

2. Some reactions of the hydrolysis and pyrolysis products are described, and the constants of the isomeric forms of 3-chloro-2-methylallyl

alcohol and of 1-chloro-2-methyl-3-phenylpropene are reported.

OAK PARK, ILLINOIS

RECEIVED MARCH 7, 1936

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

The Production of Temperatures below 1° A. The Heat Capacities of Water, Gadolinium Nitrobenzene Sulfonate Heptahydrate and Gadolinium Anthraquinone Sulfonate

BY D. P. MACDOUGALL AND W. F. GIAUQUE

Following our work on the production of temperatures below 1°K. by adiabatic demagnetization of gadolinium sulfate octahydrate¹ we investigated the effect of diluting the gadolinium atoms.

Numerous low temperature investigations of magnetic susceptibility, principally at the Kamerlingh Onnes Laboratory of the University of Leiden, indicate that ideal paramagnetic situations are more nearly approximated by compounds in which the distances between the magnetic atoms are large.

Gadolinium nitrobenzenesulfonate heptahydrate and anthraquinone sulfonate hydrate were selected because these substances, like most sulfonates, crystallize readily. The number of molecules of water of crystallization on the anthraquinone sulfonate was unknown but was presumably six or seven.

A brief summary of the results presented here has been given previously.²

Apparatus.—The magnetic and principal features of the apparatus were the same as in our previous work on gadolinium sulfate.¹ However, several parts of the apparatus were improved considerably. In a few measurements on gadolinium sulfate at a frequency of 1000 cycles/sec. the inductance changed by about 5% from the value at 60 cycles/sec. This effect was due to eddy currents set up in the surrounding metal apparatus by the alternating current used for measuring inductance. The eddy currents were almost entirely located in a brass container which surrounded the Dewar vessel used for maintaining a liquid helium bath around the sample and inductance coil. This brass container, which is shown as C in Fig. 2 of our previous paper,¹ was immersed in liquid air and served as a vacuum tight enclosure for the helium gas. The brass container was discarded and the apparatus modified to the

form shown in Fig. 1. Since the Dewar for liquid helium had to be enclosed to avoid the entry of air, and especially to permit the use of reduced pressure on the liquid helium bath, the inner tube of the solenoid case was used for this purpose. It is necessary to protect the exterior of the Dewar containing liquid helium by liquid air. This was done by passing liquid air through a non-inductively wound helical coil, E, of brass tubing 0.4 cm. o. d. which was firmly and closely attached to the exterior of the Dewar, by means of fiber separators and adhesive tape. The top of the apparatus was protected by liquid air in a cup, C, which also acted as a supply for the brass coil system. Such a system works well by gravity if the tubing is of sufficiently large diameter. However, for reasons of space economy we used small tubing and applied a vacuum at the exit end, B, of the tube. The level of the liquid air in the cup, C, was maintained constant by a float valve (not shown) attached to the end of a transfer tube connected with a 50-liter supply Dewar. The necessary flow, about 1.5 liter/hr., was maintained by means of a gas thermometer controlled magnetic valve on the vacuum line. The arrangement was very satisfactory and it was somewhat easier to solder only the inlet and outlet tubes than, as previously was necessary, to make the rather large solder joint on the brass Dewar case during assembly. The inner tube of the solenoid case was extended to the flange, D, where the joint was easily made tight by means of a gasket and stopcock grease.

We have previously¹ commented on the difficulty of maintaining a vacuum in sealed Pyrex Dewars in contact with helium and since the large outer Dewar, I, was of Pyrex a pumping line was left permanently attached at J. It was not necessary to pump the Dewar during a forty or fifty hour run. The inner Dewar was made of Jena glass and this can be used for several months without reëvacuation.

In early experiments the upper portion of the Dewar for liquid helium contained a liquid hydrogen chamber, which is shown as D of Fig. 2 in our previous paper.¹ The purpose of the liquid hydrogen was to cool the apparatus to a sufficiently low temperature before the addition of liquid helium and also to block off heat leak from above. Although the apparatus remained at liquid helium temperatures for about ten or twelve hours with one filling of liquid helium we soon reached the conclusion that the arrangement would be improved by the removal of the liquid hydrogen chamber. Actual removal of the chamber

(1) Giauque and MacDougall, (a) *Phys. Rev.*, **43**, 768 (1933); (b) **44**, 235 (1933); (c) *This Journal*, **57**, 1175 (1935).

(2) (a) Meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18–23, 1934. (b) *Phys. Rev.*, **47**, 885 (1935).

showed its presence to have been a considerable handicap as the time during which the apparatus could be kept at the temperatures of liquid helium with one filling was

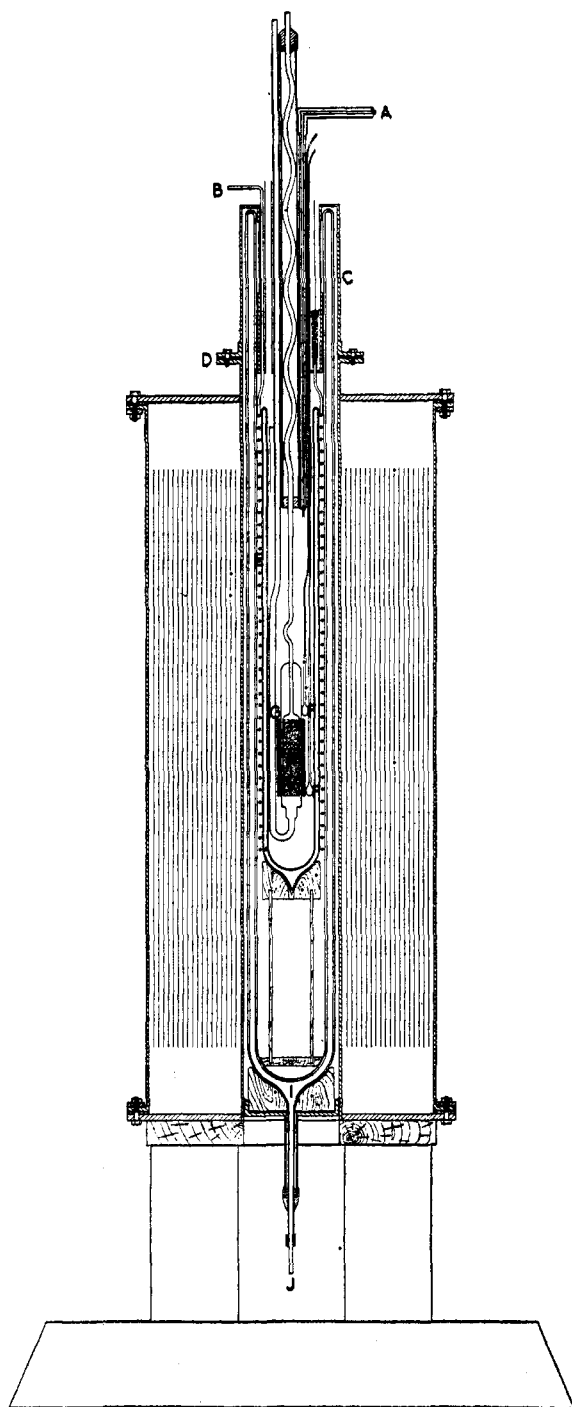


Fig. 1.—Cooling apparatus mounted in magnet.

about doubled. This was due in part to the fact that more helium could be added but the time was somewhat increased for a comparable amount and condition. In some recent work one filling of helium has sufficed for as

long as forty hours. Eliminating the use of liquid hydrogen in this connection is of course an advantage. In order to cool the apparatus from room temperature to liquid hydrogen temperatures, cold helium is circulated through the apparatus from the adjacent helium liquefier. The apparatus is first cooled to liquid air temperatures in this manner, then liquid hydrogen replaces the liquid air in the helium liquefier and the process is continued until a sufficiently low temperature is reached. The above method takes advantage of a procedure which is necessary in order to bring the helium liquefier into operation and the cold helium gas follows the same transfer path. A, from liquefier to magnet, later used for liquid helium.

The bath temperature was observed by means of helium vapor pressure thermometers located at F. F. Fig. 1.

Gadolinium Nitrobenzene Sulfonate Heptahydrate.—

The gadolinium nitrobenzene sulfonate heptahydrate, $Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$, was prepared by adding gadolinium oxide to *m*-nitrobenzene sulfonic acid. The material was placed in a sample tube of the type shown at H of Fig. 1. The sample was in the form of a cylinder 1.6 cm. in diameter and 12 cm. in length. As in previous measurements the sample was centered in an inductance coil, G, of the same length and could be insulated thermally from the coil and bath by a vacuum space. A discussion of magnetic susceptibility measurements with this arrangement has been given previously.¹⁰ With the modified apparatus the change of inductance with frequency was very small, the variation being of the order of one or two tenths of one per cent. over the range from 60 to 1000 cycles/sec. The 1000 cycles/sec. was produced with a tuning fork oscillator and a range from 60 to 550 cycles could be obtained by varying the speed of a small generator. A portion of the small frequency variation was of course due to capacity effects within the coil itself. Inductance Coil III¹⁰ was used for the measurements.

In a series of experiments on February 10–11, 1934, various exploratory measurements, made over a period of seven hours, showed that the gadolinium nitrobenzene sulfonate heptahydrate is more ideal magnetically and more effective in attaining low temperatures than is gadolinium sulfate octahydrate. We shall not present these data, as improved measurements were taken immediately afterward, and in another experiment on February 24–25, 1934. More liquid helium was added to the apparatus and the results of careful observations were recorded. The preliminary period served to season the inductance coil with respect to time lag in thermal contraction. This small but annoying effect was due to the presence of considerable organic substance as wire insulation. An accurate correction can be made but in recent work it has been found possible almost to eliminate this effect by avoiding the use of silk covered wire.

In the measurements on February 24–25 the glass apparatus was changed to the form shown in Fig. 2. The pur-

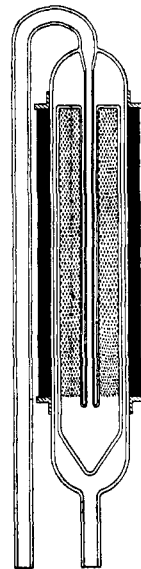


Fig. 2.—Inductance coil and inverted type sample tube.

pose of this change was to increase the thermal resistance of the small glass line leading to the sample tube and to have the bath end of this tube immersed in liquid helium even when the liquid level was low.

temperature was obtained from tables given previously.³ χ represents the molal magnetic susceptibility.

The heat capacity was obtained from the relation $dS/d \ln T = C$, a graph and Curie temperatures being used for this purpose. The results are given in Table II and are shown graphically in Fig. 3, which also includes data on gadolinium anthraquinone sulfonate, to be discussed later, and a curve for gadolinium sulfate octahydrate¹⁰ which has been included for comparison. While the curves are somewhat similar in form it is evident that no simple formula is adequate to represent the general behavior. This is not surprising when one considers the complex effects of various crystal structures on the magnetic interactions that are responsible for heat capacity in this region.

Measurements of Differential Susceptibility.—We have shown¹⁰ previously the value of measurements of differential susceptibility in a thermodynamic treatment of magnetism at low temperatures. This is especially true in connection with the determination of Kelvin temperature defined by the second law of thermodynamics. To make such measurements in strong fields it was necessary to balance the inductance bridge with headphones. The small but rapid current variations in the only direct current supply available for the magnet made it impossible to

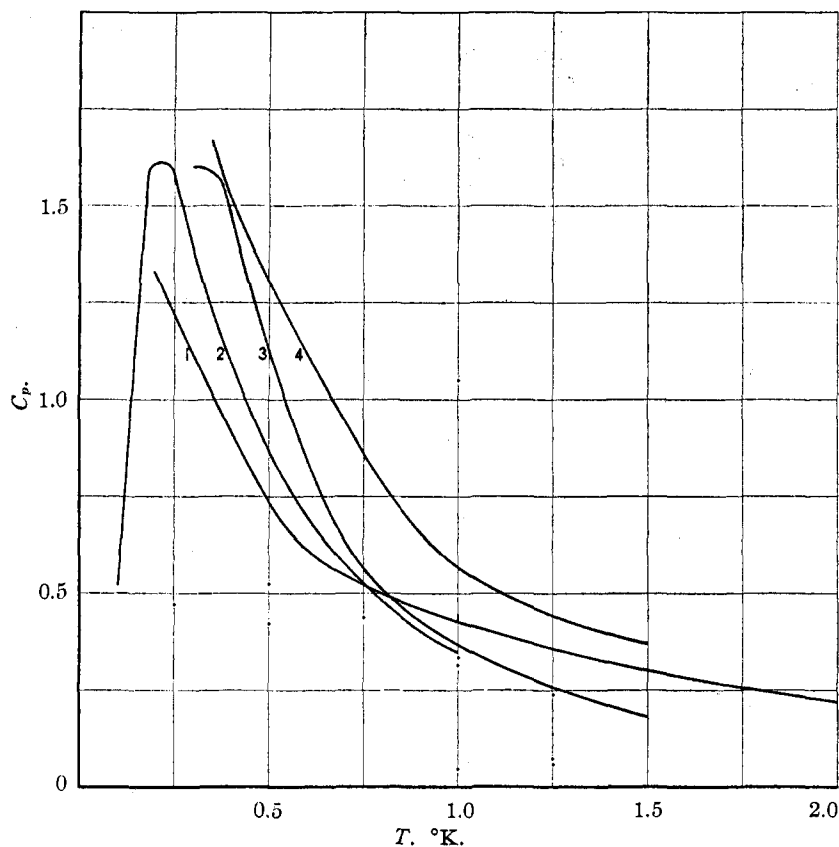


Fig. 3.—Heat capacity in calories per degree per gram atom of gadolinium: 1. gadolinium anthraquinone sulfonate hydrate; 2. gadolinium nitrobenzene sulfonate heptahydrate; 3. gadolinium sulfate octahydrate; 4. anhydrous gadolinium anthraquinone sulfonate.

The Heat Capacity of $Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$.—The results of adiabatic demagnetizations are given in Table I. The last observation was taken with the apparatus of February 25; the others on February 11. The helium gas pressure in the sample tube was about 10^{-4} mm. during the measurements. All of these observations were made with a measuring current of 60 cycles/sec. The isothermal entropy change with magnetization at the initial

TABLE I
THE CHANGE OF ENTROPY WITH TEMPERATURE PER MOLE
OF $Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$

T , °K., initial	H_{gauss}	x_{final}	T , ° Curie final	ΔS cal./deg.	$S_{1^\circ K.} - S_T$
1.62	6610	24.8	0.315	1.056	0.916
1.62	5630	21.9	.358	0.839	.699
1.56	8040	32.1	.2435	1.420	1.294
1.56	4050	15.5	.504	0.530	0.404
1.56	3215	12.2	.642	.355	.229
1.56	2840	11.3	.694	.278	.152
0.940	8090	80.1	.0978	2.348	2.372

use the sensitive galvanometer for this purpose. The decrease in accuracy was such that we preferred to regard these measurements merely as exploring the nature of the problem. No previous measurements of this kind have been made. Observations were made with measuring currents of both 550 and 1000 cycles/sec. and no difference was found within the limit of accuracy. The significant features of the measurements are shown by the smoothed data presented in Table III. All of the measurements were taken with the sample in thermal contact with liquid helium. However, the values are essentially adiabatic

TABLE II
MOLAL HEAT CAPACITY OF $Gd(C_6H_4NO_2SO_3)_3 \cdot 7H_2O$

T , °K.	C_p cal./deg.	T , °K.	C_p cal./deg.	T , °K.	C_p cal./deg.
0.10	0.52	0.30	1.39	0.70	0.58
.15	1.17	.40	1.11	.80	.48
.20	1.61	.50	0.87	.90	.41
.25	1.57	.60	.70	1.00	.35

(3) (a) Giauque, *THIS JOURNAL*, **49**, 1870 (1927); (b) Giauque and Clark, *ibid.*, **54**, 3135 (1932).

since appreciable approach to equilibrium with the bath could not be obtained in the time of one oscillation. The values given for zero field were obtained with 60 cycle current and the alternating current galvanometer. All of the measurements in Table III were taken with the apparatus of February 25 shown in Fig. 2.

TABLE III
MOLAL DIFFERENTIAL MAGNETIC SUSCEPTIBILITY OF
 $\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2\text{SO}_3)_3 \cdot 7\text{H}_2\text{O}$

H	$T = 1.31^\circ\text{K.}$	$T = 2.20^\circ\text{K.}$	$T = 4.22^\circ\text{K.}$
	$\left(\frac{\partial I}{\partial H}\right)_s$	$\left(\frac{\partial I}{\partial H}\right)_s$	$\left(\frac{\partial I}{\partial H}\right)_s$
0	5.98	3.56	1.85
500	5.19	3.35	1.80
1000	3.88	2.90	1.70
1500	2.84	2.40	1.55
2000	2.10	2.0	1.45
3000	1.30	1.5	1.3
4000	0.95	1.2	1.2
5000	.75	1.0	1.15
6000	.65	0.85	1.1
7000	.55	.8	1.1
8000	.50	.7	1.1

As we have mentioned, the values in Table III are merely to show the characteristics of such measurements and since they were taken along isotherms they are not suited for the determination of thermodynamic temperature.

Hysteresis Effects.—The absence of any frequency effect on the value of the magnetic susceptibility has been mentioned above. This was checked carefully for the initial susceptibility at 60, 550 and 1000 cycles/sec. at various temperatures from 0.1 to 4.2°K. However, since the sample tube could be used as a calorimeter we had a very sensitive means of detecting irreversible effects by the heat evolved. The sample was cooled to 0.1096° and allowed to warm by heat leak. The average warming rate from 0.1 to 0.4°K. was about 0.3° in two hours.

The sample temperature was measured at intervals with 60-cycle current in the measuring coil. Each observation required only a few seconds use of the alternating current. A 60-cycle current producing a maximum field of 15 gauss was then left on continuously with no effect on the warming rate. However, when a 550-cycle current producing a maximum field of about 25 gauss was left on continuously a very noticeable increase in warming rate was observed. Expressing the heat developed as a fraction of the total energy, $\chi H^2_{\text{max}}/2$, transferred from the field to the substance at the maximum of the sine wave it was found that 4, 3 and 2 parts in 10,000 were converted to heat at the temperatures 0.14, 0.25 and 0.28°, respectively. The 1000-cycle tuning fork oscillator supplied such a small current that no significant test could be made at this frequency.

Gadolinium Anthraquinone Sulfonate Hydrate.—Measurements were made on $\text{Gd}(\text{C}_{14}\text{H}_7\text{SO}_3)_3$ in a sample tube of the form shown in Fig. 2. The sample was 12 cm. in length and 2.50 cm. o. d. The vacuum jacketed tube was 0.31 cm. i. d. and occupied a space 0.8 cm. in diameter along the axis of the sample. Inductance coil No. 4 was wound directly on the glass insulating vacuum jacket.

The coil was made from No. 36 double silk covered copper wire: 8144 turns were wound in 18 layers. The coil diameter was 3.33 cm. i. d. and 4.2 cm. o. d. The inductance was 0.5999 henries at low temperatures. 34.40 g. (0.0338 mole) of $\text{Gd}(\text{C}_{14}\text{H}_7\text{SO}_3)_3$ and 18.17 g. of water were placed in the sample tube. This is approximately 30 moles of water for each gram atom of gadolinium. Assuming 6 or 7 moles were present as water of crystallization, some 23 or 24 moles of water per gram atom of gadolinium were mixed intimately with the sample in the form of ice. The purpose of the excess water was to enable an investigation of the heat capacity of ice near 1°K. It has been shown⁴ that the $\int_0^T C_p d \ln T$ with a reasonable extrapolation to the absolute zero does not give the correct entropy of water which is known accurately from its band spectrum. For this reason cooling experiments were carried out with the above mixture to find if ice had an anomaly in its heat capacity in the temperature region near 1°K. In the absence of such an effect the ice would not interfere with the investigation of the gadolinium compound. This point is of practical significance in connection with the necessity for careful adjustment of the water content of many hydrated substances useful for magnetic investigations.

The Heat Capacity of Gadolinium Anthraquinone Sulfonate.—The heat capacity of the gadolinium anthraquinone sulfonate hydrate plus ice was obtained from adiabatic demagnetization measurements in the manner described above. As expected the measurements showed this substance to be somewhat more ideal magnetically than gadolinium nitrobenzene sulfonate heptahydrate. The heat capacity curve had the form that we have come to recognize as being due to gadolinium so that in view of the large molal ratio of water to gadolinium it can be concluded that ice had no heat capacity within an accuracy of about one-hundredth of a calorie per degree per mole. The distribution of water molecules between two or more conceivable states would lead to a maximum of the order of a calorie per degree per mole or, in terms of the present experiment, about twenty calories per degree per gram atom of gadolinium. A negligible amount of helium gas was present in the calorimeter during the measurements. Although gadolinium anthraquinone sulfonate hydrate is more effective than gadolinium nitrobenzene sulfonate heptahydrate for producing low temperatures we did not obtain temperatures as low because of inferior starting conditions. This was partly due to an ice obstruction in the line leading to the calorimeter. This can be prevented easily by cooling the apparatus with gas at atmospheric pressure in the sample tube at least until a temperature is reached where the vapor pressure of water is negligible. This had been done in previous measurements but was overlooked in the present case. This point is important in connection with hydrated substances if it is to be assumed that no water is distilled from the sample to the outer wall of the sample tube during cooling.

Following the above experiment all of the water was removed from the sample by means of long evacuation with a mercury diffusion pump and a trap cooled with liquid air.

An attempt was then made to obtain a low initial tem-

(4) Gianque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

perature by evaporating liquid helium from the sample tube as had been done with the gadolinium nitrobenzene sulfonate. It was found that very little reduction in temperature, below that of the bath, could be obtained. The difficulty appeared to be due to convection in the tube leading from the sample to the helium bath. As may be seen from Fig. 2, the downward flow of evaporated helium permits the transfer of heat by convection to oppose the cooling effect of evaporation. The nature of gas convection is such that very low temperatures greatly increase the importance of this effect. It is evident that the balance, between conduction plus convection of heat from the bath, and the removal of heat by evaporation of liquid helium from the sample tube, may be critical and unfavorable to the production of a low temperature. It appears that fortuitous conditions existed when the above method produced a temperature of 0.94°K . in the very similar apparatus used for gadolinium nitrobenzene sulfonate.

Measurements on the anhydrous material showed it to be the most magnetically imperfect substance so far investigated. The results seem to indicate that the three large anthraquinone rings are attached like plates to the central gadolinium atom. In the absence of water about the gadolinium atoms a pile of such plates would allow close approach of the magnetic atoms in one direction.

The results in terms of the Curie scale for each substance are given in Tables IV, V and VI and the heat capacities below one degree have been represented in Fig. 3.

Excepting the anhydrous gadolinium anthraquinone sulfonate mentioned above, increased dilution of the magnetic atoms was accompanied by an increased magnetic perfection at the lower temperatures. However, above 0.8° the dilute gadolinium anthraquinone sulfonate has

TABLE IV

THE CHANGE OF ENTROPY WITH TEMPERATURE FOR 1 MOLE OF GADOLINIUM ANTHRAQUINONE SULFONATE AND 30 MOLES OF WATER

T , $^{\circ}\text{K}$. initial	H_{gauss}	χ_{final}	T , $^{\circ}\text{Curie}$ final	ΔS cal./deg.	$T_1^{\circ}\text{K} - S_T$
1.54	8000	37.8	0.207	1.458	1.311
1.52	6480	28.7	.273	1.120	0.977
1.52	5615	23.8	.328	0.915	.772
1.60	3650	15.3	.513	.510	.352
1.64	2936	9.3	.801	.270	.104
1.62	1830	7.0	1.12	.114	-.048
1.62	3836	13.8	0.568	.453	.291
1.62	8280	35.0	.224	1.358	1.196
4.22	8000	7.2	1.09	0.305	-0.034

TABLE V

THE CHANGE OF ENTROPY WITH TEMPERATURE FOR 1 MOLE OF ANHYDROUS GADOLINIUM ANTHRAQUINONE SULFONATE

T , $^{\circ}\text{K}$. initial	H_{gauss}	χ_{final}	T , $^{\circ}\text{Curie}$ final	ΔS cal./deg.	$T_1^{\circ}\text{K} - S_T$
1.56	8180	23.2	0.337	1.447	1.249
1.54	8060	23.1	.339	1.425	1.233
1.54	6485	18.5	.423	1.082	0.890
1.56	5730	16.4	.476	0.910	.712
1.56	3830	11.3	.692	.482	.284
1.56	2810	8.9	.878	.277	.079
1.56	2200	7.6	1.03	.178	-.020
1.56	8100	23.0	0.340	1.428	1.230

TABLE VI

THE HEAT CAPACITY OF 1 MOLE OF GADOLINIUM ANTHRAQUINONE SULFONATE AND 30 MOLES OF WATER AND 1 MOLE OF ANHYDROUS GADOLINIUM ANTHRAQUINONE

T	Sulfonate Hydrate plus additional H_2O C_p cal./deg.	Anhydrous C_p cal./deg.
0.20	1.33	..
.25	1.21	..
.30	1.12	..
.35	1.02	1.67
.40	0.92	1.52
.50	.74	1.31
.60	.61	1.13
.70	.55	0.95
.80	.50	.79
.90	.46	.66
1.00	.43	.57
1.50	.30	.37
2.00	.22	..
3.00	.16	..
4.00	.15	..

larger interaction effects than do the more concentrated gadolinium nitrobenzene sulfonate and gadolinium sulfate. This is consistent with the suggested explanation for the behavior of the anhydrous gadolinium anthraquinone sulfonate given above and points to the rather obvious necessity for a consideration of crystal structure detail.

It may be seen from the results given in Table VI that the vibrational heat capacity plays little part in the results discussed here. Assuming that the total heat capacity of 0.15 cal./deg. per mole at 4°K . is due to vibration and that the law $C_p = aT^3$ is valid, then the heat capacity at 1°K . would be approximately 0.002 cal./deg.

Dilution experiments with the aid of isomorphous salts have been carried out by Kürti and Simon⁵ and by de Haas and Wiersma.⁶ Kürti and Simon used $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ diluted with $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and de Haas and Wiersma used $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ diluted with $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Greater dilution did give somewhat greater magnetic perfection.

Hysteresis in Gadolinium Anthraquinone Sulfonate.—As in previous cases there was no difference in magnetic susceptibility as measured with frequencies from 60 to 1000 cycles/sec. either for hydrated or anhydrous gadolinium anthraquinone sulfonate. However a calorimetric investigation of hysteresis carried out as described above showed that two parts in ten thousand of the energy, $\chi H^2_{\text{max}}/2$, transferred to the substance at the maximum of the sine wave were converted to heat at 0.23° Curie. The effect was less than five parts in one hundred thousand at 0.38° Curie which was the limit of accuracy.

In the case of the anhydrous substance the effect was less than five parts in one hundred thousand at 0.35 and 0.40° Curie. The above measurements were made with a current of 550 cycles/sec. and $H_{\text{max}} = 20$ gauss.

From the severe test described above it is evident that the magnetic phenomena of the gadolinium compounds investigated are very reversible. This would presumably

(5) Kürti and Simon, *Proc. Roy. Soc. (London)*, **A149**, 152 (1935).

(6) De Haas and Wiersma, *Physica*, **2**, 81, 335 (1935).

be true of all reasonably dilute gadolinium compounds in which the other atoms are diamagnetic.

Summary

Adiabatic demagnetizations to temperatures below 1° A. have been carried out on gadolinium nitrobenzene sulfonate heptahydrate, gadolinium anthraquinone sulfonate x hydrate plus y water (where $x + y = 30$ moles of water) and on anhydrous gadolinium anthraquinone sulfonate.

From the relationship $dS/d \ln T = C$ the heat capacities of the three samples were calculated. The data indicate that increased dilution of the magnetic atoms results in a closer approach to the ideal magnetic situation that would result if the gadolinium atoms were controlled only by the external magnetic field.

The measurements indicate that the heat capacity of water between 0.2 and 4°K. is zero within an accuracy of about 0.01 cal./deg. per mole or less. This point is of interest in connection with the fact that the $\int_0^T C_p d \ln T$ for water gives an incorrect value for the entropy of water as reliably determined from its band spectrum.

Some exploratory measurements of differential magnetic susceptibility $(\partial I/\partial H)_S$, were made on gadolinium nitrobenzene sulfonate heptahydrate, at several temperatures and at magnetic fields up to 8000 gauss. This quantity was found to decrease rapidly to small values at the larger fields. Tables of such data for the temperatures 1.31, 2.20 and 4.22°K. have been presented. In the ideal case of no interaction between gadolinium atoms and no heat capacity $(\partial I/\partial H)_S$ would be

zero under all conditions of field and temperature. In high fields the atomic interactions would be expected to decrease in relative importance and our measurements are consistent with this. No variation of magnetic susceptibility with the frequency of the alternating measuring current could be found. Frequencies from 60 to 1000 cycles/sec. were used. However a sensitive calorimetric observation of the heat evolved due to magnetization with an alternating field showed that very small irreversible effects exist at a frequency of 550 cycles/sec. Observations were made with fields of 20–25 gauss at the maxima of the sine waves. Similar measurements could not be made at 1000 cycles/sec. since the available current at this frequency was too small.

Expressing the heat developed as a fraction of the energy, $\chi H_{\max}^2/2$, transferred from the field to the substance at the maximum of the sine wave 4, 3 and 2 parts in 10,000 were converted at 0.14, 0.25 and 0.28° Curie, respectively, by gadolinium nitrobenzene sulfonate heptahydrate. With gadolinium anthraquinone sulfonate hydrate 2 parts in 10,000 were converted to heat at 0.23° Curie. At 0.38° Curie less than 5 parts in 100,000 were converted. With anhydrous gadolinium anthraquinone sulfonate less than 5 parts in 100,000 were converted at 0.35 and 0.40° Curie. This was the limit of accuracy.

The above measurements of the small amount of irreversibility with rapidly alternating fields show that the magnetic phenomena of these gadolinium compounds are extremely reversible in character.

BERKELEY, CALIF.

RECEIVED FEBRUARY 4, 1936