3.69	.532	.520
4.17	.508	.539
4.64	.585	.582
5.26	.76	.66
6.17	1.15	.74
7.48	1.35	.92
8.79	1.34	1.12
10.12	1.44	1.35
11.34	1.54	1.52
12.53	1.09	1.92
10.49	1.80	1.52
12.12	1.43	1.84
13.69	1.66	2.21
15.32	1.66	2.61
17.16	2.01	3.08
19.20	2.16	3.66

The Heat Capacity of Ferrous Sulfate Heptahydrate between 0.9 and 20°K.—The values for the heat capacity of ferrous sulfate heptahydrate obtained during experiments of Sept. 12th–17th, 1947, between 0.9 and 20°K., are summarized in Table II and shown graphically in Fig. 2. The results have been corrected for heat leak during energy input. The heat capacity of the empty container, including the excess water of the sample, was evaluated from the observed $\Delta E/\Delta T$ between 13 and 20°K. and values of the molal heat capacity for ferrous sulfate heptahydrate read from a smooth curve through the data obtained with the copper calorimeter. The heat capacity of the container was proportional to T^3 within the probable limits of accuracy of the low temperature apparatus in this region, and was represented by $\Delta E/\Delta T = 3.99 \pm 0.09 \times 10^{-5} T^3$ cal. deg.$^{-1}$.

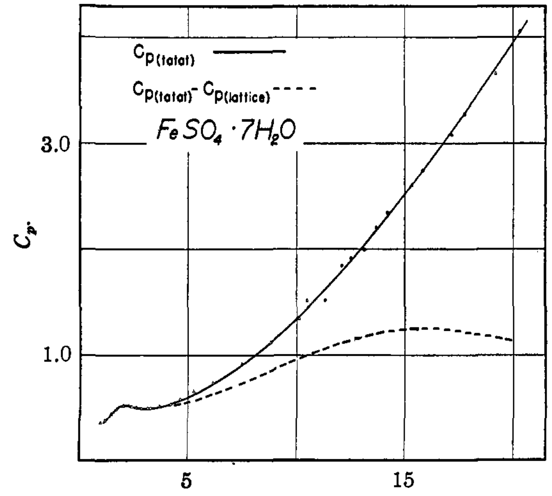

Fig. 2.—Heat capacity in calories per degree per mole.

On the basis of these data and the weight of the container, the heat capacity of Pyrex glass below 20°K. may be represented by the expression $C_p = 1.07 \times 10^{-6}\ T^3$ cal. g.$^{-1}$ deg.$^{-1}$.

Values of the heat capacity of ferrous sulfate heptahydrate taken from smooth curves through the data are given in Table III.

Table III

Heat Capacity of $FeSO_4 \cdot 7H_2O$, Cal. Deg.$^{-1}$ Mole^{-1}

Values read from a smooth curve through the data

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
1	0.35	35	10.03	170	59.54
2	.53	40	12.36	180	62.47
3	.50	45	14.70	190	65.36
4	.54	50	16.94	200	68.18
5	.62	60	21.69	210	70.94
6	.71	70	25.91	220	73.69
7	.84	80	29.90	230	76.38
8	.99	90	33.64	240	79.07
9	1.15	100	37.18	250	81.75
10	1.35	110	40.61	260	84.42
12	1.79	120	43.91	270	87.08
15	2.52	130	47.18	280	89.69
20	3.94	140	50.34	290	92.23
25	5.77	150	53.46	300	94.75
30	7.72	160	56.51		

The Initial Magnetic Susceptibility.—Values for the initial susceptibility per mole of ferrous sulfate heptahydrate, as determined from fluxmeter measurements are presented in Table IV.

Table IV

The Initial Molal Susceptibility of $FeSO_4 \cdot 7H_2O$

T, °K.	χ_m	T, °K.	χ_m
0.84	1.504	*4.204	0.552
*1.084	1.296	4.359	.539
*1.121	1.239	4.388	.532
*1.160	1.285	5.626	.438
2.182	0.890	8.20	.342
2.327	.858	*9.44	.303
*2.509	.798	10.77	.291
*2.78	.752	*14.00	.222
*3.303	.665	14.80	.199
3.455	.650	*17.03	.184
*3.530	.630	*20.31	.156
*3.804	.598		

Those entries marked with an asterisk were obtained with the sample in equilibrium with the bath during calibration measurements. The carbon thermometer was used to determine the temperature for other measurements. The experimental data are represented by the circles plotted in Fig. 3. The values of Perrier and Onnes are shown in Fig. 3 by the triangular symbols.

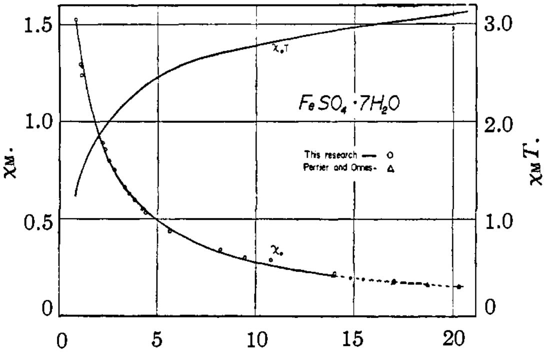

Fig. 3.—Initial magnetic susceptibility of $FeSO_4 \cdot 7H_2O$.

The Differential Magnetic Susceptibility.—Values for the molal adiabatic differential susceptibility are summarized in Table V. The values tabulated have been read, at the adopted standard fields, from smooth curves drawn through the data obtained from bridge measurements of the coil inductances during adiabatic magnetization.

TABLE V

MOLAL ADIABATIC DIFFERENTIAL SUSCEPTIBILITY OF $Fe_2SO_4 \cdot 7H_2O$

$T_{(\mathbf{H}=0)}$	$(\partial I/\partial H)_S$ at H oersteds					
	0	816	1630	3270	6530	8500
0.861	1.54	1.43	1.24	0.92	0.60	0.53
0.944	1.46	1.33	1.16	.87	.57	.50
1.304	1.23	1.17	1.08	.84	.58	.53
1.735	1.02	0.97	0.91	.80	.59	.52
2.173	0.92	.88	.84	.76	.56	.50
2.21	.89	.85	.81	.73	.54	.48
3.43	.68	.66	.64	.61	.57	.56
4.37	.56	.56	.56	.54	.51	.50
5.60	.48	.48	.48	.47	.45	.42
8.15	.35	.35	.35	.35	.35	.35
10.63	.29	.29	.29	.29	.29	.29

The differential magnetic susceptibility measurements are designated $(\partial I/\partial H)_S$, implying that the entropy is held constant during the measurement. This is true with respect to the entropy of the substance but not strictly true with respect to the system consisting of the substance plus the calorimeter. This is because the heat capacity of the calorimeter is completely out of thermal equilibrium with the substance during susceptibility measurements with a frequency of 60 cycles per second. However, this effect may be ignored in the present case since below about 5°K. the heat capacity of the calorimeter is trivial and at higher temperatures the differential susceptibility is almost independent of field. This is due to the fact that the heat capacity of the substance is large in comparison with the heat developed during magnetization, thus $(\partial \mathbf{I}/\partial \mathbf{H})_S$ is approximately equal to $(\partial \mathbf{I}/\partial \mathbf{H})_T$ and the heat capacity of the calorimeter would not alter the result even if complete thermal equilibrium were to be obtained. Under the above conditions such an equation as $\mathbf{I} = \int_0^{\mathbf{H}} (\partial \mathbf{I}/\partial \mathbf{H})_S \, d\mathbf{H}$ may be applied.

Temperature Change upon Magnetization.—Data for the temperature change of the sample and container upon adiabatic magnetization at various initial temperatures are summarized in Table VI and shown graphically in Fig. 4.

TABLE VI

TEMPERATURE CHANGE OF SAMPLE AND CONTAINER UPON ADIABATIC MAGNETIZATION

T(H = 0) °K.	ΔT, °K.	T(H = 0) °K.	ΔT, °K.	T(H = 0) °K.	ΔT, °K.
H = 3270 oersteds		H = 6530 oersteds		H = 8500 oersteds	
0.861	0.236	0.866	0.496	0.841	0.651
0.953	.204	0.957	.500	0.872	.652
1.738	.144	1.304	.458	0.963	.646
2.213	.128	1.742	.414	1.316	.618
8.15	.033	2.173	.416	1.745	.595
10.63	.015	2.221	.406	2.179	.612
		3.433	.377	3.431	.554
H = 816		4.367	.298	4.367	.513
oersteds		5.596	.227	5.60	.405
0.945	0.019	8.139	.115	8.14	.207
H = 1630		10.624	.063	10.62	.105
oersteds		14.76	.036	14.80	.057
0.949	0.061			18.14	.027

The values tabulated were obtained after correcting the observed temperature changes to the three standard fields, using a plot of $\Delta T/\mathbf{H}$ or $\Delta T/\mathbf{H}^2$ *vs.* $\mathbf{H}$ for the small interpolation over the small range of any deviation of the observed field from the standard field; thus the reported values contain all the errors of observation. Corrections

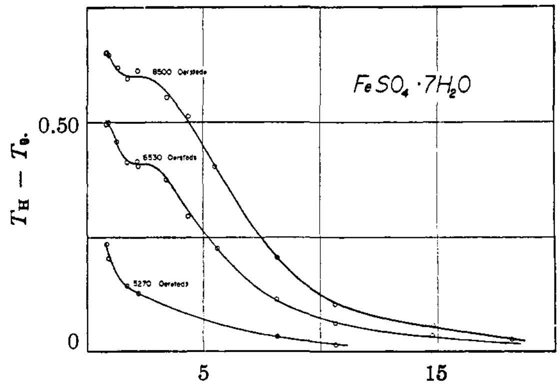

Fig. 4.—Temperature change of sample and container upon adiabatic magnetization.

were made for the effect of the magnetic field upon the resistance of the thermometer. The rapidly increasing heat capacity of the container causes the observed temperature changes to fall off more rapidly with increasing temperature than would be true for ferrous sulfate heptahydrate alone.

Reversibility of Magnetization Processes.—The second law of thermodynamics when applied to a magnetic system can be represented by the equation

$$TdS = dE + PdV - \mathbf{H}d\mathbf{I} \qquad (1)$$

where T, S, E, P, V, $\mathbf{H}$, and $\mathbf{I}$ represent temperature, entropy, energy content, pressure, volume, magnetic field strength and intensity of magnetization, respectively. Ignoring changes in volume, which are insignificant at the temperatures in question, one obtains for a process of adiabatic magnetization

$$(\partial E/\partial \mathbf{H})_S = \mathbf{H}(\partial \mathbf{I}/\partial \mathbf{H})_S \qquad (2)$$

from which the change in energy of the system upon adiabatic magnetization from field $\mathbf{H}_1$ to $\mathbf{H}_2$ is

$$\Delta E = \int_{\mathbf{H}_1}^{\mathbf{H}_2} \mathbf{H}(\partial \mathbf{I}/d\mathbf{H})_S d\mathbf{H} \qquad (3)$$

Any irreversibility in the process of magnetization, due either to magnetic hysteresis or irreversibility in the mechanism of interaction between magnetons and crystal lattice will be evidenced by a heating of the sample upon subjecting it to a cycle of magnetization.

For the case of low magnetic fields where $(\partial \mathbf{I}/\partial \mathbf{H})_S$ is essentially constant and equal to χ

$$\Delta E = \chi \mathbf{H}^2/2 \qquad (4)$$

or for an a. c. field

$$\Delta E = \chi \mathbf{H}^2_{\text{max.}} \qquad (5)$$

per cycle.

At 2.18°K., a 550 cycle a. c. field of 22.5 oersteds maximum intensity produced no detectable change in the warming rate of the sample, in the absence of an applied large d. c. field, corresponding to the dissipation of less than 20 parts per 100,000 parts of the energy change of magnetization—the limits of error of the observations under these conditions.

In the presence of large fields, a small alternating component will cause a total energy change of $\mathbf{H}(\partial \mathbf{I}/\partial \mathbf{H})_S \times \Delta \mathbf{H}$. Since, as can be seen from Table V, $(\partial \mathbf{I}/\partial \mathbf{H})_S$ for ferrous sulfate heptahydrate does not decrease with field by more than threefold, even along the isentrope which starts at the lowest temperature, it is possible to transfer much larger amounts of energy in the larger fields. Any energy dissipated in the sample due to irreversibility can be calculated from the temperature rise (after correcting for heat leak) and the measured heat capacity.

On the isentrope beginning at a zero field temperature of 0.84°K., the energy absorbed by the sample from a 60 cycle a.c. field of approximately 12 oersteds (maximum) in d. c. fields ranging from 6500 to 8500 oersteds was found to be 12 parts per 100,000 parts of the total energy change of magnetization. On the isentrope with a zero field temperature of 0.95°K., the dissipation amounted to 12 parts per 100,000 and on the one beginning at 2.18°K., 6 parts per 100,000 of the total energy change of magnetization. The magnitude of the effect decreased rapidly with increasing temperature until the decreasing sensitivity of the carbon thermometer made it impossible to observe any effect. The assignment of zero field temperatures to the above isentrope is arbitrary, since the temperature of the crystal was approximately 0.6°K. higher than the zero field temperatures, as may be seen from the data in Table VI. The high degree of reversibility indicated by these data permit one to apply the laws of thermodynamics to the system with confidence.

Susceptibility of Ferrous Sulfate Heptahydrate as Calculated from Heat Capacities and the Temperature Change upon Magnetization.—As was shown by Stout and Giauque[13b] in the case of nickel sulfate heptahydrate, the data for the temperature change of the system upon magnetization combined with heat capacity data in zero field can be used with various thermodynamic relationships to demonstrate the consistency between the magnetic susceptibility data and the entirely independent thermal data.

An adiabatic magnetization, during which the temperature of the system rises from T to $T + \Delta T$, can be realized in two steps: (1) warming of the system from T to $T + \Delta T$ in the absence of a magnetic field. The corresponding entropy change will be

$$\int_{T}^{T+\Delta T} C_p/T\, dT$$

(2) isothermal magnetization of the sample at $T + \Delta T$ from zero field to field $\mathbf{H}$. The corresponding change in entropy will be $\int_{\mathbf{H}=0}^{\mathbf{H}} (\partial S/\partial \mathbf{H})_T\, d\mathbf{H}$. Since the process is one of constant entropy, the entropy change upon isothermal magnetization to field $\mathbf{H}$ can therefore be obtained from the value of the integral in step (1).

Table VII gives the entropy change for isothermal magnetization at various temperatures. Values of ΔT were read from smooth curves for ΔT *vs.* $T + \Delta T$, and the observed values for the total heat capacity of the apparatus used to evaluate the corresponding entropy change.

Values of $1/\mathbf{H}(\partial S/\partial \mathbf{H})_T$ can be obtained from the tabulated isothermal entropy changes of Table VI, and relations such as

$$1/\mathbf{H}(\partial S/\partial \mathbf{H})_T = 2\Delta S/\mathbf{H}^2 + \frac{\partial(\Delta S/\mathbf{H}^2)}{\partial \ln \mathbf{H}} \qquad (6)$$

or

$$1/\mathbf{H}(\partial S/\partial \mathbf{H})_T = \Delta S/\mathbf{H}^2 + \frac{\partial(\Delta S/\mathbf{H})}{\partial \mathbf{H}} \qquad (7)$$

Curves were drawn through plots of $\Delta S/\mathbf{H}^2$ *vs.* $\ln \mathbf{H}$ and $\Delta S/\mathbf{H}$ *vs.* $\mathbf{H}$ so as to give consistent values

TABLE VII

ENTROPY CHANGE UPON ISOTHERMAL MAGNETIZATION OF $FeSO_4 \cdot 7H_2O$

T	$-\Delta S$ cal. deg.$^{-1}$ mole^{-1} H → 3270	6530	8500	$-\Delta S/\mathbf{H}^2$ Ergs deg.$^{-1}$ Oersted^{-2} mole^{-1} 3270	6530	8500
1.3	0.053	0.157	0.212	0.207	0.154	0.123
1.7	.045	.143	.197	.178	.140	.114
2.0	.037	.121	.180	.145	.119	.102
2.3	.030	.104	.156	.117	.102	.090
2.6	.024	.089	.137	.095	.088	.079
3.0	.019	.074	.114	.037	.072	.066
4.0	.0125	.048	.077	.049	.047	.045
5.0	.0094	.037	.062	.037	.036	.036
6.0	.0074	.028	.051	.029	.027	.030
7.0	.0058	021	.041	.023	020	.026
8.0	.0049	.017	.032	.019	.016	.019
9.0	.0038	.014	.025	.015	.013	.014
10.0	.0030	.012	.020	.012	.012	.012
12.0	.0021	.0089	.015	.0083	.0087	.0086
15.0		.0064	.0098		.0063	.0057

TABLE VIII

TEMPERATURE COEFFICIENT OF MOLAL SUSCEPTIBILITY OF FERROUS SULFATE HEPTAHYDRATE CALCULATED FROM THERMAL DATA

T, °K.	$\mathbf{H} = 0$	$\mathbf{H} = 3270$	$\mathbf{H} = 6530$	$\mathbf{H} = 8500$
0.94[a]	0.74			
1.74[a]	.38			
2.21[a]	.26			
1.50	.49	0.36	0.225	0.14
1.70	.42	.31	.20	.13
2.00	.34	.265	.18	.13
2.30	.28	.225	.17	.13
2.60	.22	.19	.15	.11
3.00	.16	.15	.125	.095
4.00	.095	.094	.088	.082
5.00	.073	.073	.072	.072
6.00	.057	.057	.056	.058
7.00	.044	.044	.043	.046
8.00	.036	.035	.034	.036
9.00	.029	.028	.027	.027
10.00	.023	.023	.023	.024
12.00	.017	.017	.017	.017

[a] Obtained by extrapolation along a constant entropy path, using the following thermodynamic relationship

$$\frac{1}{\mathbf{H}}\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{\mathrm{T}} = -\frac{C_{\mathbf{H}}}{\mathbf{H}T}\left(\frac{\partial T}{\partial \mathbf{H}}\right)_{\mathrm{S}} \tag{10}$$

$\frac{1}{\mathbf{H}T}\left(\frac{\partial T}{\partial \mathbf{H}}\right)_{\mathrm{S}}$ was plotted *versus* **H** and the curves extrapolated to $\mathbf{H} = 0$ where $C_{\mathbf{H}}$ is the experimentally observed heat capacity.

for $1/\mathbf{H}(\partial S/\partial \mathbf{H})_{\mathrm{T}}$ from either relation (6) or (7). The values obtained are given in Table VIII. The values for zero field were obtained from extrapolation of the curve indicated by the values in magnetic fields. Since

$$\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathbf{I}}{\partial T}\right)_{\mathbf{H}} \tag{8}$$

$$\frac{1}{\mathbf{H}}\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{\mathrm{T}} = \frac{1}{\mathbf{H}}\left(\frac{\partial \mathbf{I}}{\partial T}\right)_{\mathbf{H}} \tag{9}$$

Also, in small magnetic fields, $\mathbf{I}/\mathbf{H} = \chi$ so that $1/\mathbf{H}(\partial \mathbf{I}/\partial T)_{\mathbf{H}=0} = (\partial \chi/\partial T)_{\mathbf{H}=0}$. Therefore, the values of $\frac{1}{\mathbf{H}}\left(\frac{\partial S}{\partial \mathbf{H}}\right)_{\mathrm{T}}$ listed in Table VIII for zero field are values of the temperature coefficient of initial susceptibility.

The increase of the initial susceptibility of ferrous sulfate heptahydrate below 13.92°K. has been calculated by integration of the zero field values of Table VIII for the temperature coefficient, and the result is shown by the solid curves of Fig. 3, which have been drawn entirely without reference to the experimental points plotted there. The value of Perrier and Kamerlingh Onnes for the susceptibility at 13.92°K., ($\chi_{13.92} = 0.2106$) has been chosen for reference since susceptibility measurements with the apparatus used here become relatively inaccurate at and above these temperatures.

The Entropy of Ferrous Sulfate Heptahydrate.—The calculation of the increase in entropy of ferrous sulfate heptahydrate between 1 and 298.16°K. has been made by means of a plot of C_p/T against T. However, the question as to the exact value of the entropy at 1°K. is not easy to decide. The whole character of the heat capacity curve in the temperature region of liquid helium is produced by the changing populations of the quantum levels associated with the magnetic system and this influence extends to above the temperature region of liquid hydrogen. As may be seen in Fig. 2 there is a maximum in the heat capacity curve at 2.3°K. and in deciding the entropy below 1°K. a decision must be reached as to whether the heat capacity falls off continuously below 2.3°K. or whether any additional maxima occur below 0.9°K.

One method of attempting to get information about the above problem is to attempt to separate the heat capacity into one portion due to the lattice vibrations of the crystal with the remaining portion assigned to the effect of the changing populations of electronic levels. The heat capacity of the diamagnetic zinc sulfate heptahydrate has been measured by Barieau and Giauque[4] in order to assist in estimating the lattice heat capacity of other heptahydrated sulfates of the elements of this transition group. A comparison of the two substances shows that ferrous sulfate heptahydrate has a higher heat capacity than zinc sulfate heptahydrate at all temperatures up to 300°K. At higher temperatures this is presumably due to relatively stronger bonds in the case of zinc sulfate which is consistent with the fact that it has the higher heat of formation and the smaller ionic diameter of the two substances. Between 65 and 200°K., the ratio of the heat capacities is given to within 0.2% by the expression

$$\frac{C_p,\ FeSO_4 \cdot 7H_2O}{C_p,\ ZnSO_4 \cdot 7H_2O} = 1.000 + 0.000166T$$

The fact that this expression holds rather accurately above 65°K. certainly does not mean that it can be accepted with confidence at much lower temperatures but we shall adopt it as at least a reasonable representation of the heat capacity of ferrous sulfate heptahydrate due to its lattice vibrations. A broken curve representing $C_{p_{\text{total}}} - C_{p_{\text{lattice}}}$ has been shown in Fig. 2 below the curve for the total heat capacity. Below 10°K. the contribution of the lattice energy to the heat capacity is very small and the difference curve may be taken as accurate; between 10 and 20°K. it should be fairly reliable; however, above 20°K. it can only be considered as a rough approximation. The values obtained for $C_{p_{\text{total}}} - C_{p_{\text{lattice}}}$ at higher temperatures are 0.58 cal. deg.$^{-1}$ mole^{-1} at 30°K., 0.26 cal. deg.$^{-1}$ mole at 40°K., 0.11 cal. deg.$^{-1}$ mole^{-1} at 50°K., and less than 0.1 cal. deg.$^{-1}$ mole^{-1} at 60°K. The difference was arbitrarily taken as zero at 65°K.

In attempting to select some energy pattern based on a ${}^5D_4$ state to explain the difference curve, and especially the maximum at 2.3°K., some conclusions may be reached. If one assumes an ideal state in which each ferrous ion interacts only with its own immediate environment, and not with other ferrous ions, such a low maximum as 0.53 cal. deg.$^{-1}$ mole^{-1} requires two states of very low energy, with one state some 3 or 4 cm.$^{-1}$ above and additional states at considerably higher levels. No assumption including a single low lying state will satisfy the experimental data under the above ideal assumption. If there should be a doubly degenerate lower level, it would contribute the quantity $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} to the entropy below 1°K., whereas if the level be single, a reasonable extrapolation of the experimental curve leads to an estimate of a total entropy of 0.2 cal. deg.$^{-1}$ mole^{-1} at 1°K.

The detailed crystal structure of monoclinic ferrous sulfate heptahydrate is unknown; however, from the density data the average separation of the ferrous ions is of the order of 6×10^{-8} cm. At distances of this order the magnetic moments of the four electrons spins would give rise to interaction bond energies of the order of several tenths of a cal. mole^{-1} if one assumes that they act as small classical magnetic dipoles. This is much too small to be responsible for a maximum at 2.3°K. However, the actual interaction may be much greater than the above over-simplified calculation indicates and the possibility that the maximum at 2.3°K. is due to interaction of ferrous ions cannot be excluded.

If such an interaction exists, as it must to at least a small extent, then the system has begun to acquire some of the characteristics of a coöperative phenomenon and the calculation based on simple Boltzmann factors is not valid. However, it must be considered that coöperative phenomena at higher temperatures usually are associated with rather high maxima in their heat capacity curves and it was the small height of the maximum which led to a low lying doubly degenerate level as a possible explanation.

The magnetic susceptibility contributes evidence which we believe is opposed to the idea of a very low lying doubly degenerate level, since the rapid decrease of χT as shown in Fig. 3 is hard to reconcile with a doubly degenerate level which is free to orient its magnetic moment at even much lower temperatures.

Additional evidence at still lower temperatures and in much higher magnetic fields would be very desirable in arriving at a more detailed explanation of this magnetic system. We suggest that, until additional measurements are made, the best estimate of the entropy at 1°K. is 0.20 cal. deg.$^{-1}$ mole^{-1}. As is customary this value does not include the entropy due to nuclear spin or isotope effects since these cancel in ordinary chemical reactions. The entropy calculation is summarized in Table IX. The temperature range is divided into four regions so as to facilitate comparison with future data.

TABLE IX

THE ENTROPY OF FERROUS SULFATE HEPTAHYDRATE

	Cal. deg.$^{-1}$ mole^{-1}
0–1°K.	0.2
1–10°K.	1.4 ± 0.07
10–20°K.	1.7 ± 0.08
20–298.16°K.	94.5 ± 0.15
Total	97.8 ± 0.3

The entropy associated with the magnetic system, as evaluated by integration $(C_{p_{\text{total}}} - C_{p_{\text{lattice}}})/T$ *vs.* T, is 2.8 cal. mole^{-1} deg.$^{-1}$ if the entropy at 1°K. be taken as 0.2 cal. deg.$^{-1}$ mole^{-1}. If the multiplicity of 5, corresponding to the spin only case, applies, the entropy due to the electronic system would be $R \ln 5 = 3.2$ cal. deg.$^{-1}$ mole^{-1}. Considering the uncertainty of $C_{p_{\text{total}}} - C_{p_{\text{lattice}}}$ it is not possible to reach a definite conclusion but the difference is within the limits of error.

We thank J. J. Fritz, T. H. Geballe, R. H. Busey and J. E. Kunzler for assistance with the experimental measurements.

Summary

The heat capacity of ferrous sulfate heptahydrate has been measured from 0.9 to 307°K.

The entropy, less nuclear spin and isotopic contributions, has been calculated to be 97.8 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

The initial magnetic susceptibility of ferrous sulfate heptahydrate has been measured between 0.84 and 20°K.

The temperature change accompanying adiabatic magnetization has been measured in fields to 8500 oersteds and over the temperature range 0.84 to 18°K.

The magnetization and demagnetization of ferrous sulfate heptahydrate have been shown to be highly reversible processes.

The adiabatic differential magnetic susceptibility has been measured over the range 0.86 to 11°K. and at various fields up to 8500 oersteds.

The heat capacity data and the temperature change during magnetization have been used to calculate the entropy change accompanying isothermal magnetization. Values of this quantity have been used, in combination with thermodynamic relationships, to evaluate the temperature coefficient of magnetic susceptibility.

A curve of the initial magnetic susceptibility calculated by integrating the temperature coefficient of susceptibility is in complete agreement with the directly measured values.

The portion of the total heat capacity due to the electronic system has been estimated by comparing the data with the heat capacity of the diamagnetic zinc sulfate heptahydrate. Near the liquid helium temperature region the rather considerable heat capacity is almost completely due to the electronic system.

The relationship between the observed heat capacity and the electronic energy pattern responsible for it has been discussed.

The heat capacity of Pyrex glass below 20°K. has been estimated as $1.07 \times 10^{-6}T^3$ cal. g.$^{-1}$ deg.$^{-1}$.

BERKELEY, CALIFORNIA RECEIVED OCTOBER 18, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Measurement of Magnetic Susceptibility at Low Temperatures[1]

BY W. F. GIAUQUE, J. J. FRITZ AND D. N. LYON

The purpose of this paper is to describe a fluxmeter arrangement for measuring adiabatic differential magnetic susceptibilities in the region near and below 1°K. The particular instrument to be described here has been used for a research on cobaltous sulfate heptahydrate[1a] and is now in use for additional investigations in this Laboratory. For this reason, and also to separate the account from other experimental details, it has seemed desirable to give a description which can be used as a common reference in the recent and future work.

A fluxmeter is simple in principle, being based on the fact that a coil surrounding a sample will acquire an e. m. f. when a change in magnetic induction occurs within the coil. This principle is sometimes used in rough experiments in which a piece of magnetized iron is suddenly withdrawn from a coil which is attached to a ballistic galvanometer. In the present work it is very desirable not to move the sample which is surrounded by a vacuum jacket and attached to various electrical leads and other experimental facilities. Moreover the measurement of the deflection of a ballistic galvanometer is nowhere near a sufficiently accurate procedure to meet the requirements of adiabatic demagnetization work. The sample may be left stationary if the space occupied by the sample and its surrounding coil is in turn surrounded by an exciting coil which serves to produce a sudden change in magnetic induction. This requires the evaluation of the induction which would cut the coil if the sample were absent. This may be done most simply in this type of investigation by heating the sample (but not the coil) until the susceptibility is so reduced that it can be considered as a small correction. In order to obtain accuracy the e. m. f. induced in the sample coil must be measured by an essentially null point method.

An arrangement for doing this has been described and used by Giauque and Stout[2] who used a set of standard coils mounted within a second exciting coil to balance the effect of the sample coil. In their arrangement the two exciting coils were connected in series and in order to avoid magnetic interference the standard fluxmeter arrangement was located in an adjacent room well away from the adiabatic demagnetization apparatus. The major problem in any null point method arises from the fact that the two e. m. f.'s must be balanced not only in magnitude but in phase if a sensitive galvanometer is to be used.

If magnetic properties are to be investigated as a function of magnetic field, the experimental arrangement must be mounted within a magnet. This requires the presence of considerable amounts of metal near the sample and the coil surrounding it. The time required for the exciting coil to produce its change in magnetic induction will be increased by the opposing effects of various currents which are simultaneously induced in any metal objects which are within effective range of its field. Giauque and Stout[2] solved this problem so far as the measurement of initial magnetic susceptibility was concerned by placing duplicate metal parts in the same relative positions with respect to the standard fluxmeter coils and their exciting coil. They also remark "The sample and the opposing coils could be located within the same exciting magnet provided they are sufficiently isolated from each other. There are, however, some objections to this, especially in connection with low temperature investigations where the space in and near the magnet is more valuable for other purposes. Moreover, it is desirable to keep the standard coils at a fairly constant temperature to prevent dimensional changes." This latter point is the most important one because the change in turn area, when a coil is cooled from ordinary

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[1a] Fritz and Giauque, THIS JOURNAL, **71**, in press (1949).

[2] Giauque and Stout, *ibid.*, **61**, 1384 (1939).