then it is possible to calculate the vapor solubilities in equilibrium with a standard vapor state in these cases as indicated earlier in this paper.

Summary

Three different types of experimental tests are employed to test the applicability of Henry's law to aqueous solutions of slightly soluble organic liquids. It is concluded that Henry's law is applicable in concentration ranges below approximately 300 to 400 millimoles per 1000 g. of water. The calculation of vapor solubilities in cases where Henry's law is applicable is discussed.

DURHAM, N. C. RECEIVED DECEMBER 6, 1937

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

Experiments Establishing the Thermodynamic Temperature Scale below 1°K. The Magnetic and Thermodynamic Properties of Gadolinium Phosphomolybdate as a Function of Field and Temperature

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

Although summaries of the more important results described in this paper have been presented[1] several years previously, it is only recently that we have found time to prepare a full account of the work. This paper completes the presentation of the results obtained by the authors in a series of investigations over the period March, 1933–June, 1934, in which the first adiabatic demagnetization experiments producing temperatures below 1°A. were carried out and in which these low temperatures were placed on the thermodynamic scale.

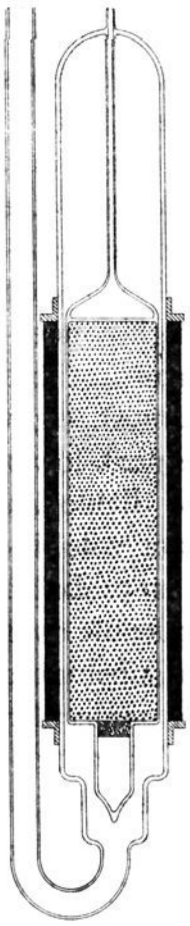

Fig. 1.

Gadolinium phosphomolybdate tridecahydrate was selected for investigation because Hoard[2] had shown that this substance is cubic, with the gadolinium atoms occupying equivalent positions in a diamond type lattice. Also this substance, $Gd(PMo_{12}O_{40})\cdot 30H_2O$, contains but one gadolinium atom in a total of 144 atoms and this dilution was expected, and was found, to lead to a closer approach to ideal paramagnetism than any of the other gadolinium compounds previously investigated. Hoard[2] has shown that the distance of closest approach of the gadolinium ions is 10.03 ± 0.02 Å.

The experimental arrangement was approximately that shown in Fig. 1 of a previous paper.[3] The sample tube, surrounded by the insulating vacuum space, and the inductance coil used for susceptibility measurements is shown in Fig. 1 of the present paper. At the upper end of the sample tube a small chamber is shown in which helium could be liquefied when desired. This permitted a temperature a little below bath temperature to be obtained at the start of demagnetization. However, this was not very useful in connection with the thermodynamic measurements as it was necessary to pump on the chamber until all the liquid helium had evaporated. The presence of an unknown amount of liquid helium in contact with the sample would have interfered with the interpretation of the measurements and when the helium was entirely evaporated the starting temperature was not accurately known when the sample was in a field. This small chamber was used as a container for an inductance heater which will be described later.

The measurement of magnetic susceptibility by means of the inductance coil has been described previously.[4] Inductance coil no. 4[3] was used for all of the measurements described in this paper. The end effect was assumed to be independent of the susceptibility. It may be well to mention here that unpublished later investigations of J. W. Stout and one of us have justified this assumption within rather small limits of error for the particular dimensions of the above apparatus and the range of susceptibility considered here.

The gadolinium phosphomolybdate was prepared by dissolving gadolinium oxide in 12-phosphomolybdic acid. The compound was then crystallized from the solution by slow evaporation of the water under vacuum at room temperature. The flask containing the solution was attached to a vacuum pump and a stream of air was allowed to pass over the surface of the liquid to facilitate evaporation. The crystals were partially dried on a filter, but it was considered desirable to leave a small excess of water since this made certain that the 30 molecules of water of crystallization were present. Analysis of a representative por-

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[1] Giauque and MacDougall, Meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18, 1934; *Phys. Rev.*, **47**, 885 (1935).

[2] Hoard, *Z. Krist.*, **A84**, 217 (1933).

[3] MacDougall and Giauque, THIS JOURNAL, **58**, 1032 (1936).

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

tion taken when the sample tube was filled showed that the sample investigated contained 94.737 g. of $Gd(PMo_{12}O_{40})\cdot 30H_2O$ + 5.456 g. H_2O. This corresponds to 0.035425 gram atom of gadolinium.

The sample tube contained approximately 28 cc. of space between the crystals and in the filling tube at the bottom. This space was filled to 1 atmosphere at room temperature with air containing 10.5% of helium. The amount of helium desirable was estimated roughly from previous experiments with hydrated crystals. A certain amount of cleanup occurs by adsorption at liquid helium temperatures and it is advantageous to have just enough helium left to assist thermal equilibrium, but not enough to contribute appreciably to the calorimetric properties of the sample. The air was added to help reduce diffusion of water to the outer surface of the sample tube as it was cooled through the temperature region in which the partial pressure of water was appreciable. This is a problem that must be considered whenever accurate work is done on hydrated crystals at low temperatures. The outer wall of the sample tube cools first and if a sufficient gradient occurs in the tube partial dehydration may occur. In the present experiments the presence of excess water was advantageous in this connection. It also appears probable that the air would be preferentially adsorbed by the more active portions of the surface and thus reduce the cleanup of helium.

The Entropy of Magnetization of Gadolinium Phosphomolybdate.—In our quantitative work on gadolinium sulfate octahydrate[4] it was possible to take advantage of the fact that Woltjer and Kamerlingh Onnes[5] had investigated the magnetization of this substance in the liquid helium temperature region. It has been shown previously[6] that the measurements of Woltjer and Kamerlingh Onnes are in agreement with the theoretical curve for the ideal paramagnetism of an octet S state within the limits of experimental error. Accordingly the use of the theoretical entropy of magnetization for an octet S state in the case of gadolinium sulfate octahydrate rests on an experimental basis.

In the present case the much greater magnetic dilution gives even more reason for expecting that the entropy of magnetization would correspond to the values given by the formula for the ideal case. However, it is preferable not to include an assumption of this kind in the treatment and it will be shown experimentally that in the case of gadolinium phosphomolybdate the intensity of magnetization also corresponds closely to the ideal values. Consequently the entropies of magnetization used in this work are those given by the formula[6]

$$\Delta S\Big|_0^{\mathbf{H}} = R \ln \Sigma \cosh(y \cos \Theta) - R \ln 4 - y \frac{\Sigma \cos \Theta \sinh(y \cos \Theta)}{\Sigma \cosh(y \cos \Theta)} \qquad (1)$$

where $y = gjM\mathbf{H}/RT$ and $\cos \Theta$ has the values 1, 5/7, 3/7, 1/7, $g = 2$, $j = 7/2$, $M = 5567$ (the molal Bohr magneton value).

Values calculated from Equation 1 have been given previously.[6,7]

The Intensity of Magnetization of Gadolinium Phosphomolybdate.—The customary methods of determining the intensity of magnetization of a substance involve the measurement of some quantity which depends on the total value of the induced magnetic moment. For example, the Gouy method depends on weighing the force which is exerted on a sample of uniform cross section when one end is in a homogeneous region of field, while the other end is in a negligible field.

During the present work a new method has been devised which lends itself more readily to the type of apparatus we have found most suitable for investigations in the temperature region below 1°K.

The procedure is as follows. The sample, mounted as in Fig. 1, is magnetized in field **H**. During the magnetization it is kept in thermal contact with the liquid helium bath by means of a small amount of helium in the insulating vacuum space. The space is then evacuated and the field reduced to zero, producing a low, but not necessarily known, temperature. A measurement of $(\partial I/\partial \mathbf{H})_S$ is then made by means of the inductance bridge. A small constant field **H** is then applied and another measurement of adiabatic differential susceptibility is made by superimposing the small alternating field oscillations on the constant field. These measurements are made at suitable intervals until the maximum field is reached. Then, using equation (14) of our previous paper,[4] the intensity of magnetization is found from the relation

$$I = \int_0^{\mathbf{H}} \left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} \qquad (2)$$

The above method requires that the magnetization be reversible and that there be no permanent magnetism left at zero field. This latter possibility is by no means excluded as a state corresponding to zero entropy at the absolute zero even though the process of magnetization

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[5] Woltjer and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 167c.

[6] Giauque, THIS JOURNAL, **49**, 1870 (1927).

[7] Giauque and Clark, *ibid.*, **54**, 3135 (1932).

occurs reversibly. Measurements showing that the magnetization is reversible and that no permanent magnetism exists in gadolinium phosphomolybdate will be presented later in this paper.

The initial susceptibility was first compared with the vapor pressure of helium and agreement was found with Curie's law in the liquid helium region. Thereafter the magnetic thermometer proved more convenient in determining bath temperatures, although two helium vapor pressure thermometers were mounted in the bath.

The quantity $(\partial \mathrm{I}/\partial \mathbf{H})_S$ is not appreciably useful in denoting temperature in large fields since it tends toward the zero value characteristic of ideal paramagnetic systems at very low temperatures. Thus the bath temperature was measured by means of susceptibility measurements in the absence of a field both before and after each adiabatic demagnetization.

The measured values of the intensity of magnetization are given in Table I where they are compared with those calculated from the theoretical equation[6]

$$\mathrm{I} = gJM\,\frac{\Sigma \cos\Theta \sinh(y\cos\Theta)}{\Sigma \cosh(y\cos\Theta)} \qquad (3)$$

where, as in equation (1), $y = gjM\mathbf{H}/RT$.

The adiabatic differential susceptibilities used to obtain the values in Table I will be discussed below in connection with their use in calculating other quantities of interest, including temperature, on the absolute thermodynamic scale.

TABLE I

THE MOLAL INTENSITY OF MAGNETIZATION OF GADOLINIUM PHOSPHOMOLYBDATE TRIDECAHYDRATE FROM ADIABATIC DIFFERENTIAL SUSCEPTIBILITIES COMPARED WITH THE IDEAL PARAMAGNETIC VALUES FOR AN OCTET S STATE

T, °K.	**H** gauss	I Theoretical	$\int_0^{\mathrm{H}} \left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}}\right)_S d\mathrm{H}$
1.433	8000	29,180	29,250
1.444	6420	26,060	26,170
1.451	5660	24,120	24,440
1.423	3750	18,380	18,490
1.430	2760	14,110	14,350
1.419	2040	10,830	10,990
1.429	1633	8,720	8,830
2.20	8040	23,150	22,570
4.22	7890	13,730	13,820

The experimental and theoretical values of the intensity of magnetization, shown in Table I, agree within the limits of experimental error. Consequently in calculating the entropy of magnetization at temperatures above 1.4°K. the theoretical formula will be considered to be representative of the experimental data.

Although the above agreement is quite good, the measurements were made under difficult experimental conditions and they are by no means representative of the accuracy obtainable with the experimental technique developed in later investigations in this Laboratory.

The Entropy as a Function of the Initial Susceptibility.—In order to correlate data in the temperature region below 1°K. it will be convenient to use the quantity $C_1/\chi = T_{\text{Curie}}$, as an arbitrary reference function. C_1 refers to the Curie constant and T_{Curie} refers to the temperatures obtained from the assumption that Curie's law is valid in the region considered.

Table II presents the results of a series of adiabatic demagnetizations carried out to determine the entropy of gadolinium phosphomolybdate as a function of C_1/χ. $C_1 = \frac{M^2g^2}{3R}S(S+1) = 7.827$ deg. per mole. In accordance with our previous convention the entropy has been referred to 1°K., since differences in entropy can be given with greater accuracy than that to which the absolute values are known.

TABLE II

THE MOLAL ENTROPY OF GADOLINIUM PHOSPHOMOLYBDATE TRIDECAHYDRATE

T, °K. initial	**H** gauss	$S - S_{\mathrm{H}=0}$ cal./deg.	$S_{1°\mathrm{K.}} - S$ cal./deg.	χ final	T_{Final} Curie
4.22	8410	0.335	0.069	10.39	0.753
4.22	6610	.215	− .051	6.20	1.263
4.22	5745	.165	− .101	4.25	1.840
4.22	3890	.080	− .186	2.40	3.26
1.423	6580	1.243	1.181	48.17	0.1625
1.428	5720	1.028	0.965	40.14	.1950
1.429	3820	0.557	.494	23.79	.3290
1.430	2840	.334	.271	17.05	.459
1.426	2285	.224	.161	13.59	.576
1.422	1630	.120	.058	10.01	.782
1.410	1220	.073	.012	8.48	.923
1.400	8220	1.642	1.582	67.18	.1165

From the data in Table II the heat capacity may be calculated in terms of temperatures on

TABLE III

THE MOLAL HEAT CAPACITY OF GADOLINIUM PHOSPHOMOLYBDATE FROM ADIABATIC DEMAGNETIZATION MEASUREMENTS

T°	C cal./deg.	T°	C cal./deg.
0.15	1.21	0.50	0.50
.20	1.07	.60	.40
.25	0.93	.70	.33
.30	.82	.80	.28
.35	.72	.90	.25
.40	.63	1.00	.22

the Curie scale for this substance. $C = \mathrm{d}S/\mathrm{d} \ln (C_1/\chi)$. The results from 0.15 to 1°K. are given in Table III. These values will be useful when the temperature scale based on Curie's law is compared to the thermodynamic scale later in this paper.

The Reversibility of the Magnetization Process.—That the magnetization process is reversible for the frequencies used is shown by the fact that no differences in susceptibility outside the limits of experimental error could be found by making inductance bridge measurements at frequencies of 60, 550 or 1000 cycles per sec.

In our previous work on gadolinium nitrobenzene sulfonate and on gadolinium anthraquinone sulfonate[1,3] a very sensitive test of reversibility was applied by comparing the normal warming rate with the rate observed when a rapidly alternating field was applied over a considerable period of time. This test was applied to gadolinium phosphomolybdate. As in previous cases, no effect could be detected with alternating fields of 60 cycles per second. The accuracy of this determination is such that it may be stated that less than 5 parts in 100,000 of the energy, $\chi \mathbf{H}^2_{\text{max.}}/2$, transferred from the field to the substance at the maximum of each sine wave, was converted to heat. However, when a field of 550 cycles per sec. was applied small effects were observed. With a field of 25 gauss at the maximum of the sine waves, 5 parts in 10,000 of the energy, $\chi \mathbf{H}^2_{\text{max.}}/2$, was converted to heat at 0.15°, 4 and 3 parts in 10,000 were converted to heat at temperatures of 0.18 and 0.20°, respectively. A similar test could not be made with the 1000 cycle field since the supply of power available at this frequency was not sufficient.

It is evident that sufficiently high frequencies would not allow time for the necessary orientations of magnetic moment to occur and a low value of the susceptibility would result. This situation would not always be accompanied by a heat effect. One might ask if some of the processes involved in the magnetization are ignored even at frequencies of 60 cycles per second? If this improbable supposition were so, the agreement between the measurements at 60, 550 and 1000 cycles per sec. would not indicate the correctness of susceptibilities measured with alternating fields of these frequencies. Fortunately it was possible to carry out an experiment that definitely eliminated the above possibility of error and at the same time permitted investigation of the possibility that permanent magnetism might be present at very low temperatures.

A Potentiometric Method of Measuring Intensity of Magnetization.—While a sample enclosed in a coil, as in Fig. 1, is being magnetized, an e. m. f. is induced in the coil. If the field is increased slowly over a period of time the e. m. f. can be measured and the $\int_0^t E\mathrm{d}t$ is a measure of the total magnetic induction within the coil. A comparison of the induction with that produced in the coil alone would give the effect due to the presence of the sample. This procedure would suffer from the disadvantage that the desired quantity is a difference between two larger quantities.

Two alternatives presented themselves. The effect on the coil alone can be balanced by another coil in the same field but removed from any influence of the sample or a constant field can be maintained while the sample is warmed at a controlled rate. Since the susceptibility decreases with increasing temperature, the change in induction produces an e. m. f. in the coil. The latter method was adopted partly because it did not involve additional equipment. This method is particularly suited to low temperature investigations since the e. m. f. is too small unless a compact coil containing a large number of turns is used and because at the same time the coil should have a low resistance if the galvanometer sensitivity is to be high. The resistance of copper is so low at the temperatures of liquid helium that in the construction of inductance coils our only criterion with respect to wire size has been that the wire should not be so small as to make precise winding difficult. Data on several coils have been given previously.[3,4]

The procedure in measuring the change in induction is as follows. The sample, protected by a high vacuum, is cooled to some low temperature by adiabatic demagnetization and a small constant field is applied. A series of e. m. f. readings is started and a small amount of helium gas is admitted slowly to the small chamber at the top of the sample tube shown in Fig. 1. The sample should not be allowed to warm too rapidly or the galvanometer reading will not be a sufficiently accurate measure of instantaneous e. m. f.

After a series of trial measurements and a calculation of the time constants of the electrical circuit the following procedure proved to be accurate enough for our present purposes. Two pieces of fine capillary tubing were sealed into a line leading to the sample tube. A one liter line volume between the stopcocks was highly evacuated by means of a by-pass before the start of a measurement. After preliminary readings had been taken with a potentiometer, a small pressure of helium gas was released into the space adjacent to the first capillary. The space between the capillaries filled slowly and thus helium passed through the second capillary and into the small chamber at the top of the sample tube very slowly. This slow acceleration of the warming rate not only permitted the galvanometer to give correct readings, but the somewhat symmetrical shape of the voltage–time curve was such that any small galvanometer lag would tend to cancel. No attempt was made to balance the potentiometer during the warming period, the field being selected so that the reading could be taken on a 100 cm. scale. The scale reading was then calibrated by means of the potentiometer. A typical curve is shown in Fig. 2.

$$\int_0^t \mathbf{E}\mathrm{d}t = 4\pi(\mathrm{I}_1 - \mathrm{I}_2)\frac{nm}{l} \times 10^{-8} \text{ volt sec.}$$

$$= 4\pi(\chi_1 - \chi_2)\frac{\mathbf{H}nm}{l} \times 10^{-8} \text{ volt sec.} \qquad (4)$$

χ_1 and χ_2 are the molal susceptibilities at the initial and final temperatures, respectively, as measured by the inductance bridge. **H** is the field in gauss; *n* the number of turns, 8144, in the coil; *m* is the number of moles, 0.035425, of substance, and *l* is the length of the sample which was 12 cm. Although the end effect when the sample is magnetized by the solenoid must be somewhat different from that when the inductance coil is used for magnetization, they should be approximately the same. Accordingly the susceptibilities used in Equation 4 were uncorrected for end effect.

Duplicate experiments were performed in which the sample was warmed, both with and without applied fields. The purpose of the latter experiment was to detect any permanent magnetism left after adiabatic demagnetization from a large field to a low temperature. In this case there was a small residual field due to the vertical component of the earth's field and a larger amount due to permanent magnetism in the reinforcing iron of the building. A measurement of this field showed that it had a value of 2.0 ± 0.1 gauss. This residual field explained, quantitatively, the $\int_0^t \mathbf{E}\mathrm{d}t$ obtained when there was no current in the solenoid. Thus it may be stated that there was no change in permanent magnetism during warming to an accuracy of 1 part in 5000 of the saturation magnetic moment. Since the residual field was nearly 10% of the magnetizing field used, the values of the $\int_0^t \mathbf{E}\mathrm{d}t$ calculated from equation (4) were corrected by adding the area due to the residual field. The data are presented in Table IV. The values calculated from the susceptibilities determined with 60 cycle current agree well with the area $\int_0^t \mathbf{E}\mathrm{d}t$ obtained by graphical integration of the data. The latter is essentially a direct current method of determining the susceptibility.

TABLE IV

COMPARISON OF DIRECT AND ALTERNATING CURRENT DETERMINATIONS OF MAGNETIC INDUCTION IN GADOLINIUM PHOSPHOMOLYBDATE

Temperature Initial T_1, °K.	Temperature Final T_2, °K.	**H**, gauss	Residual field effect $\int_0^t \mathbf{E}\mathrm{d}t$ millivolt seconds	Equation 4 + Residual field effect $\int_0^t \mathbf{E}\mathrm{d}t$ millivolt seconds	Potentiometer data $\int_0^t \mathbf{E}\mathrm{d}t$ millivolt seconds
0.132	1.403	24.3	0.25	3.43	3.31
.124	1.406	24.18	.27	3.67	3.55
.124	1.412	24.16	.27	3.66	3.51
.178	1.423	24.24	.19	2.19	2.34
.211	1.436	24.16	.17	1.76	1.93
.340	1.412	24.05	.08	0.98	1.00
.485	1.420	23.85	.05	.59	0.55

Adiabatic Differential Susceptibilities and Derived Thermodynamic Quantities.—In a previous paper[4] we have given a number of equations relating adiabatic differential susceptibilities to some thermodynamic quantities of basic importance.

$$\Delta E = \int_0^{\mathbf{H}} \mathbf{H}\left(\frac{\partial \mathrm{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H} \qquad (5)$$

where ΔE is the change in energy content of the system.

The change in heat content, ΔH, in a magnetic field is given by the equation

$$\Delta H = \int_0^{\mathbf{H}} \mathbf{H}\left(\frac{\partial \mathrm{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H} - \mathbf{H}\int_0^{\mathbf{H}}\left(\frac{\partial \mathrm{I}}{\partial \mathbf{H}}\right)_S \mathrm{d}\mathbf{H} \qquad (6)$$

The temperature on the thermodynamic scale is given by the relation

$$T = (\partial H/\partial S)_{\mathrm{H}} \qquad (7)$$

As mentioned above, the differential susceptibility determinations given below were made under difficult experimental conditions. The inductance bridge gives excellent results in the absence of a magnetizing current in the large solenoid. Current from an ordinary direct current system, which happens to be our only appreciable source, contains irregularities. This effect is presumably due to mechanical irregularities in the generator, to commutation, and to induction from parallel alternating current transmission lines. For this reason inductance bridge measurements could not be made with the sensitive vibration galvanometer. Accordingly head phones and a frequency of 550 cycles per sec. were used for all bridge measurements when the generator current was passing through the solenoid. When the bridge was balanced by means of head phones there was a considerable decrease in accuracy. Currents up to 50 amperes were available from storage cells and for this range the inductance bridge could be used with its full accuracy. Thus all measurements up to 800 gauss are quite accurate. Fortunately the values of $(\partial I/\partial H)_S$ decreased very rapidly with increasing field and for this reason it was possible to obtain considerable accuracy in the present research despite the difficulties of measurement in large fields. The procedure for obtaining a series of differential susceptibility measurements has been discussed above in connection with the determination of the intensity of magnetization.

As an example of the type of experimental data secured we present in Table V two series of observations starting with the field at 8000 gauss and the temperature about 1.4°K.

TABLE V

TYPICAL EXAMPLE OF ADIABATIC DIFFERENTIAL SUSCEPTIBILITY MEASUREMENTS

Series 1A		Series 1B	
$H_{\text{initial}} = 8060$ gauss		$H_{\text{initial}} = 8000$ gauss	
$T_{\text{initial}} = 1.455°\text{K}$		$T_{\text{initial}} = 1.433°\text{K}.$	
H	$\left(\frac{\partial I}{\partial H}\right)_S$	H	$\left(\frac{\partial I}{\partial H}\right)_S$
8060	0	8000	0
0	61.15	0	62.20
5620	0.41	122	48.02
3950	0.68	191	37.51
3150	1.09	384	21.10
2220	1.90	530	14.70
1910	2.31	673	11.04
810	8.72	804	8.65
666	11.30	1875	2.04
519	15.11	2415	1.09
363	22.20	3295	0.41
186	37.85	4130	0.27
116	47.35	6580	0
0	58.70	8240	0

Series 1A of Table V is most useful in showing the order in which these measurements should not be taken. The low temperature produced by the initial demagnetization was 0.128° whereas the final measurement corresponded to 0.133°. It is evident that the process was not entirely adiabatic. The heat leak at the lower temperatures was comparatively negligible since any helium gas in the insulating vacuum space was condensed. During the time the sample was near bath temperature the heat leak was at a maximum. Thus it was during the time required to make the several most difficult and least consequential measurements in the higher fields of Series 1A that the heat leak occurred. The measurements could have been used by correlating the final value of Series 1A with the known entropies corresponding to initial susceptibility measurements; however, Series 1A was given practically no weight except with respect to such information as it could give concerning the approximate values in large fields. The value 0 for $(\partial I/\partial H)_S$ means only that the measuring conditions were so unsatisfactory that the bridge balance was more or less meaningless. The irregularities were in proportion to the field used and interfered seriously with the use of phones in balancing the inductance bridge when high fields were applied.

Series 1B is sufficiently adiabatic for the measurements below 1000 gauss and at higher fields the values do not change much with temperature.

In Table VI, the interpolated results of seven series of measurements and some quantities calculated from them are given. In drawing the smooth curves through the susceptibility measurements, advantage could be taken of the fact that the several series constituted a family of curves. This was especially desirable in the region of high fields. Values of the intensity of magnetization, energy and heat content as a function of field are also given in Table VI.

Before proceeding further in treating the above results it will be advantageous to consider some measurements in which calorimetric energy was introduced at various temperatures.

Calorimetry by Electrical Induction Heating at Low Temperatures.—After considering numerous possible methods of introducing energy into the sample tube, shown in Fig. 1, an electrical induction heater was used. When the alternating magnetic field is of moderate frequency the amount of heat developed is inversely proportional to the specific resistance of the conductor. Thus for quantitative measurements it is desirable to induce the eddy currents in some material whose electrical conductivity is independent of temperature.

TABLE VI

MOLAL ADIABATIC DIFFERENTIAL SUSCEPTIBILITIES, INTENSITY OF MAGNETIZATION AND CHANGES IN ENERGY AND HEAT CONTENT ACCOMPANYING ADIABATIC MAGNETIZATION OF GADOLINIUM PHOSPHOMOLYBDATE

H, gauss	$\left(\frac{\partial I}{\partial H}\right)_S$	I	$\Delta E\Big\vert_0^H$ ergs/mole	$-\Delta H\Big\vert_0^H$ ergs/mole
Series 1: **H** = 8000, *T* = 1.433				
0	62.20	0	0	0
25	61.92	1553	1.94×10^{4}	1.95×10^{4}
50	60.00	3081	7.67×10^{4}	7.73×10^{4}
100	51.60	5881	2.74×10^{5}	3.14×10^{5}
250	31.20	11940	1.29×10^{6}	1.70×10^{6}
500	15.72	17470	3.29×10^{6}	5.45×10^{6}
750	9.61	20520	5.18×10^{6}	9.98×10^{6}
1000	6.52	22500	6.90×10^{6}	1.56×10^{7}
1500	3.49	24890	9.83×10^{6}	2.75×10^{7}
2000	2.11	26250	1.22×10^{7}	4.04×10^{7}
3000	0.92	27660	1.56×10^{7}	6.74×10^{7}
4000	.49	28330	1.79×10^{7}	9.54×10^{7}
5000	.30	28720	1.96×10^{7}	1.24×10^{8}
6000	.20	28960	2.10×10^{7}	1.53×10^{8}
7000	.14	29130	2.21×10^{7}	1.82×10^{8}
8000	.10	29250	2.30×10^{7}	2.11×10^{8}
Series 2: **H** = 6420, *T* = 1.444				
0	45.60	0	0	0
25	45.00	1133	1.41×10^{4}	1.43×10^{4}
50	44.00	2247	5.56×10^{4}	5.67×10^{4}
100	40.00	4350	2.13×10^{5}	2.22×10^{5}
250	28.25	9480	1.08×10^{6}	1.29×10^{6}
500	15.42	14720	2.99×10^{6}	4.37×10^{6}
750	9.48	17720	4.84×10^{6}	8.45×10^{6}
1000	6.46	19680	6.54×10^{6}	1.31×10^{7}
1500	3.47	22050	9.46×10^{6}	2.36×10^{7}
2000	2.10	23400	1.18×10^{7}	3.50×10^{7}
3000	0.92	24800	1.52×10^{7}	5.92×10^{7}
4000	.49	25470	1.75×10^{7}	8.43×10^{7}
5000	.30	25860	1.92×10^{7}	1.10×10^{8}
6000	.20	26100	2.06×10^{7}	1.36×10^{8}
6420	.17	26170	2.11×10^{7}	1.47×10^{8}
Series 3: **H** = 5660, *T* = 1.451				
0	38.30	0	0	0
25	38.20	959	1.19×10^{4}	1.20×10^{4}
50	37.90	1909	4.76×10^{4}	4.79×10^{4}
100	35.10	3744	1.84×10^{5}	1.90×10^{5}
250	25.84	8320	9.66×10^{5}	1.11×10^{6}
500	15.00	13280	2.76×10^{6}	3.88×10^{6}
750	9.38	16230	4.59×10^{6}	7.58×10^{6}
1000	6.36	18160	6.27×10^{6}	1.19×10^{7}
1500	3.41	20490	9.13×10^{6}	2.16×10^{7}
2000	2.07	21820	1.14×10^{7}	3.22×10^{7}
3000	0.92	23210	1.48×10^{7}	5.48×10^{7}
4000	.48	23880	1.71×10^{7}	7.84×10^{7}
5000	.30	24260	1.88×10^{7}	1.03×10^{8}
5660	.23	24440	1.97×10^{7}	1.18×10^{8}
Series 4: **H** = 3750, *T* = 1.423				
0	23.09	0	0	0
25	23.05	577	7.20×10^{3}	7.23×10^{3}
50	22.95	1152	2.88×10^{4}	2.89×10^{4}
100	22.20	2282	1.13×10^{5}	1.15×10^{5}
250	18.67	5312	6.44×10^{5}	6.84×10^{5}
500	12.60	9220	2.07×10^{6}	2.54×10^{6}
750	8.20	11760	3.64×10^{6}	5.18×10^{6}
1000	5.64	13460	5.12×10^{6}	8.34×10^{6}
1500	3.07	15550	7.68×10^{6}	1.56×10^{7}
2000	1.87	16750	9.76×10^{6}	2.37×10^{7}
3000	0.83	18010	1.28×10^{7}	4.12×10^{7}
3750	.53	18490	1.45×10^{7}	5.49×10^{7}
Series 5: **H** = 2760, *T* = 1.430				
0	16.06	0	0	0
25	16.00	401	5.00×10^{3}	5.03×10^{3}
50	15.95	801	2.00×10^{4}	2.01×10^{4}
100	15.45	1587	7.87×10^{4}	8.00×10^{4}
250	13.83	3800	4.62×10^{5}	4.88×10^{5}
500	10.10	6820	1.56×10^{6}	1.85×10^{6}
750	6.95	8900	2.86×10^{6}	3.81×10^{6}
1000	4.96	10370	4.14×10^{6}	6.23×10^{6}
1500	2.83	12260	6.45×10^{6}	1.19×10^{7}
2000	1.75	13380	8.38×10^{6}	1.84×10^{7}
2760	0.92	14350	1.06×10^{7}	2.90×10^{7}
Series 6: **H** = 2040, *T* 1.419				
0	11.79	0	0	0
25	11.78	295	3.68×10^{3}	3.68×10^{3}
50	11.76	589	1.47×10^{4}	1.47×10^{4}
100	11.65	1174	5.86×10^{4}	5.88×10^{4}
250	10.76	2880	3.53×10^{5}	3.68×10^{5}
500	8.09	5240	1.23×10^{6}	1.40×10^{6}
750	5.92	6970	2.30×10^{6}	2.92×10^{5}
1000	4.37	8240	3.41×10^{6}	4.84×10^{6}
1500	2.54	9920	5.47×10^{6}	9.41×10^{6}
2000	1.60	10930	7.21×10^{6}	1.46×10^{7}
2040	1.59	10990	7.34×10^{6}	1.50×10^{7}
Series 7: **H** = 1633, *T* = 1.429				
0	9.81	0	0	0
25	9.80	245	3.06×10^{3}	3.07×10^{3}
50	9.78	490	1.22×10^{4}	1.23×10^{4}
100	9.72	978	4.88×10^{4}	4.90×10^{4}
250	8.84	2375	2.90×10^{5}	3.04×10^{5}
500	7.03	4380	1.02×10^{6}	1.17×10^{6}
750	5.20	5890	1.97×10^{6}	2.45×10^{6}
1000	3.94	7020	2.95×10^{6}	4.08×10^{6}
1500	2.35	8550	4.82×10^{6}	8.01×10^{6}
1633	2.09	8830	5.31×10^{6}	9.11×10^{6}

For many years calorimetric investigations have been carried out in this Laboratory with the assistance of the ordinary type resistance thermometer-heaters which are made of gold containing a small amount of silver. The silver is added to increase the low temperature resistance sufficiently to permit a suitable rate of introduction of energy without the use of large currents at the lower temperatures. This alloy tends to lose its temperature coefficient of resistance at the temperatures of liquid hydrogen and becomes practically useless for thermometry near 10°K. A single turn of number 40 B. and S. gage wire made of gold with 0.1% silver was introduced into the small chamber at the upper end of the sample tube shown in Fig. 1. This was accomplished without the necessity of any glass blowing near the sample tube. Thus the sample was in the same condition as during the measurements described above. The loop of wire, 2.2 cm. in diameter, was collapsed and inserted in the inlet tube and then manipulated into a circular form with the assistance of a piece of wire, and several very small pieces of adhesive tape. The dimensions of the inductance heater were selected so that the alternating fields used for measuring the susceptibility would not develop enough energy to interfere with the measurements.

The measuring field introduced energy at the rate of about 2 × 10^{-7} cal./min. and since it was necessary to apply the measuring field only for a few seconds in making an observation, this source of energy was of little importance. The heat was introduced by means of a 60-cycle, 350 or 175 root mean square gauss field in the solenoid.

The rate of energy input is proportional to the square of the field and thus the square of the magnetizing current which was about 21 amperes for most of the measurements. The rate at which energy was developed in the calorimeter was about 5 × 10^{-4} or 2 × 10^{-4} cal./min. and the heating period ranged from about one-half minute to ten minutes. The induction heater was located with the plane of the circle at right angles to the axis of the cylindrical sample and was separated from the material by a glass wall about 1 mm. thick.

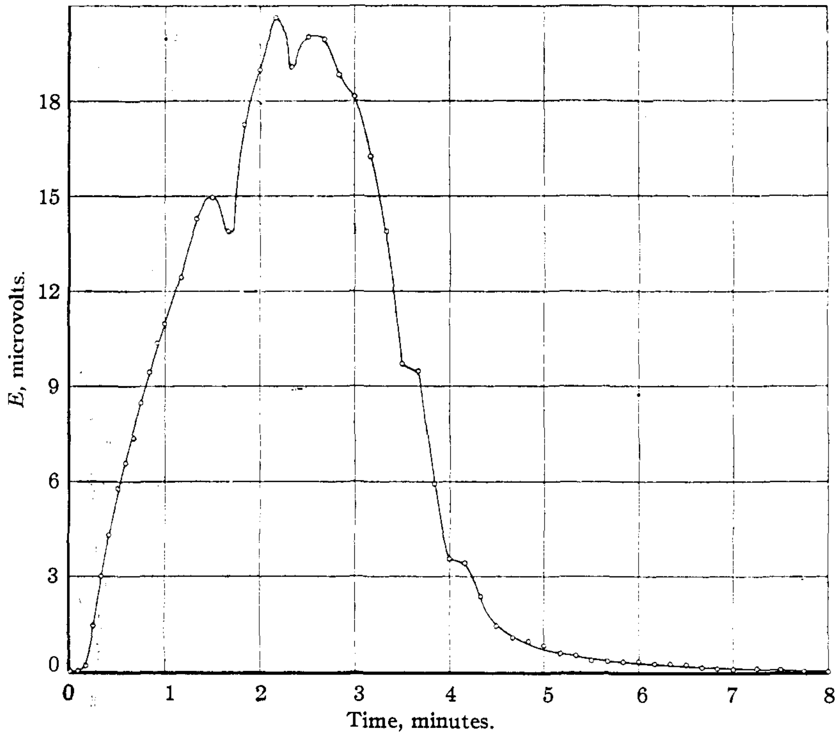

Fig. 2.—Change in magnetic induction as gadolinium phosphomolybdate is warmed in a constant field. E, in microvolts, induced in a coil surrounding sample.

In the preliminary calculation[1] of the results we made the careless assumption that the induction through the heater was proportional to the permeability of the sample. This did not affect the results greatly at the higher temperatures but produced considerable error at the lower temperatures. We were thus led to believe that the Curie scale gave results 0.03° lower than the thermodynamic scale at 0.15°K., indicating a deviation in a ferromagnetic direction. In making the correction for end effect it will be most convenient to make use of the results of an investigation[8] of the induction in the space surrounding a paramagnetic cylinder in an otherwise homogeneous field. The induction through the loop of wire may be taken as proportional to $1 + (0.40 \pm 0.01)(\mu - 1) = 0.60 + 0.40\,\mu$ at the position of the heater and over the range of permeabilities used in this research.

Due to the shielding effect of eddy currents in the metal parts of the magnet the ratio of the induction to magnet current was not known. Also the resistance and area of the induction heater were not known accurately. Thus the undeter-

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(8) Giauque and Stout, THIS JOURNAL, 60, 388 (1938).

mined constant depending on these factors was evaluated from measurements between 1 and 4°K. where the Curie and thermodynamic scales were known to be in agreement. The procedure was as follows. A plot of the measured quantity, the product of heat capacity and the unknown constant, K, was made on a log T scale and the area equated to the known entropy difference as given by the data in Table II.

The energy was calculated from the expression

$$\Delta E = [i(0.60 + 0.40\mu)]^2 t \times 1.75 \times 10^{-6} \text{ calories}$$

where i is given in amperes and t in seconds.

The results of eight series of measurements are given in Table VII. Series I to IV, V to VII and VIII were made during runs on different days. In series I and II the energy was introduced by a 60 cycle field of about 175 root mean square gauss. All of the other series were made with approximately 350 foot mean square gauss.

TABLE VII

THE HEAT CAPACITY OF GADOLINIUM PHOSPHOMOLYBDATE

T	ΔT	C	Series
0.1300	0.0414	0.82	VII
.1353	.0250	1.03	III
.1390	.0291	1.16	VIII
.1448	.0211	1.29	II
.1450	.0477	1.05	IV
.1782	.0279	1.12	III
.1860	.0332	0.94	VII
.1865	.0268	1.28	II
.2453	.0405	1.19	I
.2528	.0635	0.71	III
.2661	.0691	.71	II
.277	.1572	.66	IV
.2898	.0776	.55	VII
.3310	.0895	.70	I
.3887	.1034	.54	III
.4006	.1067	.57	II
.4569	.1053	.57	I
.464	.138	.49	VII
.525	.1191	.46	III
.531	.272	.45	IV
.554	.1152	.51	II
.608	.144	.41	I
.663	.201	.324	VII
.730	.212	.312	III
.793	.234	.309	II
.832	.102	.251	VII
.859	.254	.254	I
.977	.127	.201	VII
1.134	.458	.167	III
1.150	.903	.198	IV
1.257	.403	.172	I
1.260	.474	.161	V
1.266	.533	.159	II
1.34	.690	.148	VI
1.34	.527	.144	VII
1.90	.72	.136	I
2.06	.90	.110	VII
2.11	.72	.123	V
2.40	.93	.133	VI
2.98	.72	.208	V
3.72	1.64	.348	VI
3.81	0.76	.393	V

Incidental to the above measurements it was found that gold is not a supraconductor[1] at temperatures down to 0.11°K. Later Kürti and Simon[9] found that it is still not a supraconductor at 0.05°.

The data, which are shown graphically in Fig. 3, are compared with the heat capacity curve obtained from entropy data given in Table III. Both the points and the curve are referred to the Curie temperatures, $T_{\text{Curie}} = C_1/\chi$. The thermodynamic temperature is given by the relationship

$$T_{\text{Thermodynamic}}/T_{\text{Curie}} = \frac{\mathrm{d}E/\mathrm{d}(C_1/\chi)}{\mathrm{d}S/\mathrm{d}\ln(C_1/\chi)} \quad (8)$$

Thus if the points and curve were in agreement, the Curie and thermodynamic scales would be identical. The points below 0.3°K. are scattered, due in part to difficulty in obtaining equilibrium, and we suspect also due to the possibility that heat leak was not always the same for a given temperature difference during a measurement. While energy was being introduced the glass near the heater undoubtedly became much warmer than the sample and this is more probable the lower the temperature of the sample since there would be less helium gas conduction within the sample tube at low temperatures. This complication also leads to the possible de-adsorption of helium from the surface of the glass into the insulating vacuum space and consequently the heat leak during the cleanup interval might differ from that found from the final equilibrium data.

Although the measurements are not as accurate as might be desired, they are the first measurements[1] to give a determination of thermodynamic temperature at these low temperatures for any substance and are sufficiently good to decide that the Curie and thermodynamic temperature scales do not differ by more than 0.03° at 0.15°K. for the magnetically dilute gadolinium phosphomolybdate. Hebb and Purcell[10] recently have concluded on theoretical grounds that the Curie temperatures should be somewhat higher than the thermodynamic scale but al-

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[9] Kürti and Simon, *Nature*, **135**, 31 (1935).

[10] Hebb and Purcell, *J. Chem. Phys.*, **5**, 338 (1937).

though the points at the lower temperatures show some tendency in this direction, we do not believe that the accuracy of these preliminary results justifies any conclusion in this connection. Therefore the thermodynamic scale may be taken as identical with the temperatures given by Curie's law within the limits of accuracy of the present work.

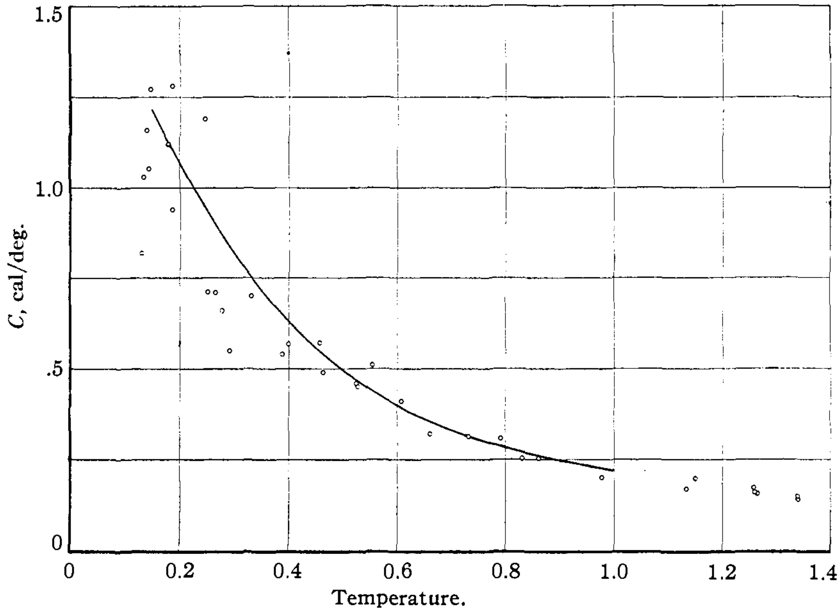

Fig. 3.—Heat capacity of gadolinium phosphomolybdate in calories per degree per mole. The solid curve is derived from demagnetizations at known entropy. The circles represent the results obtained by adding heat at the various temperatures.

The Determination of Temperature in a Magnetic Field.—As we have shown previously in the case of gadolinium sulfate,[4] the variation of temperature with magnetic field may be calculated from the measurements of adiabatic differential susceptibility

$$T_{\mathrm{H}} = \left(\frac{\partial \mathrm{H}}{\partial S}\right)_{\mathrm{H}} = \left(\frac{\partial E}{\partial S}\right)_{\mathrm{H}=0} + \left(\frac{\partial\left[\int_0^{\mathrm{H}} \mathrm{H}\left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}}\right)_{\mathrm{S}} \mathrm{dH} - \mathrm{H}\int_0^{\mathrm{H}}\left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}}\right)_{\mathrm{S}} \mathrm{dH}\right]}{\partial S}\right)_{\mathrm{H}} \quad (9)$$

$(\partial E/\partial S)_{\mathrm{H}=0}$ is the thermodynamic temperature in the absence of a field and the last term in equation (9) gives the change in temperature produced by the field.

$$T_{\mathrm{H}} = T_{(\mathrm{H}=0)} + \Delta T_{(\text{Due to H})} \quad (10)$$

It is perhaps of greatest interest to tabulate the change in temperature as the field is increased adiabatically. The values of the change in heat content between zero field and some constant field were plotted against the entropy. The necessary heat content data have been given in Table VI. The slope, $(\mathrm{d}\Delta H_0^{\mathrm{H}}/\mathrm{d}S)_{\mathrm{H}}$ was then taken and the resulting values of ΔT are given in Table VIII.

A graphical representation of the change of temperature during magnetization for the above isentropics is given in Fig. 4.

It is evident that when suitably accurate measuring conditions are available at the higher fields, calculations of the type given above will permit the determination of the low temperatures without the necessity of energy input in the region below 1°K. In fact the curves through the calculated temperatures derived from Table VIII checked the initial upper temperatures within a few hundredths of a degree for the two upper curves in Fig. 4. It is evident that the

TABLE VIII

THE CHANGE OF TEMPERATURE OF GADOLINIUM PHOSPHOMOLYBDATE DURING ADIABATIC MAGNETIZATION

$T_{\mathrm{H}=0}$	0.798°	0.664°	0.487°	0.339°	0.202°	0.172°	0.126°
H, gauss	ΔT	ΔT	ΔT	ΔT	ΔT	ΔT	ΔT
25	2.25×10^{-4}	2.25×10^{-4}	2.25×10^{-4}	2.30×10^{-4}	2.40×10^{-4}	2.8×10^{-4}	4.6×10^{-4}
50	9.4×10^{-4}	9.4×10^{-4}	9.5×10^{-4}	9.6×10^{-4}	10.4×10^{-4}	11.4×10^{-4}	14.2×10^{-4}
100	3.8×10^{-3}	3.8×10^{-3}	3.9×10^{-3}	3.9×10^{-3}	4.1×10^{-3}	5.0×10^{-3}	5.6×10^{-3}
250	0.019	0.020	0.021	0.021	0.021	0.023	0.024
500	.080	.082	.078	.072	.057	.057	.058
750	.175	.170	.152	.137	.115	.099	.094
1000	.289	.265	.234	.205	.169	.144	.132
1500	.537	.480	.421	.355	.279	.242	.214
2000	..	.738	.620	.504	.393	.343	.299
3000	..	..	..	.839	.619	.550	.465

lower temperatures could have been based on the measured upper temperatures and heat content data determined from the magnetic observations. In the other cases the temperatures from which demagnetization took place fell on the calculated curves but the calculations did not extend sufficiently close to the upper point to provide an independent check of the results.

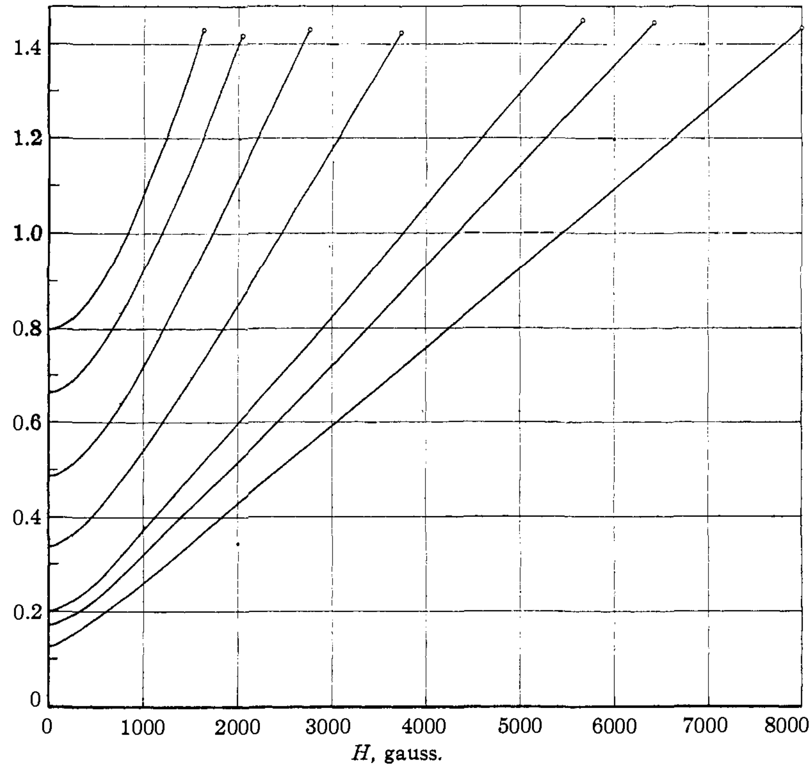

Fig. 4.—Change of thermodynamic temperature with magnetic field at constant entropy for gadolinium phosphomolybdate.

Since all appreciable thermodynamic effects below 1°K. are under the control of an applied field in such a manner that the magnetic changes are very reversible, the above method should prove of importance in avoiding the slow equilibrium which accompanies energy input by means of a heater.

Although difficulties due to poor thermal conductivity exist it should be stated that there is no evidence that the heat conductivity is phenomenally low. Accurate measurements in this temperature region involve the distribution of energy under very small thermal heads and even ordinary thermal conductivities make it more difficult to obtain a high percentage of accuracy.

The Energy Changes During Isothermal and During Adiabatic Magnetization.—In Table I we have shown by means of determinations of the intensity of magnetization that gadolinium phosphomolybdate is a very ideal paramagnetic substance at temperatures above 1.4°K. For such a substance there should be no energy change during isothermal magnetization. If this is true in the present case the energy change during adiabatic magnetization from some low temperature should be identical with the energy change along a path in zero field over the same temperature interval.

As an alternative method of showing the degree of magnetic perfection in the present case and as a check on some of the other calculations we have computed the energy change along the two paths. The results are given in Table IX. For zero field $\Delta E = \int_{T_1}^{T_2} CdT$. During adiabatic magnetization from zero field to H gauss, $\Delta E = \int_0^{\mathrm{H}} \mathrm{H} \left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}}\right)_{\mathrm{S}} d\mathrm{H}$. This latter quantity has been given in ergs per mole in Table VI. Here it has been converted to calories per mole for the present comparison. $\int_0^{\mathrm{H}} \mathrm{H} \left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}}\right)_{\mathrm{S}} d\mathrm{H} - \int_{T_1}^{T_2} CdT = \Delta E$ for isothermal magnetization at the constant temperature T_2. The difference between columns 5 and 4 in Table IX is zero within the limits of accuracy of this preliminary work.

Table IX

Comparison Energy Changes in Zero Field and During Adiabatic Magnetization over the Same Temperature Interval

T_1, initial	T_2, final	**H**, gauss. final	$\int_{T_1}^{T_2} CdT$ cal./mole	$\int_0^{\mathrm{H}} \mathbf{H} \left(\frac{\partial \mathrm{I}}{\partial \mathbf{H}}\right)_{\mathrm{S}} d\mathrm{H}$ cal./mole
0.126	1.433	8000	0.548	0.549
.172	1.444	6420	.493	.504
.202	1.451	5660	.461	.472
.339	1.423	3750	.337	.346
.487	1.430	2760	.247	.269
.664	1.419	2040	.170	.175
.798	1.429	1633	.130	.127

The perfection shown by the magnetically dilute gadolinium phosphomolybdate tridecahydrate indicates, as does our work on other gadolinium compounds, that there is little interaction between the surrounding water molecules and the octet S atom. It seems safe to conclude that deviations from perfection in more concentrated gadolinium compounds are primarily due to the magnetic interactions of the paramagnetic atoms on each other.

Hebb and Purcell[10] have based some of their theoretical predictions, referred to above, on the assumption that in a salt as magnetically dilute as gadolinium nitrobenzene heptahydrate the magnetic imperfection may be assigned entirely to interaction between the gadolinium ions and the electric fields of the crystal. This does not appear to be in agreement with our results[11] on gadolinium phosphomolybdate tridecahydrate. This latter salt is about as much more perfect than gadolinium nitrobenzene sulfonate heptahydrate as one would expect from the effect of the additional dilution on the inter-gadolinium magnetic interactions. This is a matter of some practical interest since further dilution will be ineffective in obtaining lower temperatures when the electric field of the crystal is solely responsible for the deviations from ideal paramagnetism. The gadolinium ions are undoubtedly surrounded by water in the various hydrated crystals which have been investigated and making the usual convenient simplest assumption, that the water molecules produce the same effect in the various cases, one would be led to infer that greater dilution than that in gadolinium phosphomolybdate tridecahydrate would lead to greater paramagnetic perfection.

We thank Dr. C. J. Egan for assisting with many of the calculations presented in this paper.

Summary

Gadolinium phosphomolybdate tridecahydrate has been demagnetized adiabatically to temperatures below one degree absolute.

Adiabatic differential susceptibilities have been measured up to fields of 8000 gauss and down to temperatures of 0.13°K.

These measurements form the basis of a new experimental procedure for determining the intensity of magnetization as a function of field. $I = \int_0^H \left(\frac{\partial I}{\partial H}\right)_S dH$. A knowledge of the low temperature corresponding to zero field is not necessary in applying this method.

The measurements show that gadolinium phosphomolybdate, which was selected for investigation because it is cubic with the gadolinium atoms 10.0 Å. apart in a diamond type lattice, is a very ideal paramagnetic substance at temperatures above 1°K.

The susceptibility measurements which were made with an inductance bridge using 60 cycle current were shown to be highly reversible by means of temperature observations on the thermally isolated system. No heat effect was observed and it may be stated that less than 5 parts in 100,000 of the energy, $\chi H^2_{\text{max.}}/2$, transferred from the field to the substance at the maximum of the sine waves was converted to heat.

No difference in susceptibility could be found with frequencies of 550 and 1000 cycles per sec. but very small irreversible effects were observed thermally with alternating fields of 550 cycles per sec. and 25 gauss maxima. 5, 4 and 3 parts in 10,000, respectively, of $\chi H^2_{\text{max.}}/2$, were converted to heat at 0.15, 0.18° and 0.20K.

Since it was conceivable, even if not probable, that some irreversible process might be so slow as to be ignored by the above procedure, a potentiometric method of measuring magnetic induction was devised. The electromotive force generated in a coil surrounding the sample was observed while the substance was warmed in a constant magnetic field. The $\int_0^t E dt$ measures the change in magnetic induction. The susceptibilities determined by this procedure, which is a zero frequency method, agreed with those obtained with the alternating current bridge.

It was shown that no appreciable residual magnetism is left when gadolinium phosphomolybdate is demagnetized to temperatures of 0.12°K. or above.

The thermodynamic properties, intensity of magnetization, differential susceptibility, energy and heat content have been tabulated as functions of magnetic field and temperature.

An induction heater of gold containing 0.1% of silver was devised to introduce heat for heat capacity determinations.

It was found that gold is not a supraconductor at temperatures down to 0.11°K.

By means of the adiabatic demagnetization

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[11] Giauque, *Ind. Eng. Chem.*, **28**, 743 (1936).

measurements the entropy was fixed in terms of initial susceptibility measurements.

The above measurements were combined to permit the first determination of thermodynamic temperatures in the region made available by the magnetic cooling method. Our preliminary reports on this subject were based on the data which are presented here. It is found that the thermodynamic scale agrees with the temperatures predicted by Curie's law for gadolinium phosphomolybdate down to 0.15°K.

The temperature change during adiabatic magnetization has been tabulated.

The energy change during isothermal magnetization at 1.4°K. has been shown to be practically zero, as would be expected for an ideal paramagnetic substance.

BERKELEY, CALIF. RECEIVED OCTOBER 29, 1937

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

Induction Heaters for Calorimetry below 1°K. An Investigation of the Electrical Resistance of Gold–Silver Alloys at Low Temperatures

BY W. F. GIAUQUE AND J. W. STOUT

In a previous paper it has been shown experimentally by Giauque and MacDougall[1] that induction heaters are well adapted to calorimetry below 1°K. The advantage of this type over the ordinary kind of electrical heater is the absence of direct electrical connections to contribute to calorimetric heat leak. In order to obtain a sense of proportion about the small amounts of energy concerned in calorimetry at these temperatures we will recall some of the values in the experiments on gadolinium phosphomolybdate.[1]

Although the 63-cc. calorimeter contained an 89-g. sample, the total energy change between 0 and 1°K. was only 0.03 cal. In order to investigate the rapidly varying form of the heat capacity curve below 1°K., it was necessary to add about 0.001 cal. for an individual experiment. In the previous work, this increment of energy was measured with an accuracy of the order of 10^{-5} cal. We saw no reason why this accuracy of energy measurement could not be increased easily to at least one millionth of a calorie or 0.1% if a suitable heater material could be found. The search for such a material is the subject of this paper.

In selecting a heater material it is expedient to avoid conductors that become superconducting, although such conductors conceivably could be used in a method that effected a temporary restoration of resistance. For example the application of a sufficient magnetic field could restore the resistance until the local rise in temperature of the heater was able to maintain it. The material should not be appreciably para or ferromagnetic. It is convenient to construct a heater of a substance that is chemically unreactive. When energy is being developed, the heater material will vary in temperature in some unknown manner depending on the rate of heat input and the rate at which the heat can be transferred to the sample. This makes it necessary that the electrical resistance of the material should be sufficiently constant over the possible range of temperatures that can exist during energy input. The greatest uncertainty at present is connected with what may happen to electrical conductivity below 1°K. Fortunately the heat capacity of most materials in this region is so small that the heater would be removed from this temperature region by the first, and a negligible, portion of the energy developed. To determine the temperature range over which the electrical resistance must remain constant a safe criterion would be to calculate the temperature that would be attained if all the energy introduced were retained by the heater.

A rapid survey of the available data made it clear that no pure element could meet the above requirements. Even without excluding magnetic materials and numerous superconducting substances the resistance of pure metals is not sufficiently constant. It is impracticable to design pure metal heaters of desirable form and at the same time having a proper ratio of heat capacity to energy developed in order to limit the possible temperature range during operation. It might be pointed out that this ratio can be varied by changing the value of the alternating magnetic field used for inducing the eddy currents. However, small alternating fields are often used to make magnetic susceptibility measurements by the induction method and it is desirable to have a heater that will not liberate an appreciable amount of energy unless larger fields are used. To minimize further the above effect it seems desirable that the heater should be located at some distance from the sample and measuring coil, although some means must be provided for thermal contact. Another reason for placing the heater at some distance from the magnetic sample is that the presence of magnetic material will distort the alternating field and necessitate a correction that will depend, often not in a simple manner, on the varying permeability of the sample.

Consideration of Metallic Alloys.—In general an alloy of two or more metallic elements has a much lower electrical

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