Summary

1. The high-temperature photolysis of acetone has been shown to yield methyl ethyl ketone. The yield of methane under various conditions was studied. The results are consistent with a simple mechanism involving a wall reaction between free methyl radicals and acetone.

2. Propane was found to be attacked by free radicals from photolyzing acetone. The products contained no unsaturated hydrocarbons, and it is concluded that the free propyl and isopropyl radicals are stable at 610°K. and below. From the butane–isobutane ratio in the products, it is estimated that the activation energy for removal of a hydrogen from the secondary carbon atom is 2060 cal. less than for a similar attack on a primary linkage.

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

Magnetism and the Third Law of Thermodynamics. Magnetic Susceptibility, Adiabatic Change of Temperature on Magnetization and Heat Capacity of $NiSO_4 \cdot 7H_2O$[1]

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Among the more important problems arising in the use of the third law of thermodynamics for determining chemical equilibria is the one concerned with the multiple electronic states which persist in many solids at low temperatures. The commonest indication of this situation is found in the paramagnetism of such compounds. When the magnetic susceptibility changes with temperature one may infer that the electronic system has not reached a sufficiently low temperature so that substantially all of the atoms are in the lowest electronic state. Unless heat capacity measurements on such a substance are carried to sufficiently low temperatures, they may give no indication of the entropy associated with the magnetic system. The absence of a temperature coefficient in the magnetic susceptibility may be taken to indicate that the electronic contribution to the total entropy has been lost.

The magnitude of the magnetic susceptibility and its temperature coefficient usually give an indication of the type of system which exists in the solid but will not in general give the number of states and thus permit a calculation of the entropy. We have in mind the susceptibility as determined with a sample of powdered substance since this is most easily measured and usually provides the only data available in the few compounds where any data exist. In the case of a powder it is possible for more than one situation to give the same susceptibility and thus the entropy cannot always be inferred from such incomplete magnetic data alone.

A sufficiently detailed study of the axial susceptibilities of a perfect crystal as a function of temperature should often enable the calculation of the entropy associated with the magnetic system without the necessity of actual measurements at temperatures low enough to remove the entropy concerned. It is often possible to predict the number of electronic states to be expected in the solid state at higher temperatures but at very low temperatures it remains for experiment to decide if one or more of the upper levels is practically unoccupied.

One can obtain the entropy of such substances from heat capacity data alone but it will often require measurements at temperatures below 1°K. In fact it was this problem of determining the entropy in such systems which led to the invention of the adiabatic demagnetization process of producing very low temperatures in this Laboratory. However, many experimental difficulties still remain to be overcome in the temperature range below 1°K. before the accuracy customary at higher temperatures is attained.

In this paper we will discuss measurements of the heat capacity, magnetic susceptibility and related quantities for nickel sulfate heptahydrate from 1 to 15°K. This case is of unusual interest in illustrating the effects discussed above because the energy separations in the electronic states are large enough to cause the more interesting behavior to occur above 1°K. At the same time

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[1] Presented before the Boston Meeting of the American Chemical Society, Sept. 1939.

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the energies are small enough to cause the principal phenomena to take place at a sufficiently low temperature so that the heat capacity associated with the crystal lattice has decreased to such small values that it does not appreciably complicate the heat capacity due to the magnetic system.

In a later paper we shall present heat capacity results on this and other hydrates of nickel sulfate to ordinary temperatures. These together with measurements of the entropy of hydration will be used to illustrate further the application of the third law of thermodynamics to magnetic substances.

Preparation of Nickel Sulfate.—The nickel sulfate heptahydrate used for the measurements was prepared by recrystallization of commercial analytical reagent "cobalt free" nickel sulfate. An analysis showed that it contained 0.002% cobalt, 0.0002% iron and 0.02% of alkali and alkaline earth salts.

When the small needle-shaped crystals were filtered from the saturated solution and added to the cylindrical glass sample tube it was soon apparent that random orientation could not be obtained. The crystals which originally averaged about 3 mm. long and 1 mm. in diameter were broken with a mortar and pestle until the particles were irregular in shape. The material was crushed until it passed through a sieve with 0.5 mm. holes. The particles ranged from 0.2 to 0.5 mm. in diameter. In order to prevent excessive adsorption of helium[3] on the rough surfaces of the particles, the powder was placed in the saturated solution and allowed to stand for two hours. After filtering and incomplete drying the material was placed in the sample tube.

The sample weighed 78.18 g. (*in vacuo*). Analysis by precipitating the nickel as the dimethylglyoxime salt showed that this corresponded to 0.2754 mole of $NiSO_4 \cdot 7H_2O$ and 0.0443 mole of water. The sample cylinder was evacuated, filled at room temperature with a mixture of air (P = 74.1 cm. mercury) and helium (P = 1.88 cm. mercury), and sealed.

Apparatus.—The sample was mounted in the center of the iron-free solenoid magnet described by Giauque and MacDougall.[4] It was surrounded by a glass Dewar vessel into which liquid helium or liquid hydrogen could be introduced. The arrangement of the apparatus within the Dewar vessel is shown in Fig. 1. The portion shown could be immersed in liquid helium. The nickel sulfate sample, I, was contained in the cylindrical sample tube. The end surfaces were plane. An asbestos plug, K, prevented crystals from falling into the filling tube. The sample cylinder was 12.0 cm. long and 2.78 cm. inside diameter. It is shown suspended in a space which could be highly evacuated through the tube D. On the outside of the sample chamber there was a carbon thermometer-heater of the type previously described.[5] The platinized glass leads are shown at L. They were connected by fine platinum wire to two tungsten wires sealed through the vacuum jacket. Current and potential leads were soldered to the tungsten wires outside the jacket at N. A White Double Potentiometer was used for the measurements of electrical resistance and energy.

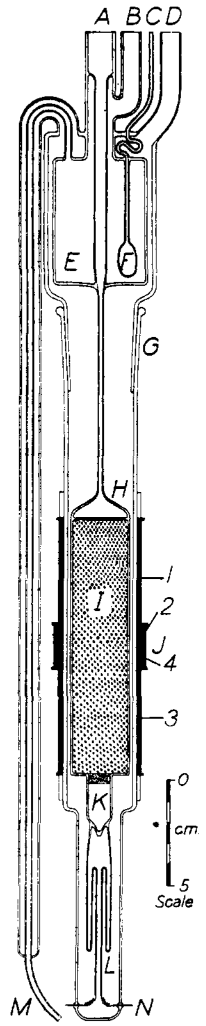

Fig. 1.—Apparatus for determining heat capacity and magnetic susceptibility at low temperatures.

The chamber E was a reservoir for liquid helium. As long as any helium remained in the Dewar it could be transferred into E through the vacuum-jacketed tube M by applying differential pressure. Thus the heat leak into the sample tube, along the glass tube from E, could be made small as long as any liquid helium remained. F indicates a helium vapor pressure thermometer. Helium could be condensed in the chamber H which was in thermal contact with the sample. This helium was used to cool the sample tube below the bath temperature and the carbon thermometer could be calibrated in terms of temperatures determined from the vapor pressures of helium in H. When the apparatus was designed we were unaware of the abnormally large rate of flow of films of liquid helium II over surfaces.[6,7,8] The apparatus behaved as we had expected above the lambda "point" of helium. Below 2.19°, however, the chamber E is an unnecessary complication since the film of helium II is sufficient to keep the upper parts of the apparatus cold as long as there is helium in the Dewar. It was not found possible to cool the sample tube more than a few hundredths of a degree below the bath temperature by pumping on the helium in H since the film of liquid inside the small tube permitted rapid thermal equilibrium between E and H. In order to make reliable calibrations of the carbon thermometer it was found necessary to introduce helium into the vacuum jacket and to have complete

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[3] Giauque and Stout, THIS JOURNAL, **60**, 393 (1938).

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

[5] Giauque, Stout and Clark, *ibid.*, **60**, 1053 (1938).

[6] Kürti, Rollin and Simon, *Physica*, **3**, 266 (1936).

[7] Rollin and Simon, *ibid.*, **6**, 219 (1939).

[8] Daunt and Mendelssohn, *Nature*, **141**, 911 (1938); **142**, 475 (1938).

temperature equilibrium between the bath and the sample.

The equations of Keesom and co-workers[9,10] for helium, of Palacios Martinez and Kamerlingh Onnes[11] for liquid hydrogen, and of Giauque, Johnston and Kelley[12] for solid hydrogen were used to find the temperature from the observed vapor pressure.

The measurements were made in January, 1936. In this run the calibration of the carbon thermometer below 2.19° was somewhat uncertain because of the rapid temperature drift due to the helium film. In April, 1938, the same carbon thermometer was recalibrated against helium and hydrogen vapor pressures, this time with the insulating vacuum broken. In the two-year interval the resistance of the thermometer had increased by about 7.5% throughout the range above 2.19°. The new calibration, together with the calibration of a similar carbon thermometer used for gadolinium phosphomolybdate,[13] served to determine the course of the resistance temperature curve below the lambda point. A smoothed table of resistance of the thermometer as a function of temperature was constructed.

The ground glass joint, G, was introduced to facilitate the assembly of the apparatus. The sample tube cannot be allowed to touch the vacuum jacket at any point. During assembly the sample tube was held in position by a holder fitted with a female ground joint slipped on at G. The small tube leading from H was sealed to the similar tube leading down from E. The holder was then slipped off and the vacuum jacket put in place. The small platinum wires between L and N were welded together through a temporary opening blown in the bottom of the vacuum jacket. The ground-glass joint was lubricated with rubber cement diluted with kerosene. Tight rubber bands were attached to keep the joint firmly closed while it was at room temperature. Some difficulty was encountered with maintaining the insulating vacuum at liquid helium temperatures and in later experiments the ground glass joint was abandoned. This did not, however, entirely eliminate the vacuum leak and we are convinced that it was due to a small crack along the tungsten seal.[14] A vacuum leak is particularly unfortunate in an apparatus such as this because the carbon thermometer heater adsorbs the gas during the period of rapid leak when the bath is below the lambda point of helium and allows it to evaporate slowly and prevents a good vacuum when the bath is above 2.19° and no appreciable amount of gas is leaking in.

The differential magnetic susceptibility of the sample was measured by means of the inductance bridge described by Giauque and MacDougall.[4] The inductance coils are shown at J in Fig. 1. The coils have been described by Giauque, Stout, Egan and Clark.[13] For the measurements when the field produced by the large magnet was off, the three inner coils were connected in series to give one continuous inductance coil 12 cm. long. This arrangement is termed Coil 1 + 2 + 3. When the large magnet was on, the two symmetrically placed end coils, 5 cm. long each, were connected in series but in opposite senses. Any e. m. f. generated in the upper coil by fluctuations in the field strength of the large magnet was exactly cancelled by an equal and opposite e. m. f. induced in the lower coil. This arrangement of coils, called Coil 1–3, completely eliminated the "jitters" which, when the large field was on, prevented accurate measurements of susceptibility by Coil 1 + 2 + 3.

The Heat Capacity of Nickel Sulfate Heptahydrate.—The heat capacity measurements were made by introducing a measured amount of electrical energy into the heater and calculating the rise in temperature from the change in resistance of the carbon thermometer. Corrections were made for the heat leak during the energy input. One calorie was taken as 4.1833 international joules. The heat capacity of the excess ice in the sample and of the glass sample tube was subtracted from the measured heat capacity. The heat capacity of the glass was estimated to be $0.9 \times 10^{-6}T^3$ cal. deg.$^{-1}$ g.$^{-1}$. That of the excess ice was obtained from the measurements of Simon and of Giauque and Stout.[15] The total correction was $1.42 \times 10^{-4}T^3$ cal. deg.$^{-1}$ mole^{-1} of $NiSO_4 \cdot 7H_2O$. The results of the heat capacity measurements are given in Table I and illustrated in Fig. 2.

TABLE I

HEAT CAPACITY OF $NiSO_4 \cdot 7H_2O$

T, °K.	ΔT (approx.)	C_p, cal. deg.$^{-1}$ mole^{-}
1.345	0.17	1.045
2.080	.22	1.206
2.412	.31	1.144
2.850	.44	1.057
3.439	.63	0.942
4.563	1.0	.697
5.708	1.4	.517
6.903	1.9	.433
7.032	2.2	.439
9.072	2.4	.421
10.28	2.6	.492
12.05	3.1	.698
14.20	2.5	1.05
16.10	2.3	1.42

The Adiabatic Change in Temperature with Magnetic Field.—Measurements were made of the adiabatic change in temperature when a magnetic field is applied at temperatures between 1.2 and 15°K. and at fields up to 8330 gauss. The quantity directly measured was the change in resistance of the carbon thermometer when a magnetic field was applied.

In order to calculate the change in temperature the change in resistance of the thermometer at constant temperature when a field is applied must be known. This quantity was measured in an

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(9) Keesom, Weber and Schmidt, *Commun. Phys. Lab. Univ. Leiden*, No. 202c.

(10) Keesom, *ibid.*, No. 219a.

(11) Palacios Martinez and Kamerlingh Onnes, *ibid.*, No. 156b.

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

(13) Giauque, Stout, Egan and Clark, *ibid.*, **63**, 405 (1941).

(14) See Giauque, Stout and Barieau, *ibid.*, **61**, 654 (1939), for a description of this leak.

(15) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

independent series of experiments made with helium in the insulating vacuum jacket so that the carbon thermometer remained at the temperature of the surrounding bath. It was found that at constant temperature the change in the resistance of the thermometer was positive. Within the experimental limit of error the effect was proportional to the square of the field strength at all temperatures above 2°K. and deviated only slightly from the square law at lower temperatures.

In Table II are presented the experimental results. The observed change in resistance, ΔR_1, was always negative. ΔR_2 is the difference between the resistance at the field **H** and the resistance the thermometer would have at the same temperature but in zero field. This quantity was calculated from the measurements with the insulating vacuum broken. $\Delta R = \Delta R_1 - \Delta R_2$ is the difference in resistance in zero field corresponding to the adiabatic change in temperature when the field was applied. The change in temperature, ΔT, was calculated from ΔR using the table of resistance against temperature.

TABLE II

ADIABATIC CHANGE IN TEMPERATURE WITH MAGNETIC FIELD

$NiSO_4 \cdot 7H_2O$ + Ice + Sample Tube

T, °K. (**H** = 0	R, ohms (**H** = 0)	**H** gauss	$-\Delta R_1$ ohms	ΔR_2 ohms	$-\Delta R$ ohms	ΔT °K.
1.226	85221	8070	313	307	620	0.075
1.229	85190	6200	208	187	395	.047
1.232	85166	3270	67	54	121	.0141
1.939	81161	3210	65	24	89	.0230
1.947	81126	6220	206	84	290	.076
1.955	81104	8430	352	145	497	.136
2.224	80167	8410	346	112	458	.152
2.232	80143	6200	202	64	266	.087
2.240	80118	3270	62.0	18.6	80.6	.0262
2.599	79106	3270	54.8	13.9	68.7	.0268
2.609	79080	6200	175	49	224	.089
2.618	79056	8380	312	82	394	.160
3.086	77979	8410	287	60	347	.177
3.102	77946	6200	158	34	192	.096
3.107	77936	3270	52	10	62	.0302
4.042	76417	8270	261	36	297	.232
4.043	76416	6200	157	21	178	.137
4.044	76414	3270	45	6	51	.0388
5.063	75253	3270	36.5	4.0	40.5	.0428
5.059	75259	6200	128	14	142	.152
5.052	75264	8270	219	25	244	.266
6.121	74383	8240	173	17	190	.275
6.079	74413	6200	100	10	110	.156
6.072	74418	3270	27.5	2.9	30.4	.0424
6.905	73873	3270	22.2	2.2	24.4	.0425
6.855	73903	6200	86	8	94	.163
6.819	73925	8200	144	14	158	.274
9.521	72648	8100	54.2	7.1	61.3	.164
9.451	72674	6200	31.6	4.3	35.9	.097
9.332	72720	3270	9.6	1.3	10.9	.0282
11.12	72110	3270	4.4	0.9	5.3	.0174
11.01	72143	6200	18.2	3.2	21.4	.070
10.95	72162	8200	31.6	5.4	37.0	.119
13.25	71517	8140	13.9	3.2	17.1	.067
15.23	71040	8330	6.8	2.3	9.1	.040

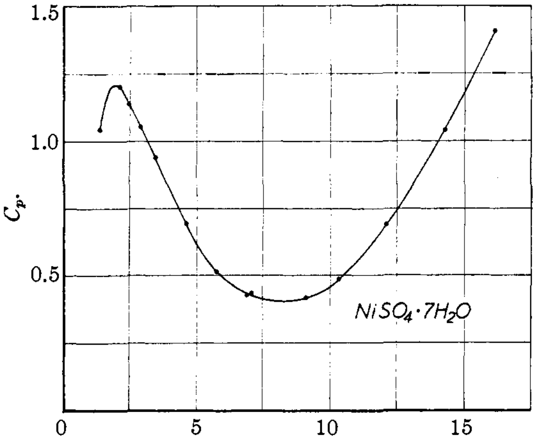

Fig. 2.—Heat capacity in calories per degree per mole of $NiSO_4 \cdot 7H_2O$.

The data in Table II are taken at fields close to 3270, 6200, or 8330 gauss. Making use of the fact that $\Delta T/\mathbf{H}^2$ does not change much with field, small corrections have been made to convert the ΔT's to the values corresponding to the three fields mentioned above. The values of ΔT so obtained are listed in Table III and illustrated in Fig. 3. The values of ΔT listed in Tables II and III are those for the entire calorimeter and contents whose heat capacity includes that of the glass sample tube and the excess ice as well as that of the $NiSO_4 \cdot 7H_2O$. At the higher tempera-

TABLE III

ADIABATIC CHANGE IN TEMPERATURE WITH MAGNETIC FIELD. VALUES CONVERTED TO THREE STANDARD FIELDS

H = 3270 gauss		**H** = 6200 gauss		**H** = 8330 gauss	
T, °K.	ΔT, °K.	T, °K.	ΔT, °K.	T, °K.	ΔT, °K.
1.232	0.0141	1.229	0.047	1.226	0.080
1.939	.0240	1.947	.076	1.955	.133
2.240	.0262	2.232	.087	2.224	.150
2.599	.0268	2.609	.089	2.618	.158
3.107	.0302	3.102	.096	3.086	.174
4.044	.0388	4.043	.137	4.042	.236
5.063	.0428	5.059	.152	5.052	.270
6.072	.0424	6.079	.156	6.121	.275
6.905	.0425	6.855	.163	6.819	.283
9.332	.0282	9.451	.097	9.521	.173
11.12	.0174	11.01	.070	10.95	.123
				13.25	.069
				15.23	.040

tures the heat capacity of the glass and the ice serves to make the observed rise in temperature smaller than would be observed with a calorimeter consisting only of $NiSO_4 \cdot 7H_2O$.

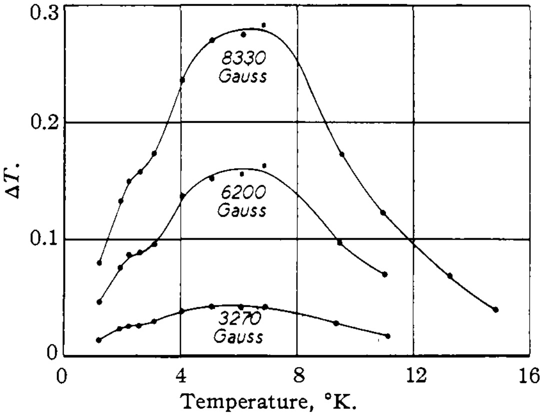

Fig. 3.—Temperature change upon adiabatic magnetization of $NiSO_4 \cdot 7H_2O$.

Magnetic Susceptibility of $NiSO_4 \cdot 7H_2O$.—In order to calculate the susceptibility from the measured inductances use has been made of the data of Giauque, Stout, Egan and Clark[13] on gadolinium phosphomolybdate using the same coils. In their experiment simultaneous measurements were made of the inductance of coil 1 + 2 + 3 and of the susceptibility by an induction method which made use of the coil factors for a cylindrical sample tabulated by Giauque and Stout.[16] Factors were determined relating the inductance, L, less the inductance at unit permeability, $L°$, to the volume susceptibility of the sample. The factor relating the increase in inductance of Coil 1-3 to that of Coil 1 + 2 + 3 was determined from the present measurements. The factors are independent of the susceptibility over the range covered by the present data. Using factors obtained in this way, and converting to the molal susceptibility, χ_M, we obtain the equations

$$L - L° = 2.25 \times 10^{-2}\,\chi_M\,L° \text{ for Coil } 1 + 2 + 3$$
$$L - L° = 1.91 \times 10^{-2}\,\chi_M\,L° \text{ for Coil } 1\text{-}3$$

In choosing the factor for Coil 1-3 use was also made of the data on $NiSO_4 \cdot 7H_2O$ where measurements of the inductances of both coils were made at the same temperature and in zero field. The values of $L°$ for both coils were obtained from measurements of the inductances with the coils at 4.22°K. and the sample at 40° and at 48°K. The small correction for $L - L°$ at these temperatures was obtained from the susceptibility measurements of Gorter, de Haas and van den Handel[17] on $NiSO_4 \cdot 7H_2O$. By having the coils at helium temperatures changes in $L°$ due to thermal expansion were avoided. $L°$ was 0.7402 henry for Coil 1 + 2 + 3 and 0.5208 henry for Coil 1-3.

It is important that the value of $L°$ shall not change during a series of measurements. The present coils were made of enameled wire and their inductance proved more stable at helium temperatures than that of coils made from silk covered wire used in earlier experiments. The stability of the coils and the measuring system may be seen from the data in Table IV.

TABLE IV

INDUCTANCE WITH COILS AND SAMPLE AT 4.22°

Date	Time	L, henries Coil 1 + 2 + 3	Coil 1-3
1-8-36	6:20 p.m.	0.7452	0.5237
1-10-36	11:32 a.m.	.7450	.5236
1-12-36	6:00 a.m.	.7451	.5237

The measurements were made during one continuous experiment. Between 1-8-36 and 1-10-36 the coils remained at liquid helium temperatures. Between 1-10-36 and 1-12-36 they were warmed to liquid air temperatures and recooled.

The quantity that is measured is the adiabatic differential susceptibility, $(\partial \mathbf{I}/\partial \mathbf{H})_S$.

$$(\partial \mathbf{I}/\partial \mathbf{H})_S = (\partial \mathbf{I}/\partial \mathbf{H})_T + (\partial \mathbf{I}/\partial T)_{\mathbf{H}}\,(\partial T/\partial \mathbf{H})_S$$

$(\partial T/\partial \mathbf{H})_S$ approaches zero as $\mathbf{H}$ approaches 0; so the adiabatic and isothermal differential susceptibilities become the same for small fields. Also $\partial \mathbf{I}/\partial \mathbf{H}$ and $\mathbf{I}/\mathbf{H}$ become identical. The fields produced by the inductance coils are sufficiently small, about 30 gauss, so that the measurements with the large magnet turned off yield values of the susceptibility at zero field. The

TABLE V

MOLAL MAGNETIC SUSCEPTIBILITY OF $NiSO_4 \cdot 7H_2O$ IN ZERO FIELD

T, °K.	χ_M	T, °K.	χ_M
1.23	0.57	4.22	0.29
1.94	.47	5.07	.24
2.22	.45	6.21	.20
2.32	.45	6.9	.18
2.60	.41	6.8	.20
2.97	.38	9.7	.13
3.10	.36	11.1	.13
3.82	.31	13.9	.10
4.04	.30	15.0	.09

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(16) Giauque and Stout, THIS JOURNAL, 61, 1384 (1939).

(17) Gorter, de Haas and van den Handel, *Commun. Phys. Lab. Leiden*, No. 218d.

susceptibility data on $NiSO_4 \cdot 7H_2O$ in zero field are listed in Table V.

The values are based principally on measurements with Coil 1 + 2 + 3. When several measurements were taken at the same temperature the average has been entered in the table. The uncertainty in the susceptibility values is estimated at between 0.01 and 0.02 unit.

Using Coil 1–3 the adiabatic differential susceptibilities of $NiSO_4 \cdot 7H_2O$ were measured at fields of 0, 3270, 6200 and 8330 gauss. The fields used sometimes differed slightly from the values listed and in such cases a small correction has been applied. The results are given in Table VI.

TABLE VI

MOLAL ADIABATIC DIFFERENTIAL SUSCEPTIBILITY OF $NiSO_4 \cdot 7H_2O$

T, °K. ($\mathbf{H} = 0$)	$(\partial I/\partial \mathbf{H})_S$ $\mathbf{H} = 0$	$\mathbf{H} = 3270$	$\mathbf{H} = 6200$	$\mathbf{H} = 8330$
1.23	0.57	0.54	0.46	0.42
1.95	.47	.45		.40
2.23	.45	.42	.42	.39
2.60	.41	.38	.36	.34
3.10	.36	.34	.34	.31
3.82	.31	.29	.27	.25
4.04	.30	.30	.28	.26
5.06	.24	.23	.23	.21
6.1	.20	.20	.19	.20
6.9	.18	.18	.18	.17
9.4	.14	.14	.14	.12
11.1	.13	.13	.13	.13

Thermodynamic Treatment of the Data.—From the thermal measurements on $NiSO_4 \cdot 7H_2O$ the isothermal change in entropy upon magnetization has been calculated. If the temperature changes from T to $T + \Delta T$ upon the reversible adiabatic magnetization from field 0 to $\mathbf{H}$ then the isothermal change in entropy at the temperature $T + \Delta T$ caused by the application of the field $\mathbf{H}$ is given by

$$\Delta S = \int_{T}^{T + \Delta T} C_p \, d \ln T$$

C_p is the heat capacity in zero field of the entire calorimeter and contents. To the values given in Table I must be added the heat capacity of the glass sample tube and of the excess ice. The values of ΔT used in the calculation were obtained from smooth curves through the data of Table III. The calculated values of ΔS are presented in Table VII. There are also listed values of $\Delta S/\mathbf{H}^2$ in (ergs gauss^{-2}) deg.$^{-1}$ mole^{-1}. 1 calorie = 4.185×10^7 ergs.

The values of $\Delta S/\mathbf{H}^2$ were plotted as a function of ln $\mathbf{H}$ and from the slope of the curves and the relation

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

the values of $1/\mathbf{H}\ (\partial S/\partial \mathbf{H})_T$ listed in Table VIII have been obtained. The values have been smoothed and those at zero field obtained by extrapolation of the smooth curves.

TABLE VII

ISOTHERMAL CHANGE IN ENTROPY UPON MAGNETIZATION OF $NiSO_4 \cdot 7H_2O$

	$-\Delta S$ cal. deg.$^{-1}$ mole^{-1}			$(-\Delta S/\mathbf{H}^2) \times 10^2$ (ergs gauss^{-2}) deg.$^{-1}$ mole^{-1}		
T, °K.	$\mathbf{H} =$ 3270	$\mathbf{H} =$ 6200	$\mathbf{H} =$ 8330	$\mathbf{H} =$ 3270	$\mathbf{H} =$ 6200	$\mathbf{H} =$ 8330
1.2	0.0097	0.0304	0.0491	3.80	3.31	2.96
1.4	.0126	.0400	.0674	4.93	4.35	4.07
1.6	.0142	.0450	.0766	5.56	4.90	4.62
1.8	.0148	.0465	.0807	5.79	5.06	4.87
2.0	.0149	.0463	.0805	5.83	5.04	4.86
2.4	.0127	.0427	.0754	4.97	4.65	4.55
2.8	.0105	.0352	.0634	4.11	3.83	3.82
3.0	.0099	.0325	.0590	3.86	3.54	3.56
3.5	.0093	.0307	.0527	3.64	3.34	3.18
4.0	.0080	.0282	.0480	3.13	3.07	2.89
5.0	.0053	.0197	.0349	2.09	2.14	2.10
6.0	.0038	.0141	.0253	1.48	1.54	1.53
7.0	.0029	.0111	.0198	1.14	1.21	1.19
8.0	.0023	.0088	.0161	0.91	0.96	0.97
10.0	.0014	.0060	.0103	.56	.65	.62
12.0	.0011	.0043	.0074	.42	.47	.45
15.0			.0048			.29

TABLE VIII

TEMPERATURE COEFFICIENT OF MAGNETIC SUSCEPTIBILITY OF $NiSO_4 \cdot 7H_2O$ CALCULATED FROM THERMAL DATA

$$-\frac{1}{\mathbf{H}}\left(\frac{\partial S}{\partial \mathbf{H}}\right)_T = -\frac{1}{\mathbf{H}}\left(\frac{\partial I}{\partial T}\right)_{\mathbf{H}} \text{ (ergs gauss}^{-2}\text{) deg.}^{-1}\text{ mole}^{-1}$$

T, °K.	$\mathbf{H} = 0$	$\mathbf{H} = 3270$	$\mathbf{H} = 6200$	$\mathbf{H} = 8330$
1.2	0.084	0.069	0.056	0.049
1.4	.104	.090	.074	.071
1.6	.115	.101	.090	.083
1.8	.116	.103	.094	.090
2.0	.116	.103	.094	.090
2.4	.099	.093	.089	.085
2.8	.081	.078	.075	.074
3.0	.076	.072	.069	.067
3.5	.073	.068	.063	.059
4.0	.064	.061	.059	.056
5.0	.042	.042	.042	.042
6.0	.031	.031	.031	.031
7.0	.023	.023	.023	.023
8.0	.019	.019	.019	.019
10.0	.013	.013	.013	.013
12.0	.009	.009	.009	.009
15.0	.006	.006	.006	.006

The second law of thermodynamics requires that $(\partial S/\partial \mathbf{H})_T = (\partial I/\partial T)_{\mathbf{H}}$. The entries in Table VIII are therefore values of $1/\mathbf{H}\ (\partial I/\partial T)_{\mathbf{H}}$ from which one may calculate I as a function of

TABLE IX

COMPARISON OF VALUES OF I/**H** CALCULATED FROM THERMAL MEASUREMENTS WITH THOSE CALCULATED FROM MAGNETIC MEASUREMENTS

	H = 0			**H** = 3270 gauss			**H** = 6200 gauss			**H** = 8330 gauss	
T, °K.	I/**H** Thermal	I/**H** Magnetic	*T*, °K.	I/**H** Thermal	I/**H** Magnetic	*T*, °K.	I/**H** Thermal	I/**H** Magnetic	*T*, °K.	I/**H** Thermal	I/**H** Magnetic
1.23	0.550	0.57	1.24	0.524	0.55	1.28	0.505	0.54	1.31	0.491	0.51
1.95	.469	.47	1.97	.454	.46	2.03	.440	.44	2.08	.427	.44
2.23	.437	.45	2.26	.425	.44	2.31	.414	.43	2.38	.401	.42
2.60	.400	.41	2.63	.392	.40	2.69	.381	.39	2.76	.370	.38
3.10	.360	.36	3.13	.354	.36	3.20	.344	.34	3.27	.336	.34
3.82	.308	.31	3.86	.305	.30	3.95	.297	.30	4.04	.290	.29
4.04	.294	.30	4.08	.291	.29	4.18	.284	.29	4.27	.278	.29
5.06	.242	.24	5.1	.241	.24	5.21	.235	.23	5.33	.230	.23
6.1	.206	.20	6.1	.206	.20	6.3	.199	.20	6.4	.196	.20
6.9	.185	.18	6.9	.185	.18	7.1	.179	.18	7.2	.176	.18
9.4	.138	.14	9.4	.138	.14	9.5	.135	.14	9.6	.134	.14
11.1	.116	.13	11.1	.116	.13	11.2	.114	.13	11.2	.114	.13

temperature if it is known at any one temperature. The measurement of the susceptibility at 14.35° by Gorter, de Haas and van den Handel[17] yields I/**H** = 0.088 at this temperature and throughout the range of fields which we have used. An alternative method is to plot values of $T^2/\mathbf{H}\ (\partial S/\partial \mathbf{H})_T$ against $1/T$, extrapolate to $1/T = 0$, where I = 0, and then by graphical integration under the extrapolated portion of the curve determine the value of I/**H** at some temperature within our range of measurement. In making this extrapolation one can make use of the fact that the high temperature limit of $T^2/\mathbf{H} \times (\partial S/\partial \mathbf{H})_T$ is the Curie constant. A calculation of this type yields I/**H** = 0.092 at 14.35°. Although the latter method has the advantage of making use of only thermal data we prefer to use the accurate magnetic data that are available at 14.35° to fix one value of I/**H**. It should be noted, however, that the error that would be introduced by the extrapolation to infinite temperature is only 0.004, or less than 1% of the value of I/**H** at the lowest temperatures.

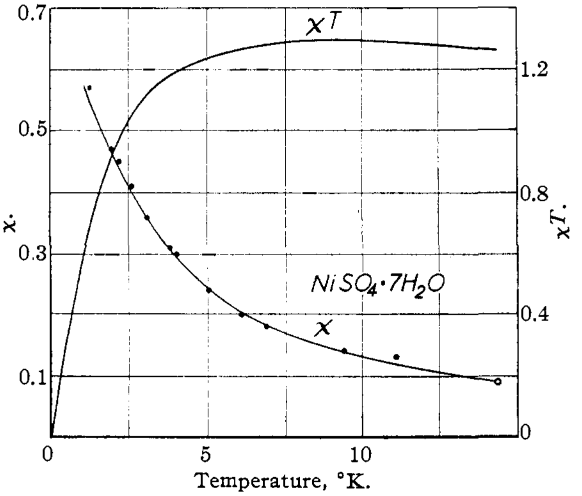

Fig. 4.—Magnetic susceptibility of $NiSO_4 \cdot 7H_2O$. The curves are obtained from the thermal data. The points represent the values obtained by magnetic induction measurements.

Table IX is a comparison of the values of I/**H** calculated from the thermal measurements using the second law of thermodynamics with those calculated from direct magnetic measurements.

$$\frac{\mathrm{I}}{\mathbf{H}}\,(\text{thermal}) = \frac{1}{\mathbf{H}}\int_{14.35}^{T}\left(\frac{\partial S}{\partial \mathbf{H}}\right)_T \mathrm{d}T + 0.088$$

$$\frac{\mathrm{I}}{\mathbf{H}}\,(\text{magnetic}) = \frac{1}{\mathbf{H}}\int_{0}^{\mathbf{H}}\left(\frac{\partial \mathrm{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H}.$$

The values of $(\partial \mathrm{I}/\partial \mathbf{H})_S$ are taken from Table VI. The integration for I/**H** (thermal) is at constant field strength and that for I/**H** (magnetic) at constant entropy. Within the limit of error of the magnetic measurements there is complete agreement between the two sets of values. The agreement shows that the equations based on the second law of thermodynamics may be successfully applied to measurements on this magnetic system.

In Fig. 4 the susceptibility data for zero field have been shown graphically. The curve of χ is obtained entirely from the more accurate thermal measurements. The points represent the values obtained from the magnetic induction data. The measurement of Gorter, de Haas and van den Handel,[17] at the lowest temperature of their investigation, has been included on the graph and is indicated by the open circle. Our method of susceptibility measurement becomes very inaccurate at low susceptibilities. Within the limit of error our measurements agree with the more accurate result of the Leiden workers at 14.35°K.

For a substance obeying Curie's law $\chi_m T$ is independent of temperature. It is seen from Fig. 4 that below 4° the susceptibility decreases rapidly below the Curie law value. That Curie's law must fail at sufficiently low temperatures is a consequence of the third law of thermodynamics. Figure 4 shows one type of deviation which is approaching the thermodynamic requirement that $(d\chi/dT)_H = 0$ at 0°K. The character of deviations from Curie's law is also of interest in connection with the use of this law in magnetic thermometry.

Discussion.—The maximum at 1.8°K. in the heat capacity curve of $NiSO_4 \cdot 7H_2O$, the deviation of the magnetic susceptibility from the Curie law value, and the drop in the isothermal entropy of magnetization below 2° may be explained qualitatively as due to the changing population of the magnetic ions among a group of energy states in the crystal. At high temperatures the magnetic ions are randomly distributed among all the available states whose energy separation is small compared to kT. As the temperature is lowered they will drop down to the lowest of the group of energy states until at the absolute zero all randomness is lost and the entropy is zero.

The ground state of gaseous Ni^{++} is, according to Hund,[18] a ^3F. In the crystal the electrostatic fields of the ions surrounding the nickel atoms will radically change the pattern of the energy levels. Schlapp and Penney[19] have calculated the energy level distribution to be expected from a crystalline field that is predominantly cubic but with a small field of rhombic symmetry added. They find that when the effect of the spin-orbit coupling is taken into account the lowest level splits into three closely spaced non-degenerate states. They have not estimated the separation between these states except to say that it is small compared to the energy separating the group from the next highest levels. The susceptibility calculations of Schlapp and Penney yield an expression for the susceptibility of the form

$$\chi = (C/T) + B$$

The susceptibilities calculated from their equation are in good agreement with the measurements of Gorter, de Haas and van den Handel[17] on $NiSO_4 \cdot 7H_2O$ except for the points at the temperatures of liquid hydrogen. At lower temperatures the equation deviates widely from the values of susceptibility which we have presented in Table IX and is qualitatively not in agreement with our data. The equation evidently cannot be valid at low temperatures since $\partial\chi/\partial T$ calculated from it does not approach zero at the absolute zero of temperature as required by the third law of thermodynamics. In their susceptibility calculations Schlapp and Penney have expanded the Boltzmann exponentials in a series in $1/T$ and neglected all powers higher than the second. Such a procedure would evidently become very inaccurate at low temperatures.

We have made calculations of the heat capacity to be expected assuming that each ion of nickel has available three equally spaced states, each of weight one, and that there is no interaction among the magnetic ions. The distribution function is

$$Q = 1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT}$$

The shape of the curve assuming an energy difference of 2.6 cm.$^{-1}$ between adjacent states is in qualitative agreement with the observed heat capacity curve although the agreement is not exact. Better agreement is obtained using a function

$$Q = 1 + e^{-\epsilon/kT} + e^{-2.14\epsilon/kT}$$

which has been chosen to give the same maximum value of the heat capacity as that found experimentally. This function corresponds to a spacing of 2.5 cm.$^{-1}$ between the first and second levels and 2.8 cm.$^{-1}$ between the second and the third. Since slight errors in the temperature scale used for the carbon thermometer can greatly affect the height of the maximum in the observed heat capacity curve and since the model used for the calculation may be over simplified we do not believe that the heat capacity data allow a choice between the two energy spacings.

The entropy, however, is little affected by small errors in the temperature scale. Since the crystalline heat capacity is very small in the region where the magnetic heat capacity is largest an accurate correction may be made for the entropy associated with the crystalline vibrations. By a graphical method the entropy between 1.345° and 10° was evaluated. Using the function

$$Q = 1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT}$$

with $\epsilon = 2.6$ cm.$^{-1}$ the magnetic entropy between 0 and 1.345°K. and between 10° and infinite temperature has been estimated. The crystalline

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[18] Hund, "Linienspektren," Berlin, 1927, p. 165.

[19] Schlapp and Penney, *Phys. Rev.*, **42**, 666 (1932).

entropy at 10°K. was obtained by fitting the points above this temperature, corrected for a small calculated magnetic heat capacity, to a T^3 law. The calculation is presented in Table X.

Table X

Calculation of Magnetic Entropy of $NiSO_4 \cdot 7H_2O$

$S_{10°} - S_{1.345°}$ (graphical)	1.68
$S_{1.345°}$ (magnetic)	0.49
$S_{T = \infty} - S_{10°}$ (magnetic)	.09
	2.26
$-S_{10°}$ (crystalline)	−0.06
Total magnetic S	2.20 cal. deg.$^{-1}$ mole^{-1}
R ln 3 =	2.18 cal. deg.$^{-1}$ mole^{-1}

A similar calculation making the extrapolations with the function

$$Q = 1 + e^{-\epsilon/kT} + e^{-2.14\epsilon/kT}$$

gives a total magnetic entropy of 2.24 cal. deg.$^{-1}$ mole^{-1}. The entropy associated with three states per atom of nickel is R ln 3 = 2.18 cal. deg.$^{-1}$ mole^{-1}. The agreement is evidence that at high temperatures each magnetic ion is randomly distributed among three states. The usual "third law" calculation of the entropy at high temperatures of a substance makes use of an extrapolation from about 15°K. to the absolute zero using the Debye function for crystalline heat capacity. Such an extrapolation for $NiSO_4 \cdot 7H_2O$ would completely miss the magnetic entropy which is lost well below 15° and would give a so-called "third law entropy" 2.18 cal. deg.$^{-1}$ mole^{-1} too small. In applying the third law to paramagnetic substances it must be kept in mind that a Debye extrapolation to the absolute zero can be safely made only from a temperature where the temperature coefficient of magnetic susceptibility, and therefore the entropy of the magnetic system, has become zero.

Summary

The heat capacity of $NiSO_4 \cdot 7H_2O$ has been measured by means of an amorphous carbon thermometer heater from 1 to 15°K.

The adiabatic change of temperature on magnetization has been measured over the same temperature range and in fields up to 8000 gauss.

The differential magnetic susceptibility was measured by the method of opposed identical coils to eliminate effects due to fluctuations in the field of the magnet.

The ordinary magnetic susceptibility was calculated from the differential susceptibility.

The susceptibility was also calculated from the observed heat capacity and temperature change on magnetization using equations based only on thermodynamics. The values so calculated are more reliable than the directly observed susceptibilities, which agree within the limit of error.

The electronic system makes a large contribution to the heat capacity at temperatures where the lattice heat capacity is unimportant. A maximum in the heat capacity occurs near 1.8°K.

The heat capacity data have been used to show that the entropy associated with the electronic system is R ln 3. This shows that the system has three electronic levels. They are about equally separated, the separation being about 2.6 cm.$^{-1}$ which is equivalent to 7.4 cal. mole^{-1}.

The character of the heat capacity curve of $NiSO_4 \cdot 7H_2O$ down to 15°K. gives no indication that electronic entropy exists and the usual extrapolation would be in error by 2.2 cal. deg.$^{-1}$ mole^{-1}.

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