THE CONDITIONS FOR PRODUCING TEMPERATURES BELOW 1° ABSOLUTE BY DEMAGNETIZATION OF $Gd_2(SO_4)_3 \cdot 8H_2O$. TEMPERATURE-MAGNETIC FIELD ISENTROPICS

BY W. F. GIAUQUE AND C. W. CLARK

Several years ago one of us[1] devised a method for producing temperatures below those which it has been found possible to obtain by means of liquid helium.

Briefly, the method in its simplest form consists in: (a) magnetizing a suitable paramagnetic substance; (b) absorbing the resulting heat by means of thermal conduction to liquid helium; (c) thermal isolation of the working substance from the helium bath; (d) reversible adiabatic demagnetization with consequent lowering of the temperature.

A few remarks on progress may be of interest here. From the beginning of this problem seven years ago, it has been planned not merely to produce a low temperature but rather to make such temperatures as can be obtained available for experimental work. This has meant the acquisition of apparatus on a scale which has necessitated very slow progress.

The principal requirements are a magnet to produce considerable and very homogeneous fields throughout a large volume and liquefaction cycles of considerable capacity for hydrogen and helium, the liquid hydrogen being required for precooling the helium gas.

A specially built hydrogen compressor with a delivery of 50 cubic feet per minute has been obtained. A very satisfactory hydrogen liquefaction cycle has been constructed. The capacity is about 15 liters of liquid per hour and this can be increased to about 25 liters per hour when a suitable vacuum pump can be obtained for more effective evaporation of the liquid air used for precooling the hydrogen. Storage facilities for 2000 cubic feet of pure hydrogen have been provided.

A helium compressor with a delivery of 25 cubic feet per minute has also been installed and storage facilities for 2000 cubic feet of helium are available. A purification system for removing oil and air or other gases from the helium cycle has been built and it is hoped that the liquefier can be completed in the near future. Acquisition of vacuum pumps permitting recovery of hydrogen evaporated at reduced pressures in the helium cycle and for the reduction of the temperature of liquid helium by reduced pressure is not possible at present.

[1] Giauque, (a) Author's method presented by Professor W. M. Latimer at the meeting of the California Section of the American Chemical Society, April 9 (1926); (b) THIS JOURNAL, **49**, 1864 (1927); (c) *ibid.*, **49**, 1870 (1927). Also see P. Debye, *Ann. phys.*, **81**, 1154 (1926).

An iron-free solenoid magnet with oil-cooled conductors and necessary accessories has been placed in operation. A very homogeneous field is obtained in the central portion of a three-foot cylinder with six inches inside diameter. The magnet has been constructed to take 1000 k. v. a., producing a field of over twenty thousand gauss. At present 100 k. v. a. are available, giving a field of about 8000 gauss. The design of the magnet and helium cycle has been carried out by D. P. MacDougall and one of us. G. F. Nelson has been responsible for mechanical construction of apparatus.

The object of the work reported in this paper was to supply information which would determine the magnetic field requirements and thus provide a sound basis for the design of the magnet referred to above.

Gadolinium sulfate octahydrate is a suitable working substance and a full discussion of its magnetic susceptibility with references to the excellent experimental work of Kamerlingh Onnes, Perrier, Oosterhuis and Woltjer has been given previously.[1b,c] Before the temperature effect produced by the demagnetization of gadolinium sulfate could be determined, it was necessary to know the heat capacity of this substance. It would be preferable to have these data at the temperatures of liquid helium. However, rather than delay until this is possible, it was decided to utilize results at liquid hydrogen temperatures with a Debye heat capacity extrapolation since only approximate results are necessary for our present purpose. Later the heat capacity will be investigated accurately in the liquid helium temperature range. Since no previous measurements have been made on the heat capacity of rare earth compounds at low temperatures it was thought desirable to cover the range to room temperature.

Purity of the Gadolinium Sulfate.—The gadolinium sulfate was obtained from the Welsbach Company, Gloucester, New Jersey, and the analysis furnished by them was Gd 98.5%, Sa 0.5%, Tb 1.0%. These impurities are sufficiently like gadolinium as to introduce a negligible error. A difference of several per cent. in the respective heat capacities would introduce an error of only a few hundredths of one per cent. The average atomic weight of the mixture is but 0.02% lower than that of gadolinium, so the difference may be neglected; 275.804 g. or 0.36926 mole was used in the measurements, the molecular weight of $Gd_2(SO_4)_3 \cdot 8H_2O$ being taken as 746.90.

Heat Capacity Measurements.—The apparatus and calorimetric method were similar to those used in many of the previous low temperature investigations[2] in this Laboratory.

The calorimeter was of copper on which was wound a gold resistance thermometer-heater. The resistance was 365 ohms at 290°K. with a

² (a) Gibson and Giauque, THIS JOURNAL. 45, 93 (1923); (b) Giauque and Johnston, *ibid.*. 51, 2300 (1929).

dR/dT of about 1 ohm per degree from 40 to 290°K. Twelve radial vanes improved the distribution of heat, which was also facilitated by helium gas in the spaces between the gadolinium sulfate crystals. A massive electrically-heated hollow cylinder constructed of copper and lead surrounded the calorimeter and provided a practically constant temperature environment during measurements. The apparatus was enclosed in an evacuated container.

The resistance thermometer was calibrated by means of the standard copper–constantan thermocouple number 16 which was compared with the hydrogen gas thermometer by Giauque, Buffington and Schulze.[3] The thermocouple was attached to the calorimeter during the heat capacity measurements. All low temperatures were produced by liquid air or by liquid hydrogen. The results are given in Table I.

TABLE I

HEAT CAPACITY OF $^1/_2$ MOLE $Gd_2(SO_4)_3 \cdot 8H_2O$ (M. W., 746.90)

T_{av}.°K.	ΔT	$C_p/^1/_2$ mole in cal./deg.	T_{av}.°K.	ΔT	$C_p/^1/_2$ mole in cal./deg.
15.42	2.595	1.159	149.59	4.572	42.00
16.55	4.269	1.469	153.73	4.618	43.10
17.64	1.935	1.735	158.63	5.118	44.10
20.23	3.394	2.387	163.73	4.950	45.20
23.60	3.630	3.208	168.88	5.195	46.41
27.25	3.512	4.243	174.31	5.468	47.40
31.56	4.509	5.961	179.78	5.186	48.69
36.02	4.095	7.423	184.94	4.975	49.66
42.67	4.177	9.939	190.12	5.186	50.86
46.93	4.074	11.61	195.30	4.918	52.52
51.26	4.441	13.28	200.20	4.789	52.61
56.15	5.277	15.19	205.23	5.046	53.85
61.82	5.836	17.59	210.35	4.865	54.64
67.55	5.574	19.24	215.35	4.870	54.82
73.22	5.728	21.31	220.36	4.596	55.67
81.28	4.871	23.44	226.97	4.156	57.92
86.12	4.802	25.35	231.89	4.864	58.60
90.76	4.474	26.67	236.92	4.723	59.14
95.33	4.568	28.26	241.95	4.675	61.02
100.17	5.112	29.25	247.00	4.808	61.35
104.88	4.672	30.87	252.13	5.087	62.27
109.46	4.417	32.13	257.34	4.893	63.73
113.98	4.576	33.29	262.46	4.773	63.87
118.64	4.698	34.55	267.56	4.670	64.86
123.19	4.363	35.80	272.62	4.530	66.71
128.47	5.158	37.01	277.82	5.315	66.20
133.69	5.255	38.36	283.25	5.156	66.46
139.06	5.349	39.59	288.86	5.353	68.04
144.53	5.409	41.08			

---

[3] Giauque, Buffington and Schulze, THIS JOURNAL. **49,** 2343 (1927).

The data are not as accurate as the various low temperature calorimetric investigations made with similar apparatus in this Laboratory within recent years. During the course of the measurements it was found that the thermometer-heater wound on the exterior of the cylindrical calorimeter had an unusually large thermal head with respect to the calorimeter. This greatly increased the usually small correction for radiation to the protective cylinder during heat input and also made it somewhat difficult to obtain equilibrium for the temperature measurements. Following the completion of the measurements the calorimeter was destroyed in order to learn the reason for the difficulty. It was found that the lacquer used on the closely wound thermometer-heater had not adhered to the calorimeter as in previous cases. However, the experimental results are sufficiently accurate and a smooth curve through the points is believed to represent the heat capacity to about 1% at 250°K. and about 0.5% at 100°K.

Since the completion of these measurements, S. Freed[4] has carried out a magnetic investigation on the electronic levels existing in $Sa_2(SO_4)_3 \cdot 8H_2O$. In this connection he has desired to compare the heat capacities of gadolinium and samarium sulfates. We have suggested that the accuracy required in this matter makes it desirable to have the present measurements repeated. We have accordingly given the gadolinium sulfate to Dr. J. E. Ahlberg, who is collaborating with Dr. Freed in this investigation, which should lead to results of increased accuracy. Moreover, for the purposes of comparison some accuracy is gained by measuring both substances in the same calorimeter.

The Entropy of Gadolinium Sulfate Octahydrate at Low Temperatures.—At the temperatures of liquid hydrogen the heat capacity has decreased to such an extent that it seems plausible that the degrees of freedom ordinarily assumed to be represented by the Einstein function are not appreciably active. It is further assumed that the remaining vibrational heat capacity can be represented by the Debye equation. Error resulting from this will be in such a direction as to make the conditions for producing low temperatures more favorable than calculations based on these assumptions will indicate.

Adopting a $\beta\nu = 110$ for $1/2$ mole of gadolinium sulfate, the Nernst–Lindemann limiting expression for the Debye equation gives

$$C = \frac{12}{5} \frac{\pi^4 R}{(\beta\nu)^3} T^3 = 3.5 \times 10^{-4} T^3 \tag{1}$$

The arbitrariness in selecting $1/2$ mole for determining $\beta\nu$ is of little consequence near the T^3 region. The Debye entropy for the T^3 region is given by

$$S_v = \frac{1}{3} \frac{12\pi^4 R}{5(\beta\nu)^3} T^3 = \frac{3.5 \times 10^{-4}}{3} T^3 \tag{2}$$

---

[4] Freed, THIS JOURNAL, **52**, 2702 (1930).

The entropy due to the distribution of the gadolinium ions in the eight states associated with the seven additively coupled electron spins of this ion has been previously considered.[1c]

The expression for the decrease in entropy which accompanies the application of a magnetic field is given by

$$\Delta S^{\overline{H}}_{\overline{H}=0} = R \left[\ln \sum \cosh \frac{gjM\overline{H} \cos \theta}{RT} - \ln 4 - \frac{gjM\overline{H}}{RT} \frac{\sum \cos \theta \sinh \dfrac{gjM\overline{H} \cos \theta}{RT}}{\sum \cosh \dfrac{gjM\overline{H} \cos \theta}{RT}} + 0 \right]$$

$$(3)$$

Since the gadolinium ion is an ^8S state, $g = 2$ is the ratio of magnetic to mechanical moment. $j = S = 7 \times \frac{1}{2}$, the total momentum. M is the molal unit Bohr magneton value. $M = 5567$ ergs/gauss. The summations require four values of $\cos \theta$, namely, $1, \frac{5}{7}, \frac{3}{7}$ and $\frac{1}{7}$. The negative values ordinarily used in addition to these are included by the use of hyperbolic functions.

The above expression assumes that the eight spatial orientations of the magnetic moment are equally probable in the absence of a magnetic field. This cannot be quite true but the magnetic susceptibility data extending to 1.3°K. indicate that the states differ but little in energy.[1c] Further magnetic susceptibility measurements and heat capacity determinations near 1°K. are needed to increase our information concerning the separation of the octet levels. However, the most promising method of obtaining this information appears to be the study of absorption spectra of the solid.

The measurements of Freed and Spedding[5] and more recent work by Spedding[6] and by Spedding and Nutting[7] include observations on $GdCl_3\cdot 6H_2O$ which has the same crystal structure and very nearly the same absorption spectrum as $Gd_2(SO_4)_3\cdot 8H_2O$. It would be expected that the two substances have quite similar characteristics. Dr. Spedding informs us that preliminary results indicate disturbances in the ideal separation of the Zeeman components amounting to two or three-tenths of a reciprocal centimeter. Energies of this magnitude become of importance below 1°K. Spedding and Nutting[7] have recently pointed out that the hexagonal crystals $Gd(BrO_3)_3\cdot 9H_2O$ and $Gd(C_2H_5SO_4)_3\cdot 9H_2O$ have energy levels which are affected by the crystal forces only to about one-half the extent of the monoclinic crystals $Gd_2(SO_4)_3\cdot 8H_2O$, $GdCl_3\cdot 6H_2O$ and $GdBr_3\cdot 6H_2O$. It is evident that the greater symmetry will produce conditions favorable to maximum magnetic cooling effect. Moreover, it is well known from the many investigations of Kamerlingh Onnes and his collaborators that greater dilution of the paramagnetic atoms by diamagnetic ones permits an increased perfection of magnetic behavior. For these reasons it appears

[5] Freed and Spedding, THIS JOURNAL, **52**, 3747 (1930).

[6] Spedding, *Phys. Rev.*, **38**, 2080 (1931).

[7] Spedding and Nutting, *ibid.*, **38**, 2294 (1931).

that $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, the magnetic susceptibility of which has been investigated to low temperatures by Jackson and Kamerlingh Onnes,[8] will prove superior to $Gd_2(SO_4)_3 \cdot 8H_2O$ as a working substance. It is also evident that best results will eventually be obtained by placing the crystal axis in proper relationship with the magnetic field.

For our present purposes which are purely for determining the order of magnitude in connection with the design of apparatus it will be possible to neglect the effect of the splitting of the energy levels mentioned above. However, as a result of the ideal conditions assumed, the calculated reduction in temperature for a given change in field is greater than will be found experimentally. In fact it may be shown that effects of the order of magnitude found in $Gd_2(SO_4)_3 \cdot 8H_2O$ by Spedding will produce a considerable effect below 1°K. and an appreciable effect extending to several degrees absolute. Nevertheless the figures to be presented in Table IV show the order of magnitude of the ideal limit for a magnetic cooling process utilizing a gadolinium compound. It is possible that a well-diluted crystal with cubic symmetry may make a reasonably close approach to such a limit even below 1°K.

Another consideration that may be of importance is the perfection of the crystals used. Dr. Spedding states that strained crystals give absorption lines which have been broadened to an extent that may lead to an appreciable effect on the magnetic and thermal properties at one or two degrees absolute.

The calculations were made in the following manner. The total entropy, excluding the effect of nuclear spin, and at zero field strength, was taken as $S_T = R \ln 8 + (3.5/3) \times 10^{-4} T^3$. Let ΔS_M be the change (reduction) in entropy caused by the application of the field $\mathfrak{H}$ at temperature T. Then the total entropy for a given situation is

$$S_{T,\mathfrak{H}} = R \ln 8 + \Delta S_M + \frac{3.5 \times 10^{-4}}{3} T^3$$

This must remain constant during a reversible adiabatic change.

Values of ΔS_M were calculated from equation 3 and represented on a large graph. The calculated values have been given in Table II as a function of $(gjM/R) \cdot (\mathfrak{H}/T)$. Table II is for the most part a repetition of the similar values given previously.[1c] However, a correction of the previous values on the basis of 1 calorie (15°) equals 4.185×10^7 joules instead of the value 4.182×10^7 has been made. The table is included to facilitate appreciation of the relatively large amount of entropy under the control of obtainable magnetic fields compared to the small amount concerned in ordinary vibration.

For comparison several values of the vibrational entropy calculated from the expression $S_V = (3.5 \times 10^{-4}/3)T^3$ are given in Table III.

[8] Jackson and Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 168a.

TABLE II

THEORETICAL ENTROPY OF MAGNETIZATION OF $1/2$ $Gd_2(SO_4)_3 \cdot 8H_2O$ AS A FUNCTION OF $gjM\mathcal{H}/RT$

$4.687 \times 10^{-4}\,\mathcal{H}/T$ gauss/deg.	$-\Delta S_M$ cal./deg.	$4.687 \times 10^{-4}\,\mathcal{H}/T$ gauss/deg.	$-\Delta S_M$ cal./deg.
0.1	0.004	2.8	1.673
.2	.017	4.2	2.396
.4	.068	6.3	3.064
.7	.196	7.0	3.220
1.4	.663	∞	4.132
2.1	1.195		

TABLE III

VIBRATIONAL ENTROPY OF $1/2$ $Gd_2(SO_4)_3 \cdot 8H_2O$

T, °K.	S, cal./deg.	T, °K.	S, cal./deg.
1	0.000117	6	0.0252
2	.000934	7	.0400
3	.00315	8	.0598
4	.00747	9	.0851
5	.0146	10	.117

For example, when a field of 12,000 gauss is applied at a temperature of 10°K.

$$S = R \ln 8 - 0.1275 + 0.1167 = R \ln 8 - 0.0108$$

Then at 0.5°K.

$$R \ln 8 - 0.0108 = R \ln 8 + \Delta S_M + 0.0000146$$

From this ΔS_M is found to be -0.0108 E. U., which corresponds to a value of $gjM\mathcal{H}/RT = 0.160$ and $\mathcal{H} = 171$ gauss.

This means that $Gd_2(SO_4)_3 \cdot 8H_2O$ should cool from 10 to 0.5°K. when the magnetic field is reduced from 12,000 gauss to 171 gauss. As may be seen from Table IV, the particular isentropic which was considered above shows that the temperature will fall from 4 to 0.5°K. when the field is reduced from 1780 gauss to 171 gauss.

The results for a number of isentropics are summarized in Table IV.

TABLE IV

TEMPERATURE-MAGNETIC FIELD ISENTROPICS FOR $Gd_2(SO_4)_3 \cdot H_2O$

Each column represents a line of constant entropy

T, °K.	Gauss							
10		20000	15000	12000	11400	11100	10100	7800
9		17000	12300	9320	8650	8260	7220	4180
8		14300	10100	6990	6320	5960	4860	0
7		12100	8180	5180	4530	4120	2790	
6		10000	6550	3710	3060	2620	0	
5		8130	5160	2590	1920	1430		
4		6410	3960	1780	1060	0		
3		4750	2880	1170	448			
2	10000	3150	1890	709	0			
1	4970	1570	940	342				
0.5	2430	786	470	171				

The possibilities shown by the tabulated data need little comment. As mentioned above, the amount of entropy under the control of the magnetic field is large compared to the amount concerned in vibration. For this reason conditions appear favorable to the production of extremely low temperatures even if several members of the magnetic octet are rendered inactive at such temperatures by energy differences comparable with kT. It is evident that the cooling effect available is not only sufficient for producing very low temperatures in the gadolinium sulfate octahydrate itself, but is also sufficient to cool simultaneously other materials in addition.

Summary

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been measured from 14 to 290°K. Extrapolation of the heat capacity results combined with the entropy of magnetization previously given has been used to determine the conditions for producing temperatures below 1°K. by reversible adiabatic demagnetization of gadolinium sulfate octahydrate.

The magnetic field–temperature isentropics have been tabulated. The data indicate that the demagnetization of gadolinium sulfate at the temperatures of liquid helium not only provides enough cooling effect to produce temperatures considerably below 1° absolute, but that in addition other substances may be cooled by gadolinium sulfate for investigation of their properties.

BERKELEY, CALIFORNIA

THE CONDUCTIVITY OF SOLUTIONS OF GERMANIC OXIDE[1]

BY CHARLES E. GULEZIAN AND JOHN H. MÜLLER

There are known to exist several modifications of germanium dioxide, the physical and chemical properties of which differ very definitely.[2] The ordinary form—the so-called "hydrolyzed" oxide—is soluble in water and is obtained by the hydrolysis of the tetrachloride. When solutions of this modification are evaporated to dryness, ignition of the residue gives varying yields of a very insoluble variety—the amount depending on the conditions under which the evaporation is carried out and on the temperature at which the residue is ignited. Only traces of this insoluble form can be obtained by directly igniting large quantities of the "hydrolyzed" oxide, whereas repeated evaporations and ignitions of the "evaporated" oxide bring about complete conversion of the soluble to the insoluble

---

[1] From a thesis presented by C. E. Gulezian in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Müller and Blank, THIS JOURNAL, **46**, 2358 (1924).