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

Magnetism and the Third Law of Thermodynamics. Magnetic Properties and Heat Capacity of $CoSO_4 \cdot 7H_2O$ from 0.1 to 15°K.[1]

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This paper presents the results of a low temperature magnetic and calorimetric investigation on cobaltous sulfate heptahydrate. The work is part of a series of researches on magnetic properties near 1° K. which is utilizing the adiabatic demagnetization method. The only other low temperature investigation on $CoSO_4 \cdot 7H_2O$ is that of Jackson[1a] whose measurements extend to 14.76° K.

According to Hund's rule, the ground state of Co^{++} is $^4F_{9/2}$. However, as in other elements of this transition group the contribution which the orbital momentum makes to the total magnetic moment of the ion in the gas state is largely "quenched" in the solid state at low temperatures. Jackson's magnetic susceptibility measurements show a considerable orbital contribution at ordinary temperatures but at 15° K. the total susceptibility is only 20% above the "spin only" case, with $S = 3/2$.

Material Used.—The material used in the investigation was obtained from C. P. "Nickel Free" Cobaltous Chloride Hexahydrate. The commercially available material was first converted into cobaltic hexammine trichloride by oxidation with ammoniacal silver chloride. The cobaltammine was decomposed to anhydrous cobaltous chloride, which was then converted to the sulfate with sulfuric acid. $CoSO_4 \cdot 7H_2O$ was obtained by fractional crystallization. The analysis is given in Table I.

TABLE I

ANALYSIS OF $CoSO_4 \cdot 7H_2O$ SAMPLE

Iron (as $FeSO_4 \cdot 7H_2O$)	0.001 mole %
Nickel (as $NiSO_4 \cdot 7H_2O$)	.01 mole %
Alkali and alkaline earth elements (as K_2SO_4)	.01 mole %

A spectroscopic examination of the material agreed with the above analysis; it indicated the absence of other elements of the iron group with the possible exception of a trace of copper.

The crystals were in the form of plates whose thickness was about half their width. After breaking and screening, the sample consisted of irregular particles whose average diameters ranged from 0.2 to 0.8 mm.; most of them were about 0.5 mm. across. The material was allowed to stand for several hours in contact with a saturated solution of $CoSO_4 \cdot 7H_2O$ so as to remove rough edges from the particles and to restore any water of crystallization which might have been lost from their surfaces during preparation.

A representative sample was analyzed by dehydration to $CoSO_4$ at 550°. The sample was found to contain 6.97 moles of water per mole of $CoSO_4$. Since the hepta- and hexa-hydrate should exhibit quite similar thermal and magnetic behaviors, the results will be considered representative of the properties of $CoSO_4 \cdot 7H_2O$.

The material actually used in the investigation weighed 45.655 g. *in vacuo*. It contained 0.1627 mole of Co^{++}.

Experimental Arrangement.—Figure 1 shows the assembly of the sample and the coils used for the measurement of susceptibility. The Pyrex sample container (F) was ellipsoidal in shape. It was constructed by sealing together two half-ellipsoids, each of which had been formed on an accurately machined steel mold. The seal was in the equatorial plane of the completed ellipsoid. The inside shape of each half was that of a prolate ellipsoid of revolution to within 0.1 mm. at all points except at the lower extreme, where an 8 mm. Pyrex filling tube was sealed on. The inside semi-major axis of the finished container was 5.90 cm.; the inside semi-minor axis was 1.247 cm.

The powdered crystalline sample was firmly packed inside its container and was held in place at the lower end by a small plug of fine glass wool, which was shaped so as to maintain the ellipsoidal shape as closely as possible. The space about the powder was filled with a mixture of nitrogen and helium. At room temperature the partial pressure of helium was 2 cm.; the total pressure was 1 atm. The filling tube was sealed off at the bottom. The volume of the ellipsoid, 38.4 cm.^{3}, plus the volume of the filling tube, 1.0 cm.^{3}, totalled 39.4 cm.^{3}. The volume of the cobalt sulfate heptahydrate was 23.4 cm.^{3} and that of the 0.02 g. of glass wool was negligible. Thus the sample tube contained 1.7×10^{-5} mole of He and 6.3×10^{-4} mole of nitrogen.

The chamber (E) at the top of the sample tube had a volume of about 1.4 cc.; it could be filled with liquid helium through tube (D). At the top of the chamber was a thin glass diaphragm pierced by a hole 0.56 mm. in diameter. This constriction was provided to make possible the attainment of low vapor pressures of liquid helium inside the chamber by providing a restriction of the flow of liquid helium II into tube (D) as used by Cooke and Hull.[2] The tube (D) was 0.35 cm. o.d., 0.27 cm. i.d., and 10 cm. long; the cross sectional area of the glass in it was 0.039 sq. cm. At the upper end it connected through an 8 mm. tube (A) to an external pumping system, which contained an oil-diffusion pump having a speed of 275 liters/sec. Upon application of this pump considerable quantities of liquid helium could be evaporated rapidly from the chamber (E) at pressures well below 1 mm.

The total weight of glass in the sample container and tube (D) was 35.46 g., of which 34.68 g. were considered to be in equilibrium with the sample.

A carbon thermometer, constructed as described by Giauque, Stout and Clark,[3] was placed on the outside of the glass ellipsoid. Electrical connection to the thermometer was furnished by thin platinized strips running up the outside of the tube (D). At the lower end these strips were branched out, so as to provide a large contact area without having any extensive unbroken metal surface, minimizing heating by eddy currents in alternating fields. At the top of tube (D) the strips were connected by means of coiled pieces of no. 36 platinum wire to tungsten-glass seals (B) which led to the external connections. The glass seal was made by coating the tungsten lead with Nonex glass and sealing this to the Pyrex by means of uranium glass.

At the top another 8-mm. glass tube (behind tube A and not visible in this diagram) led to a vacuum system for pumping the space inside the glass jacket (C). During assembly the ellipsoid was carefully centered inside the jacket (C). The average equatorial spacing between them was 0.8 mm.

Two helium vapor pressure thermometers are shown at J, J of Fig. 1.

Magnetic susceptibilities were measured by means of a

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

(1a) Jackson, Comm. Phys. Lab. Univ. of Leiden, No. 163 (1923).

(2) Cooke and Hull, *Nature*, **143**, 799 (1939).

(3) Giauque, Stout and Clark, THIS JOURNAL, **60**, 1053 (1938).

coil assembly which surrounded the sample container and its jacket. The coil system was designed to be used as part of a fluxmeter arrangement which depended on balancing the effect produced by a small change in the applied magnetic field as described by Giauque and Stout.[4] However, in the present case the arrangement was improved by the addition of an intermediate set of reference coils which were immersed in the helium bath and located in nearly the same environment as the sample. A detailed description of this arrangement has been given by Giauque, Fritz and Lyon.[5] The upper set of two coils (G) each contained about 2100 turns wound in 12 layers. The set of intermediate reference coils (I) consisted of 13 coils which were centered about a point 13 cm. below the center of the sample and co-axial with it.

The coils surrounding the sample could also be used as part of an Anderson Inductance Bridge arrangement for measuring magnetic susceptibility, as described by Giauque and MacDougall[6] and Giauque, Stout, Egan and Clark[7].

Figure 1 also shows the apparatus assembled inside a double glass Dewar vessel. This vessel was used in the same manner as that described by Giauque, Stout, Egan, and Clark.[7] Its construction differed from the other in two important details. It was made 20 cm. longer overall, with the inner (liquid helium) chamber (M) 25 cm. longer and of about 20% greater capacity. The volume of this chamber was about 4500 cc. The glass spiral used to connect the two Dewar vessels in the previous apparatus was replaced by a straight length of thick-walled glass tubing (N). The connection of this tube to the inner tube of the outer vessel provided sufficient flexibility with respect to sidewise motion; the tube itself was not as susceptible to breakage in the event of a sudden longitudinal thrust. The breakage of a previous apparatus when a vacuum was applied, after it had been filled with liquid nitrogen, was attributed to the collapse of the spiral when the refrigerant "bumped." The small extension on the bottom of the innermost tube prevented appreciable displacement of this tube on the occasions when the entire vessel was in a horizontal position. The outer Dewar vessel was strengthened by the usual type of asbestos supports between the walls. A coil of no. 22 double cotton insulated copper wire wound on the outermost tube of the Dewar vessel served as an exiciting coil of the fluxmeter.

The glass line (K) connected the high vacuum system to the space inside jacket (C) of Fig. 1. Two glass spirals (L) were used to prevent radiation from travelling down these tubes.

The solenoid magnet and most of the associated equipment have been described by Giauque and MacDougall.[8] A battery of high-capacity lead cells sufficient to produce as much as 260 volts was used in parallel with or in place of the ordinary 240-volt d.c. source of current in order to obtain sufficiently steady currents in the magnet circuit. A 110 c.f.m. Kinney DVD-8-8-10 vacuum pump was used to reduce the pressure of the liquid helium inside the Dewar vessel. Under normal conditions it was possible to obtain a pressure as low as 0.4 mm. above the liquid helium; this corresponds to a bath temperature of about 1.14°K.

Characteristics of the Carbon Thermometer.—The carbon resistance thermometer was used over almost all of the range investigated. Its resistance was compared with vapor pressures of liquid helium at seven calibration points, with vapor pressures of liquid and solid hydrogen at four points, and with the vapor pressure of liquid nitrogen at a single point. The comparisons were made in zero field and in various magnetic fields up to the maximum available. Temperatures were obtained from vapor pressures of liquid helium by using the data of Schmidt and Keesom[9] for the range 4.4 to 1.6°K. and those of Bleaney and Simon[10] for the range 1.6 to 0.9°K. The equations of Martinez and Kamerlingh Onnes[11] were used for vapor pressures of liquid hydrogen, and those of Giauque, Johnston and Kelley[12] for vapor pressures of solid hydrogen.

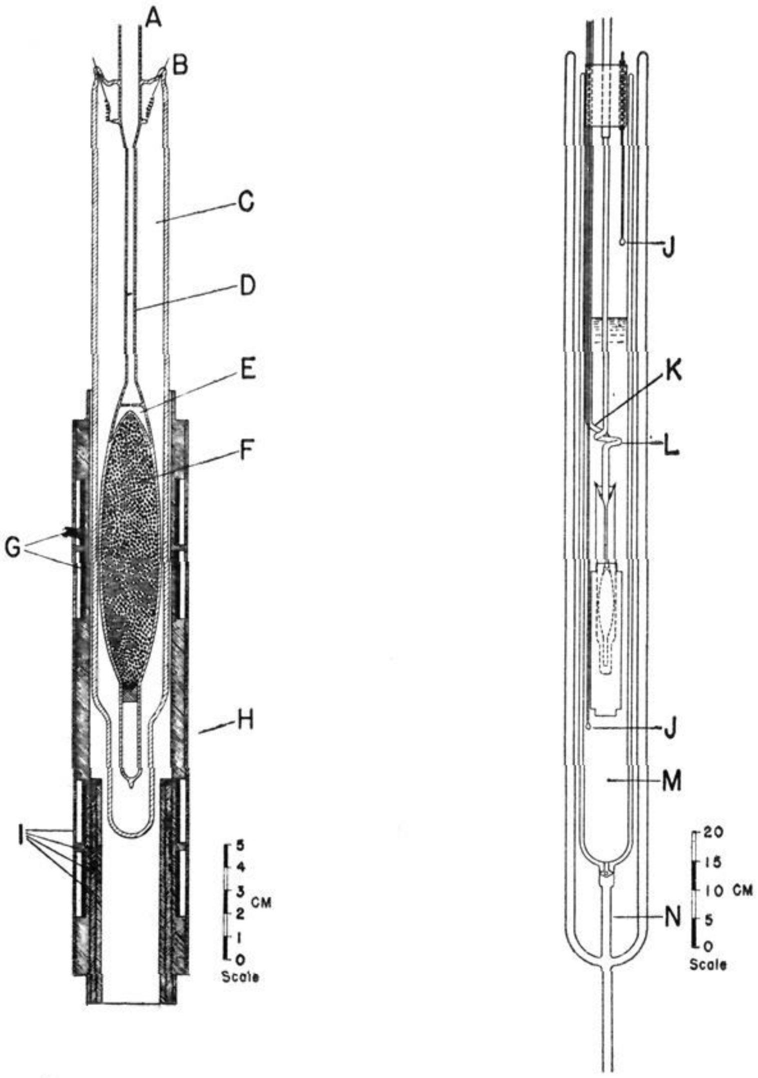

Fig. 1.—Apparatus for measurement of heat capacity and magnetic properties of $CoSO_4 \cdot 7H_2O$.

From the observations of zero-field resistance a continuous calibration curve was constructed for the resistance as a function of temperature from 1.1 to 20°K. The increase in the thermometer resistance produced by a magnetic field was found to be proportional to $\mathbf{H}^2$ for all temperatures and fields used. Table II gives the values of the resistance and of $\Delta\mathbf{R}/\mathbf{R}_0\mathbf{H}^2$ for the various calibration points. The last column of Table II gives values of $(\Delta\mathbf{R}/\mathbf{R}_0)(T/\mathbf{H})^2$. A curve of values of this function as ordinates against T shows that it is not far from linear near the boiling point of helium, however the curve is definitely concave downward and it should eventually bend enough to reach zero at 0°K. An extrapolation of this curve is used later in estimating the change of resistance of the carbon thermometer in magnetic fields below 1°K.

Between 4°K. and room temperature the relative rate of change of resistance with temperature was quite similar to that of the thermometer described by Giauque, Stout and Clark.[3] Below 4°K. the resistance changed somewhat more gradually than did that of the previous thermometer. This thermometer, like all previous carbon thermometers used in this Laboratory, was made from the supply of lamp black used by Giauque, Stout and Clark.[3] However, some differences in characteristics are to be expected, because it is impracticable to exactly duplicate details of construction, such as the amount of collodion used. Table

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[4] Giauque and Stout, THIS JOURNAL, **61**, 1384 (1939).

[5] Giauque, Fritz and Lyon, *ibid.*, **71**, 1657 (1949).

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

[7] Giauque, Stout, Egan and Clark, *ibid.*, **63**, 405 (1941).

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

[9] Schmidt and Keesom, Comm. Phys. Lab. Univ. Leiden, No. 250 (1937).

[10] Bleaney and Simon, *Trans. Far. Soc.*, **35**, 1205 (1939).

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

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

TABLE II

CALIBRATION DATA OF CARBON RESISTANCE THERMOMETER

Temperature, °K.	Resistance, ohms	$(\Delta R/R_0H^2)$ × 10^{12} (oersted)$^{-2}$	$(\Delta R/R_0)$ $(T/H)^2$ × 10^{12}
1.145	32,386.8	68.0	89
1.772	31,477.0	34.1	107
2.164	31,098.0	25.0	117
2.641	30,761.7	16.9	118
3.112	30,521.5	12.7	123
3.723	30,277.1	9.5	132
4.216	30,060.2	7.7	137
8.720	29,320.0	1.6	120
13.86	28,918.2	0.66	130
16.95	28,736.0	...	...
20.33	28,561.4	0.1	...
77.2	26,826.6	...	...
295 (approx.)	24,200		

TABLE III

TYPICAL EXAMPLES OF THE INCREASE IN RESISTANCE OF A CARBON THERMOMETER IN A MAGNETIC FIELD AT CONSTANT TEMPERATURE

T = 1.145°K.			T = 2.656°K.			T = 4.224°K.		
H	$\Delta R_{obs.}$	$\Delta R_{calcd.}$	H	$\Delta R_{obs.}$	$\Delta R_{calcd.}$	H	$\Delta R_{obs.}$	$\Delta R_{calcd.}$
2512	12.9	13.9	2368	2.9	3.0	2400	1.9	1.4
5808	74.2	74.5	6000	18.7	19.2	6000	7.9	8.5
6640	97.4	(97.4)	6784	23.5	24.5	6800	11.3	10.9
			8528	38.7	(38.7)	8500	17.2	(17.2)

III gives a comparison for several temperatures between the observed ΔR due to field and that calculated from the value at the highest field, assuming $\Delta R \propto H^2$. The differences between the observed and calculated values are within the limit of error.

Since Curie's law could not be assumed, especially since χT was known to be variable even above 1° K., temperatures below 1° K. could be obtained only by combining the magnetic and calorimetric data as done by Giauque and MacDougall.[6,13] The quantity $(\partial I/\partial H)_S$ enables the calculation of I, the intensity of magnetization, at any field, H, along a series of constant entropy paths. These start at some unknown low temperature and zero field and proceed to the region above 1° K. where temperatures can be measured.

$$I = \int_0^H \left(\frac{\partial I}{\partial H}\right)_S dH$$

By this method I can be measured as a function of H and T above 1° K. for all obtainable values of the field. From these measurements and the thermodynamic relationship $(\partial S/\partial H)_T = (\partial I/\partial T)_H$ the entropy of magnetization can be computed

$$\Delta S = \int_0^H \left(\frac{\partial I}{\partial T}\right)_H dH$$

When the change of heat content has been obtained, either from the magnetic measurements or calorimetrically, the equation $T = (\partial H/\partial S)_H$ may be applied, where H represents the heat content.

In the present work the change in heat content in zero field was measured calorimetrically. Unfortunately the rather low temperatures obtained with cobaltous sulfate heptahydrate were unexpected and insufficient preparation had been made for obtaining values of $(\partial I/\partial H)_S$ at numerous fields in the region between 0 and 800 oersteds as would be desirable. However enough values were obtained at various fields, up to 8600 oersteds, to enable a rough application of the method. The values of I obtained in the region just above 1° K. corresponded roughly to those which would be found for an ideal "spin only" case with $S = 3/2$. That this can be only roughly true is shown by the fact that the product χT is quite appreciably larger than the Curie constant calculated for the ideal case. However the ideal character of the magnetic system above 1° K. is shown by the fact that it makes practically no contribution to the heat capacity of the substance in this region. Accordingly the entropy change on magnetization of an ideal $S = 3/2$ substance was taken as an approximate measure of the entropy change. More accurate results could have been obtained by additional measurements of $(\partial I/\partial H)_S$ but these did not seem justified since it is expected that a more detailed magnetic investigation as a function of axial direction in single crystals will soon be possible.

The resistance of the carbon thermometer in the range below 1° K. obtained on the above assumption is given in Table IV and smoothed values are presented in Table V. The magnetic and calorimetric data utilized will be given below.

TABLE IV

RESISTANCE OF CARBON THERMOMETER BELOW 1°K.

Temp., °K.	Resistance, ohms
0.22	35,866
.27	35,532
.32	35,277
.36	35,132
.54	34,150
1.145	32,387

TABLE V

SMOOTHED VALUES OF RESISTANCE OF CARBON THERMOMETER BELOW 1°K.

Temp., °K.	Resistance, ohms
0.3	35,435
.4	34,834
.5	34,320
.6	33,917
.7	33,575
.8	33,272
.9	32,995
1.0	32,735

Below about 0.2° K. the resistance thermometer no longer gave results consistent with the susceptibility measurements. Immediately after a demagnetization the resistance fell rapidly from an initial high value and then changed only quite slowly, while the susceptibilities indicated that the bulk of the sample was warming at a roughly constant rate. After the temperature of the sample reached about 0.2°, as indicated by the susceptibility measurements, the thermometer behaved in a normal manner. The explanation of this is that at the lowest temperatures thermal contact between the sample and the thermometer

[13] Giauque and MacDougall, THIS JOURNAL, **60**, 376 (1938).

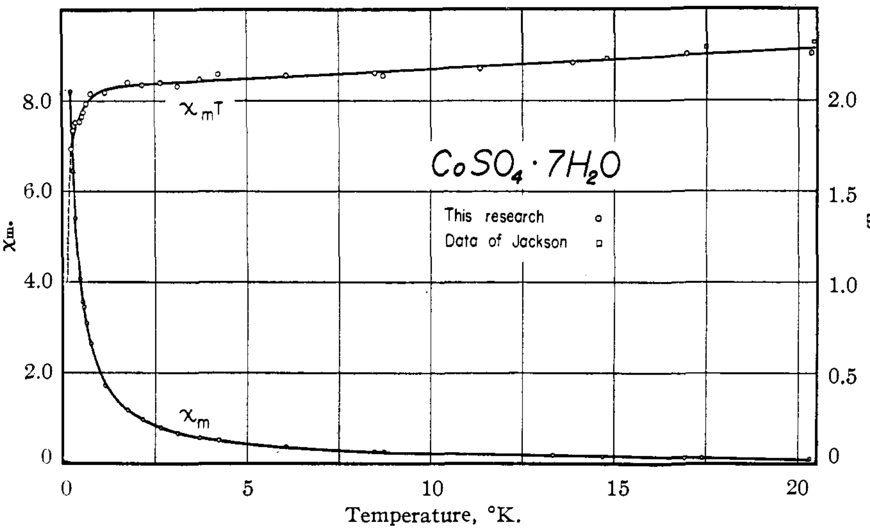

Fig. 2.—Initial susceptibility of $CoSO_4 \cdot 7H_2O$.

was exceedingly poor. Under these circumstances the thermometer and the outside of the sample tube could rapidly warm due to heat leaking in from the outside, and then remain at a temperature higher than that of the bulk of the sample until the entire sample had warmed sufficiently for the reëstablishment of thermal equilibrium. A similar effect has been observed in this laboratory with gadolinium phosphomolybdate tridecahydrate.

The Initial Magnetic Susceptibility of Cobaltous Sulfate Heptahydrate.—Some of the magnetic susceptibility measurements considered in this section were made under adiabatic conditions, however, the limiting values at zero field approach the initial isothermal susceptibility, χ.

$$(\partial I/\partial H)_S = (\partial I/\partial H)_T, \text{ when } H = 0$$

In using either the fluxmeter or inductance bridge methods referred to above it is necessary to compare the observations with the readings which would be obtained if the coils were at unit permeability. The product of turn area and field must be obtained when the coils have been cooled to liquid helium temperatures. Also it is very convenient to avoid moving the substance being investigated out of the coil. As in previous work in this laboratory the sample alone was heated until the susceptibility had reached a small value which could be applied as a correction. In this case the material was heated to 30° K. and the work of Jackson[1a] was used to make the correction.

Table VI gives the zero-field magnetic susceptibilities as a function of temperature. The values tabulated are those obtained at the temperature calibration points, together with approximate values below 1° K. and two points (at 6.07° and 8.48°) which lay between the liquid helium and liquid hydrogen calibration points.

The value of $\chi_m T$ falls off very slowly with decreasing temperature from 20 to 1° K., then appears to drop off much more rapidly below this temperature. The value at 1° K. is about 10% higher than the theoretical "spin-only" value of 1.864. The shape of the curve below 1° K. is approximate, since the temperatures were not known accurately in this region. Figure 2 shows χ_m and $\chi_m T$ *vs.* T.

TABLE VI

THE INITIAL MOLAL MAGNETIC SUSCEPTIBILITY OF COBALTOUS SULFATE HEPTAHYDRATE AS A FUNCTION OF TEMPERATURE

T, °K.	χ_m	$\chi_m T$	T, °K.	χ_m	$\chi_m T$
0.212	8.19	1.735	2.656	0.790	2.098
.289	6.35	1.835	3.125	.665	2.078
.348	5.40	1.879	3.732	.567	2.116
.464	4.06	1.884	4.224	.508	2.146
.537	3.56	1.912	6.07	.352	2.135
.564	3.43	1.935	8.48	.254	2.150
.646	3.07	1.983	8.72	.245	2.136
.763	2.67	2.037	11.35	.192	2.176
1.145	1.786	2.045	13.86	.159	2.204
1.772	1.185	2.100	16.95	.133	2.254
2.164	0.965	2.088	20.33	.113	2.26

The circles refer to the points listed above; the squares represent the values obtained by Jackson[1a] in the liquid hydrogen range. The agreement is probably within the accuracy of the present measurements in this temperature range, where the effects measured are considerably smaller than those at helium temperatures.

In addition to the measurements listed above, susceptibilities were determined below 0.2° K. Due to the absence of thermal data in this range, these cannot be presented as a function of temperature. The highest value found for χ_m was 19.35. From this the minimum temperature attained can be estimated as about 0.1° Curie (probably about 0.08° K.).

The Susceptibility of Cobaltous Sulfate Heptahydrate in Magnetic Fields.—The adiabatic differential susceptibility, $(\partial I/\partial H)_S$, was determined along various constant entropy paths produced by adiabatic magnetizations and demagnetizations. The observed values are given in Table VII. The measurements were all made in order of increasing fields because values at the lower temperatures are more important and most subject to the effect of heat leak. At higher fields and temperatures the differential susceptibility is relatively insensitive to these variables.

Many of the measurements in Table VII were made at temperatures where the calorimeter had a considerable heat capacity. Measurements made with either the fluxmeter or the inductance bridge yield a value of $(\partial I/\partial H)_S$ in which S is constant with respect to the substance but not with respect to the total entropy of the substance plus calorimeter. This is because the time required for a measurement is small compared to the time required for thermal equilibrium between the substance and its container.

When a large field is increased slowly the intensity of magnetization, I, will increase at constant entropy with respect to the total entropy of the substance and its container. Thus strictly speaking the values of $(\partial I/\partial H)_S$ cannot be used with complete accuracy in the equation

$$I = \int_0^H (\partial I/\partial H)_S \, dH$$

at temperatures where the calorimeter has a substantial heat capacity.

TABLE VII

MOLAL DIFFERENTIAL SUSCEPTIBILITY OF COBALTOUS SULFATE HEPTAHYDRATE

H	$(\partial I/\partial H)_S$	H	$(\partial I/\partial H)_S$	H	$(\partial I/\partial H)_S$
0	11.47	0	6.21	0	2.92
776	2.17	800	1.40	800	0.81
1185	1.15	1600	0.365	1600	.21
2373	0.231	2400	.152	2400	.18
5390	0.028	6000	.036	6000	.13
$T_{max.}$ = 1.68°K. gjMH/RT = 0.644		$T_{max.}$ = 3.01°K. gjMH/RT = 0.400		$T_{max.}$ = 4.69°K. gjMH/RT = 0.257	
$T_{min.}$ = 0.14°K.		$T_{min.}$ = 0.29°K.		$T_{min.}$ = 0.67°K.	
0	0.926	0	0.352	0	0.254
704	.575	800	.341	800	.242
1600	.415	1600	.332	1600	.240
2384	.352	2400	.298	2400	.239
6000	.22*	6000	.22*	8880	.24*
8528	.22*	8752	.24*		
$T_{max.}$ = 6.04°K. gjMH/RT = 0.284		$T_{max.}$ = 7.27°K. gjMH/RT = 0.242		$T_{max.}$ = 8.99°K. gjMH/RT = 0.198	
$T_{min.}$ = 2.31°K.		$T_{min.}$ = 6.03°K.		$T_{min.}$ = 8.41°K.	
0	0.215	0	0.181	0	0.154
2400	.200	768	.177	2000	.148
5200	.185	1920	.175	5200	.146
8640	.18*	8512	.18*	8832	.14*
$T_{max.}$ = 10.46°K. gjMH/RT = 0.166		$T_{max.}$ = 12.61°K. gjMH/RT = 0.136		$T_{max.}$ = 14.73°K. gjMH/RT = 0.121	
$T_{min.}$ = 10.00°K.		$T_{min.}$ = 12.45°K.		$T_{min.}$ = 14.66	

Fortunately at temperatures below a few degrees absolute the heat capacity of the calorimeter is trivial and the equation may be used with accuracy. Moreover, at higher temperatures the situation mentioned above is not very serious because the adiabatic differential susceptibility is small and has become very insensitive with respect to the several variables. At the higher temperatures the values approximate the isothermal differential magnetic susceptibility, because the considerable heat capacity of the substance, and the small amount of heat produced by a change in field, combine to keep the temperature nearly constant as may be seen by comparing the values of $T_{max.}$ and $T_{min.}$ given at the bottom of Table VII.

Most of the measurements given in Table VII were made with the fluxmeter and have a precision of 0.003 unit. The several observations at the higher fields which have been marked by asterisks were made with the induction bridge and 60 cycles per second; these have a precision of 0.01 unit.

An ideal paramagnetic substance with zero heat capacity would have a differential adiabatic susceptibility of zero. The observations given in Table VII show that cobaltous sulfate heptahydrate approximates this condition in the region just above 1° K. The differential susceptibility decreases very rapidly with increasing field until very low values are reached.

The results of the integration $I = \int_0^H (\partial I/\partial H)_S \, dH$ have not been tabulated here since the absence of data in the range 0 to 800 oersteds, at the lower temperatures, makes it impossible to do

TABLE VIII

INTENSITY AND ENTROPY OF MAGNETIZATION FOR IDEAL CASE OF $S = 3/2$

gjMH/RT	I	$\Delta S_{mag.}/R$
0.1	930	0.0028
.2	1853	.0110
.3	2762	.0246
.4	3651	.0431
.5	4514	.0663
.8	6906	.1586
1.0	8307	.2337
1.5	11090	.4388
2.0	12976	.6338
2.5	14213	.7986
3.0	15024	.9309
4.0	15925	1.1154
5.0	16345	1.2267
10.0	16744	1.3765
∞	16758	1.3863

TABLE IX

ENTROPY DATA FOR REGION BELOW 1°K.

T_{initial}	$\mathbf{H}_{\text{initial}}$	$gj\mathbf{MH}/RT$	$-\Delta S$ isothermal magnetization	$S_T - S_{1°K.}$ $\mathbf{H} = 0$	$S_{1°K.} - S$	Carbon thermometer ohms	Molal susceptibility
1.650	8640	1.052	0.506	0.009	0.497	36,240	...
1.827	8528	0.938	.416	.011	.405	36,202	...
2.238	8752	.786	.305	.013	.292	36,183	14.14
2.569	8768	.686	.239	.014	.225	36,063	11.40
3.462	5936	.345	.064	.017	.047	34,847	4.97
3.589	5952	.333	.060	.017	.043	34,739	4.68
4.800	8608	.360	.070	.022	.048	34,588	4.34
1.040	6816	1.317	.721	.000	.721	36,600	...
1.228	8400	1.374	.767	.004	.763	36,603	...
1.300	8512	1.315	.719	.005	.714	36,600	...
1.163	2384	.412	.091	.001	.090	35,509	6.58
2.683	6000	.404	.088	.014	.074	35,505	6.55
3.045	6800	.449	.107	.015	.092	35,500	6.50
3.720	8576	.463	.114	.018	.096	35,496	6.46
1.156	692	.139	.012	.003	.009	33,997	3.31
1.530	1046	.210	.024	.008	.016	33,967	3.30
2.119	2400	.227	.030	.012	.018	33,938	3.26

more than conclude that the intensity values correspond approximately to those which would arise from the $S = 3/2$, "spin-only," case in the region 1 to 5° K.

Ideal values of the intensity and entropy of magnetization for the $S = 3/2$ case are given in Table VIII. $g = 2$, $j = 3/2$, $M = heN/4\pi m = 5586$ = the molal Bohr magneton value. h = Planck's constant, e/m the ratio of charge to mass of the electron in e. m. u. N = Avogadro's number. R represents the gas constant = 1.9872 cal. deg.$^{-1}$ mole^{-1}. The values of the entropy change have been given as the dimensionless ratio $\Delta S/R$.

The calculated values of $\Delta S_{\text{mag.}}$, in conjunction with the heat capacities measured above 1° K., were used to calculate $S_{1°K.} - S_T$ for the states reached after demagnetizations to temperatures below 1° K. The final state was specified initially in terms of resistance or of zero-field susceptibility.

The observations and calculated quantities are given in Table IX. The values are listed in chronological order.

The Heat Capacity of Cobaltous Sulfate Heptahydrate.—The heat capacity of $CoSO_4 \cdot 7H_2O$ was measured from 0.20 to about 15° K. It was necessary to divide the investigation into three parts comprising the temperature ranges 0.20 to 1° K., 1 to 4° K. and 4 to 15° K.

The measurements in the range 4 to 15° K. were made in the usual manner. The calibrated carbon thermometer-heater was used to add energy, record the temperature increase and drift so that heat leak corrections could be made. The data are recorded in Series 1 and 3 of Table X.

The values were corrected for the heat capacity of the Pyrex glass container by means of the equation C_p (Pyrex) = $1.07 \times 10^{-6}T^3$ cal. deg.$^{-1}$g.$^{-1}$, The constant in this equation was obtained from data of Lyon and Giauque.[14] In the present case the total correction for 34.7 g. of Pyrex glass was $2.28 \times 10^{-4}T^3$ cal. deg.$^{-1}$ mole^{-1} of cobaltous sulfate heptahydrate.

TABLE X

HEAT CAPACITY OF COBALTOUS SULFATE HEPTAHYDRATE

Series 1			Series 2		
Temp., °K.	ΔT, °K.	C_p, cal./mole deg.	Temp., °K.	ΔT, °K.	C_p, cal./mole deg.
0.25	0.154	0.205	0.21	0.016	0.15
4.48	.83	.046	.24	.056	.17
5.46	1.27	.074	.44	.159	.10
6.41	1.68	.125	.96	.331	.033
7.88	1.59	.210		Series 3	
9.17	2.43	2.96	9.66	1.80	.353
11.19	2.67	5.27	11.37	1.79	.541
			13.33	2.46	.836

Series 1 was measured with liquid helium in the Dewar vessel and Series 3 was made with the calorimeter immersed in liquid hydrogen. Several heat capacity measurements were made in the range up to 22°; however, they were erratic and appeared to be low. An alteration in the energy circuit was made prior to measurements above 15° and defects in this circuit were later found to have been responsible. These unreliable data have not been included.

Between 1 and 4° K. the heat capacity was so small that differential measurements were impractical. In this region the heat capacity was evaluated from measurements with relatively large temperature differences. The data are given in Table XI.

TABLE XI

CHANGE OF HEAT CONTENT IN REGION 1° TO 5°K.

T_1, °K.	T_2, °K.	ΔH cal. mole^{-1}
2.12	4.35	0.0506
2.49	4.53	.0570
1.30	2.61	.0158
1.45	4.63	.0627

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(14) Lyon and Giauque, THIS JOURNAL, 71, 1647 (1949).

These observations, combined with adjacent heat capacity points, were used to obtain heat capacity values in the range 1 to 4° K.

In the range 0.20 to 1° K. the data were recorded in terms of either the initial susceptibility or the uncalibrated resistance thermometer or both. In order to apply the equation $T = (\partial H/\partial S)_{H=0}$, it was necessary to utilize the heat content data in advance of actually computing the values of the heat capacity. The data are given in Table XII.

At the very low temperatures the resistance thermometer was not in good equilibrium with the sample and was also not quite as sensitive as the magnetic susceptibility in the present case. Accordingly the initial susceptibility was used as the intermediate reference for heat content at the lower temperatures. However, the resistance thermometer was a better reference in the upper part of the region below 1°K.

TABLE XII

HEAT CONTENT DATA ON COBALTOUS SULFATE HEPTAHYDRATE BELOW 1°K.

Ohms		Molal		ΔH
R_1	R_2	χ_1	χ_2	cal. mole^{-1}
36,025	35,277	10.43	5.87	0.0316
35,954	35,905	9.21	8.44	.0023
35,857	35,602	8.15	7.18	.0094
35,077	34,223	5.17	3.65	.0158
33,280	32,235	...	..	.0111

The rate of change of heat content with entropy was then obtained for each of the several heat capacity points and these served to establish thermodynamic temperature in the region above 0.2° K. The values have been given above in Table IV. The entries in the table correspond to the several beginning or end points of the heat capacity measurements which were evaluated by interpolations in terms of $1/\chi$ since this is approximately linear with respect to temperature. Although this calculation depends on the assumption of values of the entropy change on magnetization from the "spin only" ideal case, as mentioned above, it is believed that they represent the true thermodynamic temperatures within an accuracy of from one to two hundredths of a degree. The values of C_p were then calculated at several points in the region below 1° K. The data have been given in Table X as Series 2 and the first entry in Series 1.

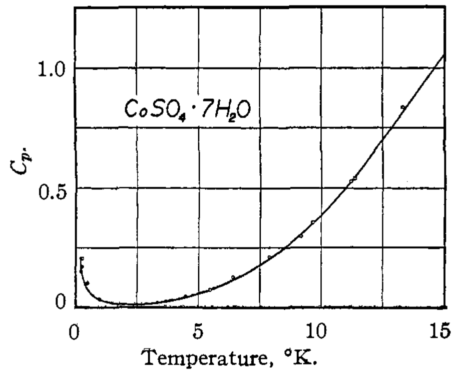

Fig. 3.—Heat capacity in calories per mole per degree.

The results are shown graphically in Fig. 3. Above 1° K. the curve was drawn through the points. Below 1° K. the curve was derived from a plot of entropy against log T from the experiments on adiabatic demagnetization. Values taken from the curve are given in Table XIII.

TABLE XIII

HEAT CAPACITY OF COBALTOUS SULFATE HEPTAHYDRATE

Values taken from a smooth curve cal. deg.$^{-1}$ mole^{-1}

T, °K.	C_p	T, °K.	C_p
0.20	0.232	4.0	0.037
.30	.147	4.5	.054
.40	.102	5.0	.071
.50	.070	6.0	.105
.60	.054	7.0	.150
.70	.038	8.0	.214
.80	.035	9.0	.288
.90	.031	10.0	.380
1.0	.027	11.0	.494
1.5	.016	12.0	.627
2.0	.008	13.0	.764
2.5	.005	14.0	.91
3.0	.011	15.0	1.06
3.5	.023		

Temperature Changes on Magnetization.—Temperature changes on magnetization were determined by means of the resistance thermometer. Corrections for the effect of the field on the resistance were made as indicated earlier. The most uncertain of these corrections amounted to only about 0.01° near 0.26°K.

Table XIV gives the temperature changes for magnetizations (or demagnetizations) with the lower temperatures below 1° K. Table XV gives the temperatures obtained on magnetization after small corrections to standard fields and initial temperatures. The corrections to standard fields have been made using the observed rate of change of ΔT with **H**.

Measurements on Remanent Magnetism and Hysteresis.—The thermodynamic considerations used in the interpretation of the measurements below 1°K. would not be valid if there were an appreciable amount of hysteresis or remanent magnetism at the low temperatures. A variety of experiments were performed to explore this possibility.

I. The e. m. f. induced in the measuring coils immediately after completion of demagnetization from a d. c. field of 8600 oersteds was observed. The very slight effect observed in the first thirty seconds corresponded to a loss of intensity of magnetization of 1 part in 40,000 of the saturation value and even this small effect may have been due to the iron in the reinforced concrete build-

TABLE XIV

TEMPERATURE CHANGE ACCOMPANYING ADIABATIC MAGNETIZATION

T_1, °K.	H, oersted	T_H, °K.
0.12[a]	1648	0.270
.12	2416	0.366
.12	6000	0.937
.12	6816	1.045
.12	8512	1.300
.285	928	0.550
.286	1592	0.845
.287	2384	1.163
.288	6000	2.683
.289	6800	3.045
.290	8576	3.720
.355	592	0.494
.389	5932	3.46
.407	5952	3.59
.445	8608	4.80
.580	800	1.156
.588	1600	1.530
.596	2400	2.12
.611	6000	4.31
.619	8576	5.24

[a] At the lowest temperature in this series, the carbon thermometer was not in equilibrium with the sample. The zero-field temperature was estimated; the other temperatures were measured.

TABLE XV

CHANGE OF TEMPERATURE WITH MAGNETIC FIELD AT CONSTANT ENTROPY

		Magnetic field in oersteds			
0	800	1600	2400	6000	8640
		Temperature degrees K.			
..	..	0.262	0.362	0.937	1.32
0.290	0.51	0.86	1.18	2.78	3.75
0.60	1.15	1.55	2.12	4.25	5.2
2.35	2.79	3.38	3.84	5.37	6.04
3.20	3.42	3.89	4.25	5.52	6.14
5.80	5.83	5.82	5.99	6.57	7.01
8.20	8.21	8.22	8.24	8.50	8.67
10.00	..	..	10.03	10.17	10.37
12.30	..	..	12.32	12.39	12.47
15.30	..	..	..	15.33	15.37

ing. The temperature after demagnetization was 0.16° K.

II. The application of a 60-cycle a. c. field produced no d. c. e. m. f. which could be observed on the sensitive galvanometer. The a. c. field might be expected to break down any residual magnetization and thereby induce an e. m. f. in the coils.

III. During a number of heat capacity measurements, including those at the lowest temperatures, the change in intensity of magnetization during the heating period was observed in terms of the e. m. f. induced in the coils surrounding the sample. The coils were connected in opposition to about the same turn area of fluxmeter coils to balance out small effects due to external sources such as the variations in the earth's field. A high sensitivity galvanometer was connected into this circuit. The steady field, due to the earth's field and iron of the building, induced a small e. m. f. due to decreasing susceptibility as the sample warmed, causing very small deflections. They could be explained by assuming a field of 2–3 oersteds, compared with the field of 2.0 oersteds previously measured by Giauque and MacDougall[13] under similar conditions in the same location. In the event that there was residual magnetism at the lower temperatures, one would expect an effect of considerable magnitude.

IV. The rate of temperature increase was observed before and after the application of a. c. fields to the measuring coils. Fields up to 14 oersteds, 60 cycles, and up to 29 oersteds, 550 cycles, were used for time intervals from 1 to 15 minutes. These fields, applied via the measuring coils, were not uniform, the value given is the average over the sample. At 0.15–0.20° K. the energy retained by the sample amounted to about 1 part in 8000 of the total energy introduced and removed by the a. c. field during the period of application. This represents an upper limit for the amount of hysteresis of the sample at these frequencies.

V. The initial susceptibilities as measured with the induction bridge at 60 cycles sec.^{-1} agreed with the fluxmeter values within the lesser accuracy of the induction bridge. The induction bridge could also be used at 550 cycles sec.^{-1} but it was necessary to use head phones in balancing it and it was only possible to obtain results of the same order of magnitude as those obtained with the fluxmeter.

The Entropy of Cobaltous Sulfate Heptahydrate.—Neglecting isotope and nuclear spin effects, as is customary, the entropy of cobaltous sulfate in the region below 1 °K. is due essentially to the distribution of the substance among the four levels of the limiting "spin only" state, $S = 3/2$. The total increase in entropy due to these levels in the region just above 1° K. has been estimated at 0.02 cal. deg.^{-1} mole^{-1}. Thus the entropy at 1° K. $= R \ln 4 - 0.02 = 2.73$ cal. deg.^{-1} mole^{-1}. By graphical integration above 1° K. the following values of the entropy are found: at 10° K., 2.89; and at 15° K., 3.16 cal. deg.^{-1} mole^{-1}.

Discussion of Results

The heat capacity of $CoSO_4 \cdot 7H_2O$ follows a T^3 law approximately in the region between 3 and 15° K. There is no indication that any heat capacity in this region is associated with the changing population of magnetic levels. Below 1° K. the heat capacity rises rapidly with decreasing temperature and probably reaches a maximum below 0.1° K. The increasing heat capacities are due to a set of low-lying magnetic levels, with over-all spacing of the group a few tenths of a wave number.

The magnetic susceptibility in zero field, in the region from 1 to 4° K., is somewhat above the theoretical value for an ideal "spin only" paramagnetic material with $S = 3/2$. The curie constant increases gradually from 4° K. to room temperature. This increase may be attributed to increased orbital contribution. The value of 3.07 at 292° K., given by Jackson,[1a] is 65% above the spin-only value, but still below the value calculated for complete spin-orbit coupling.

The magnetic and thermal data indicate that $CoSO_4 \cdot 7H_2O$ behaves approximately as an ideal paramagnetic substance in the region near 1° K. There is essentially no hysteresis or remanent magnetic moment in zero field. The separation between the magnetic levels in the absence of an applied magnetic field is quite small. This is in marked contrast to the behavior of the closely analogous salts $NiSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$. In the former case the three lowest magnetic states are separated by about 2.5 cm.$^{-1}$ from each other. In the latter case the over-all separation of five states has been estimated[14] at about 25 cm.$^{-1}$. The crystal structures and molar volumes of the three salts are quite similar, and the "dilution" of the magnetic ions by diamagnetic atoms should be about the same in each case. Apparently the ideal behavior observed with $CoSO_4 \cdot 7H_2O$ is characteristic of the nature of the cobalt ion itself.

The entropy associated with the population of the four low-lying magnetic levels is $R \ln 4 = 2.74$ cal. deg.$^{-1}$ mole^{-1}. It has been found possible to remove 0.8 cal. deg.$^{-1}$ mole^{-1} of this by a field of 8400 oersteds at 1.22° K.

We thank D. N. Lyon, T. H. Geballe, R. H. Busey and J. E. Kunzler for assistance with the experimental measurements and Mrs. B. J. Hurd for making the spectroscopic examination of the cobaltous sulfate.

Summary

The magnetic susceptibility and heat capacity of $CoSO_4 \cdot 7H_2O$, together with associated thermodynamic data, have been measured between about 0.2 and 15° K. The thermodynamic temperature has been estimated for measurements in zero field to 0.25° K.

The magnetic data and heat capacities agree with the assumption of a set of low-lying levels of the ground state multiplet with an over-all spacing of the order of a few tenths of a wave number. The data on intensity of magnetization can be explained at the lower temperatures by the assumption of four magnetic levels of very small separation, such as could arise from the electron spins alone, with the orbital contribution "quenched."

The residual magnetism after demagnetization to temperatures as low as 0.16° K., from magnetic fields sufficient to produce about 25% saturation, is at most 1 part in 40,000 of the "spin-only" saturation value. The energy absorbed due to magnetic hysteresis is no more than 1 part in 8000 at about 0.2° K. for a. c. fields up to 14 oersteds, 60 cycles, and 29 oersteds, 550 cycles.

The entropy of $CoSO_4 \cdot 7H_2O$ at 1° K. is 2.73, and at 15° K. is 3.16 cal. deg.$^{-1}$ mole.$^{-1}$.

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

The Entropy of Ethylene Oxide. Heat Capacity from 14 to 285 °K. Vapor Pressure. Heats of Fusion and Vaporization

BY W. F. GIAUQUE AND JOSEPH GORDON

This paper presents the results of a low temperature calorimetric investigation on ethylene oxide. The purpose of the measurements was the determination of the entropy of ethylene oxide gas from the third law of thermodynamics and the comparison of this value with one calculated from molecular data.

The measurements were made in a calorimeter which has previously been given the laboratory designation Gold Calorimeter II. References to its description and a discussion of the temperature scale are given by Gordon and Giauque.[1] The results in the previous paper were based on 0° C. = 273.10° K.; however, the values given here have been corrected to the basis 0° C. = 273.16° K.

Ethylene Oxide.—Ethylene oxide better than 99.5% pure was obtained from the Matheson Chemical Company. It was transferred from the cylinder in which it was received to a glass purification system by means of a connecting line containing rubber pressure tubing. The material was dried with phosphorus pentoxide and condensed as a solid by liquid air. The glass bulb in which it was condensed was protected from the liquid air by means of a removable metal sheath to prevent mixing in case of breakage. The system containing the solid was evacuated by means of a mercury diffusion pump to a pressure of 10^{-6} mm., followed by several repetitions of melting, freezing and pumping to remove any volatile impurities. The complete removal of all inert gas was desirable since very small amounts would have interfered with condenser operation during subsequent purification by fractionation.

The material was distilled in a silvered, vacuum jacketed, column with an ice-cooled condenser. Heat was supplied to the boiler of the column electrically by means of wire wound on its outer surface. The column which was about 1.3 cm. i. d.

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(1) Gordon and Giauque, THIS JOURNAL, 70, 1506 (1948).