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

The Measurement of Adiabatic Differential Magnetic Susceptibility Near 1° Absolute. The Heat Capacity of Gadolinium Phosphomolybdate Tridecahydrate from 0.17 to 4.7° Absolute

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The observations reported here were made some four years ago, primarily to gain experience in the measurement of magnetic and calorimetric properties in the temperature region near 1°K. We selected gadolinium phosphomolybdate tridecahydrate for investigation because it is a comparatively ideal magnetic substance whose properties have been studied by Giauque and MacDougall[1]; in fact we used the same sample and tube which had been used in the previous research. Otherwise the measuring coils and low temperature apparatus were entirely reconstructed.

On the basis of helium adsorption measurements made previously[2] we reduced the amount of helium used to facilitate heat conduction in the sample tube. For the present experiments the 28 cc. of gas space in the tube was filled at 90°K., with helium to a pressure of 0.25 cm. and with air to a pressure of 10 cm. The tube was evacuated and the gas added at a low temperature to avoid the loss of water from the sample.

The gadolinium phosphomolybdate had been analyzed during the previous work by precipitation of gadolinium oxalate and ignition to oxide. Using the later atomic weight of gadolinium, 156.9, and making a small correction for the fact that the 0.5% Sm and 1% Tb would act differently than gadolinium, we estimate the total number of moles of gadolinium phosphomolybdate as 0.03515 rather than the value 0.03543 mole given in the previous work. It should be pointed out that the method of treatment used in the previous paper[1] made the results independent of the number of moles of gadolinium phosphomolybdate used.

In order to make sure that no decomposition to gadolinium phosphate occurred during the three years between the two sets of measurements the sample was removed, after the present experiments and found to be completely soluble in water.

The apparatus is shown in Fig. 1. The whole arrangement was placed in the center of a solenoid magnet. As can be seen from the drawing the two dewar vessels have a single vacuum space which could be pumped continuously if desired. However this was not necessary for although the dewars were made of Pyrex, which is permeable to helium, it was found sufficient to pump a vacuum and then turn off the vacuum pumping system during the course of an experiment which usually extended over two days. Although a considerable area in the outer tube was at room temperature or even warmer during this period any helium diffusing through the warm parts of the dewar was cleaned up by adsorption on the cold portions. Such a cleanup of helium in a Pyrex dewar has been observed previously in this Laboratory.

The space between the two dewar vessels contains a coil, A, of brass tubing through which liquid air is circulated in order to keep the outer wall of the liquid helium dewar at the temperature of liquid air. The liquid air is supplied from a 100 liter container under a small pressure and a small fraction not evaporated is discharged into a cup (not shown) which cools the top of the apparatus. An oxygen vapor pressure thermometer near the top of the cup controls the pressure on the liquid air supply dewar with the assistance of a magnetic valve and thus the liquid level in the cup is kept constant.

The coil was wound double so as to be non-inductive and to have both inlet and outlet at the top. The coil is held in shape with the assistance of small pieces of wood which prevent electrical short circuiting of the turns. It was desired to have the coil non-inductive to reduce eddy current effects when alternating fields are used. A similar coil has been described previously.[3]

The sample tube, B, is shown in the central portion. The platinized glass leads are shown at the bottom. They are connected by means of a fine platinum wire to tungsten seals, C—C, in the glass wall.

The measuring coil system is shown at 1, 2, 3 and 4. The sample was surrounded by four coils which could be used in various combinations. Coils 1 + 2 + 3 constituted a simple solenoid similar to the coil used in the previous measurements. The inductance of this arrangement was measured by an Anderson inductance bridge as described previously.[4] Coils 2 and 4 were designed to operate in connection with the fluxmeter described by Giauque and Stout.[5] The original reason for having two coils for this purpose was to permit extrapolation to the condition of a coil on the sample. This condition was of course not experimentally possible since the sample must be isolated by a vacuum space. However the investigation of the flux distribution in the space around a cylinder which has been carried out previously[5] made two separate coils unnecessary and they were treated as a single unit, 2 + 4, in the measurements given here.

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(1) Giauque and MacDougall, *ibid.* **60**, 376 (1938).

(2) Giauque and Stout, *ibid.*, **60**, 393 (1938).

(3) MacDougall and Giauque, *ibid.*, **58**, 1032 (1936).

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

(5) Giauque and Stout, *ibid.*, **61**, 1384 (1939).

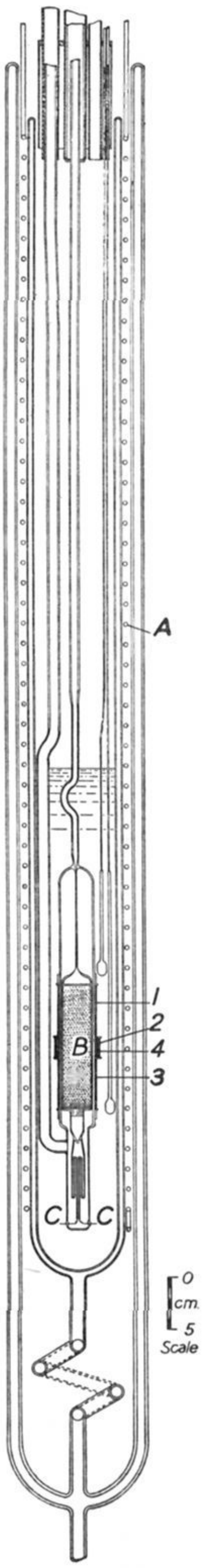

Fig. 1.—Adiabatic demagnetization apparatus.

The principal feature of the coil system was that coils 1 and 3 could be used in opposition for inductance measurements. These coils were carefully made duplicates so that when the system was subjected to a strong magnetic field, the effects of fluctuations associated with a generator supply of current were balanced out so completely that the effect was less than 0.01% on an inductance measurement. The operation of coils 1 and 3 in opposition reduces the measured effect somewhat, *e. g.*, if the combination $1 - 3$ were arranged to give an inductance equal to a single coil of the same length as the sample the inductance contribution due to the sample would be reduced by about 15%. The field applied to the sample by coils $1 - 3$ was very non-uniform but since this small alternating measuring field was only a small increment of the total applied field the magnetization of the sample was not appreciably complicated by this fact. In order to interpret the observations with coils $1 - 3$ experimental factors could be determined relating these coils to the simpler arrangements with coils $1 + 2 + 3$ and $2 + 4$.

An amorphous carbon thermometer–heater was placed on the outer surface of the sample tube. This particular thermometer–heater has been discussed in a previous paper[6] relating to the properties of such instruments. A further description here is unnecessary except to recall that the leads consisted in part of a silver film deposited from silvering solution instead of the usual platinized leads. The gadolinium phosphomolybdate sample tube could not be subjected to the temperature required for platinizing without decomposition of the sample so the substitution of silver was tried. The heating which resulted from eddy currents in the silver film made it necessary to remove this thermometer after the heat capacity determinations so that reliable measurements could be made with alternating fields.

The carbon thermometer was not in good equilibrium with the entire sample below a few tenths of a degree although it was definitely shown that those portions of the sample which adhered to the wall of the sample tube were in good equilibrium with the carbon thermometer. This rapid equilibrium between the sample and thermometer which has been discussed previously[6] showed that even at 0.13°K. heat could flow from the carbon thermometer on the outside of the sample tube, to and through the glass wall, and after transfer to the crystal lattice, come to substantial equilibrium with the magnetic system within the few seconds required to make an observation. However the small portion of the sample in good contact with the wall warmed faster than the interior, establishing a temperature lead of several hundredths of a degree and it was decided that observations with coils $1 + 2 + 3$ gave the best average of the entire sample. Coils $2 + 4$ largely measured the condition of the central portion of the sample while coils $1 - 3$ were principally influenced by material somewhat out from the central portion.

The data obtained with coils $2 + 4$ in combination with the field distribution factors given by Giauque and Stout[5] permitted the determination of the values which the inductances of coil combinations $1 + 2 + 3$ and $1 - 3$ would have had in the absence of the sample. The corresponding value for coils $2 + 4$ using the fluxmeter was determined at the boiling point of helium since the susceptibility of the sample may be calculated at this temperature.

Coils 2 and 4 each contained 1502 turns wound in twelve layers 2 cm. long. The i. d. and o. d. of the inner coil, no. 2, were 3.504 and 3.910 cm., respectively, and diameters of coil no. 4 were 3.925 and 4.332 cm. Coils 1 and 3 were of the same diameter as coil 2. They were wound in 12 layers and were 4.9 cm. long. Coil 1 contained 3722 turns and coil 3 had 3725, the additional three turns being added to equalize the coils. All the coils were wound of no. 36 B. and S. double enameled copper wire. They were supported on glass covered by a layer of rice paper and Bakelite lacquer, but coil no. 4 was wound over coil no. 2, being separated by a layer of rice paper impregnated with lacquer.

Some data were obtained on the stability of the coils with time and the decrease in size with temperature. For coils 2 and 4 the decrease in area corresponded to a linear decrease in coil circumference of 0.29 and 0.34%, respectively, over the range from room temperature to 4°K. For copper the corresponding decrease is 0.33%. The above result is practically identical with a similar observation made on coils wound on Dilecto tubing and reported previously.[5]

In Table I are collected some data on the flux through the coils calculated to the value they would have in the absence of the sample at the boiling point of liquid helium. The numbers are in arbitrary units and the constancy of the ratio leads us to believe that the coils in the large solenoid were at least in part responsible for the change rather than the measuring coils 2 and 4. The solenoid was of course not built as a precision instrument and it was used to supply the induced measuring flux in this preliminary investigation only as a matter of convenience. It is planned to add a carefully constructed coil for the express purpose of inducing the flux used for measuring purposes.

The Measurement of Heat Capacity.—The carbon thermometer–heater was used to introduce electrical energy for all the heat capacity

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[6] Giauque, Stout and Clark, This Journal, **60**, 1053 (1938).

TABLE I

EFFECT OF TIME ON MAGNETIC FLUX THROUGH MEASURING COILS AT 4°K.

Magnetic flux is in arbitrary units.

Date	Coil no, 2	Coil no. 4	Ratio coil 4/2
6-12-36	210.829	261.908	1.2423
6-20-36	210.649	261.702	1.2424
11-27-36	210.096	261.015	1.2424
12- 5-36	209.925	260.811	1,2424
12- 8-36	210.043	260.970	1.2425
12-19-36	209.985	260.890	1.2424
12-20-36	209.997	260.900	1.2424
12-29-36	210.051	260.965	1.2424
1- 5-37	210.025	260.988	1.2427

measurements which extended from 0.17 to 4.7°K. On account of equilibrium difficulties we preferred to base the low temperature observations on inductance measurements with coils 1 + 2 + 3. However, above 1°K. the higher precision of the carbon thermometer was used for measuring the temperature increments and drifts associated with the heat capacity measurements. The calibration of the carbon thermometer was accomplished by comparison with coils 2 + 4 and the fluxmeter.

The heat capacity results are given in Table II and have been shown in Fig. 2. The heavier portion of the curve below 1°K. is drawn from the $dS/d \ln (C_1/\chi)$ values of Giauque and MacDougall[1] in order to compare it with the present experimental values. C_1 is the Curie constant for gadolinium and χ the magnetic susceptibility. $C_1/\chi = T_{(\text{curie})}$ and the thermodynamic temperature

$$T = T_{(\text{curie})} \times \frac{dE}{dT_{(\text{curie})}} \bigg/ \frac{dS}{d \ln T_{(\text{curie})}} \quad (1)$$

TABLE II

HEAT CAPACITY OF GADOLINIUM PHOSPHOMOLYBDATE TRIDECAHYDRATE

0.03515 mole of $GdPMo_{12}O_{40} \cdot 30H_2O$ in calorimeter; C_p in cal. deg.$^{-1}$ mole^{-1}.

$T_{av.}$	ΔT	C_p
0.187	0.0411	1.01
.272	.0374	0.93
.391	.0484	.72
.545	.0740	.471
.704	.104	.336
.862	.125	.280
1.027	.167	.212
1.325	.216	.164
1.622	.275	.129
1.902	.309	.117
2.210	.601	.119
2.576	.480	.150
2.835	.674	.175
3.408	1.100	.261
4.192	1.132	.461

Above 0.5° the calorimetric results are in good agreement with those obtained from the entropy. Below this temperature the poor equilibrium which was evident from the observations is probably sufficient to account for the deviations. In agreement with the previous research we conclude that there is no difference between the thermodynamic and Curie temperatures, within the accuracy of the experiments, over the range investigated.

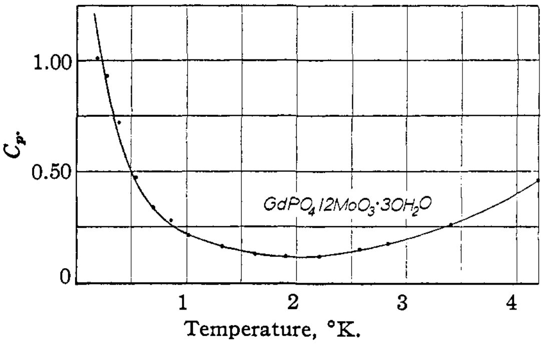

Fig. 2.—Heat capacity in cal. deg.$^{-1}$ mole^{-1} of gadolinium phosphomolybdate tridecahydrate. Points represent calorimetric measurements. The heavier curve below 1°K. is taken from measurements of $ds/d \ln(C_1/x)$ by Giauque and MacDougall.

It is perhaps desirable to point out that the requirements as to completeness of distribution of thermal energy increase roughly in inverse proportion to the temperature in such measurements. For example, at 10°K. one might measure a heat capacity using a 1° temperature increment while at 0.1° the corresponding rise would be only 0.01°. It is evident that irregularities in thermal distribution which would cause a 0.1% error at 10°K. would produce a 10% error at 0.1°K. The precision of the measuring system is not appreciably concerned in the deviations since this increases roughly in inverse proportion to the temperature in ideal cases.

The heat capacity results are in agreement with the calorimetric results of Giauque and MacDougall although the present work is more accurate due to elimination of errors introduced by the preliminary form of induction heater[7] used in their work.

The Adiabatic Differential Susceptibility.—Before coils 1 − 3 could be used to obtain values of the adiabatic differential magnetic susceptibility, $(\partial I/H)_S$, in the presence of large fields, it was necessary to determine factors relating the

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[7] *E. g.*, see Giauque and Stout, THIS JOURNAL, **60**, 388 (1938).

observations to the simple coil system 2 + 4. However, it soon became evident that these factors could not be determined with good accuracy at the lower temperatures because of faulty thermal distribution in the sample tube. As we have mentioned above the portions of the material affecting coils 2 + 4 were not the same as those affecting 1 − 3 and we assume that the variable results were due to chance temperature differences originating from the faulty distribution of the small normal heat leak into the sample. For this reason we have discarded observations made at the lowest temperatures and have given only those at fields from 1000 gauss up to extend and improve the similar results of the previous work.[1]

The experiments of Giauque and MacDougall were carried out with fields produced by storage cells up to 800 gauss. These fields did not have the fluctuations of those produced with the usual current supply. At higher fields they were obliged to balance the inductance bridge with phones instead of the sensitive vibration galvanometer. Their measurements up to 800 gauss were made with 60-cycle fields and above 800 gauss a frequency of 550 was used. In the present work 60-cycle current was used throughout.

After each measurement of a differential susceptibility the field was removed and a value of the initial susceptibility observed. Measurements were always made at certain values of the field so that the results could be plotted as a function of initial susceptibility and curves drawn through the values at each field. In this way we read off results along the same adiabatic paths used in the previous work. Above 800 gauss the fields used were 816, 1143, 1633, 3265, 6204 and 8410 gauss.

In the numerous experiments which have been done with gadolinium compounds we have found it necessary to have tables of the intensity and entropy of magnetization as a function of field and temperature. The very brief tables which have been given previously[8,9] have proved inadequate. Since such values will be useful to anyone making calculations based on existing data, and in the considerable amount of work with this substance which is planned, we have given the values in Table III. The formulas have been given in previous papers.[8,9]

The values are given as a function of $gj\mathrm{MH}/RT$ and are thus independent of natural constants. In the present work $gj\mathrm{M}$ was taken equal to a total magnetic moment of 38,970 per gram atom of gadolinium and $R = 8.315 \times 10^7$ ergs deg.$^{-1}$ mole^{-1}.

TABLE III

THE INTENSITY AND ENTROPY OF MAGNETIZATION OF AN IDEAL GADOLINIUM COMPOUND

$\frac{gj\mathrm{MH}}{RT}$	$\mathrm{I}/\mathrm{I}_{\mathrm{Sat.}}$	$\Delta S/R$	$\frac{gj\mathrm{MH}}{RT}$	$\mathrm{I}/\mathrm{I}_{\mathrm{Sat.}}$	$\Delta S/R$
0.07	0.02999	0.00105	3.57	0.83952	1.05960
.14	.05990	.00419	3.64	.84436	1.07704
.21	.08965	.00940	3.71	.84901	1.09413
.28	.11918	.01663	3.78	.85348	1.11088
.35	.14840	.02583	3.85	.85778	1.12729
.42	.17725	.03693	3.92	.86192	1.14337
.49	.20567	.04986	3.99	.86592	1.15913
.56	.23359	.06452	4.06	.86975	1.17458
.63	.26097	.08081	4.13	.87344	1.18972
.70	.28775	.09862	4.20	.87701	1.20456
.77	.31388	.11783	4.27	.88045	1.21911
.84	.33934	.13832	4.34	.88376	1.23338
.91	.36410	.15997	4.41	.88696	1.24738
.98	.38812	.18266	4.48	.89005	1.26111
1.05	.41139	.20627	4.55	.89303	1.27458
1.12	.43390	.23068	4.62	.89591	1.28779
1.19	.45563	.25578	4.69	.89870	1.30076
1.26	.47659	.28146	4.76	.90139	1.31349
1.33	.49678	.30761	4.83	.90400	1.32596
1.40	.51620	.33412	4.90	.90651	1.33822
1.47	.53487	.36089	4.97	.90895	1.35025
1.54	.55278	.38784	5.04	.91131	1.36206
1.61	.56997	.41490	5.11	.91360	1.37365
1.68	.58644	.44200	5.18	.91581	1.38503
1.75	.60222	.46905	5.25	.91795	1.39621
1.82	.61732	.49600	5.32	.92003	1.40719
1.89	.63177	.52280	5.39	.92204	1.41798
1.96	.64559	.54940	5.46	.92400	1.42858
2.03	.65880	.57576	5.53	.92589	1.43899
2.10	.67143	.60184	5.60	.92773	1.44921
2.17	.68350	.62761	5.67	.92951	1.45926
2.24	.69504	.65304	5.74	.93124	1.46914
2.31	.70606	.67811	5.81	.93292	1.47885
2.38	.71658	.70280	5.88	.93456	1.48839
2.45	.72665	.72710	5.95	.93614	1.49776
2.52	.73626	.75099	6.02	.93768	1.50697
2.59	.74545	.77446	6.09	.93918	1.51603
2.66	.75424	.79751	6.16	.94063	1.52494
2.73	.76264	.82014	6.23	.94205	1.53370
2.80	.77067	.84235	6.30	.94342	1.54231
2.87	.77837	.86414	6.37	.94476	1.55078
2.94	.78571	.88551	6.44	.94606	1.55911
3.01	.79276	.90646	6.51	.94732	1.56730
3.08	.79950	.92700	6.58	.94855	1.57535
3.15	.80596	.94713	6.65	.94975	1.58327
3.22	.81215	.96685	6.72	.95092	1.59106
3.29	.81809	.98617	6.79	.95205	1.59872
3.36	.82378	1.00509	6.86	.95316	1.60626
3.43	.82924	1.02363	6.93	.95432	1.61368
3.50	.83449	1.04180	7.00	.95528	1.62098

The values of $(\partial \mathrm{I}/\partial \mathrm{H})_S$ are given in Table IV beside those of the previous research which they

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(8) Giauque, THIS JOURNAL, **49**, 1870 (1927).

(9) Giauque and Clark, *ibid.*, **54**, 3135 (1932).

replace. Revised and extended values of the molal intensity of magnetization I, are also given. These values were obtained by means of the equation $I = \int_0^H (\partial I/\partial H)_S \, dH$. We have not included a recalculation of the heat content and energy tables of the previous paper or the thermodynamic temperature in the field as the more interesting values are those at the lower temperatures which are unchanged. Also the calculated change of thermodynamic temperature with field would be less accurate at higher temperatures.

TABLE IV

THE INTENSITY OF MAGNETIZATION AND ITS RATE OF CHANGE WITH FIELD AT CONSTANT ENTROPY

H	$(\partial I/\partial H)_S$ (Giauque and MacDougall)	$(\partial I/\partial H)_S$ (This Research)	I
0	45.60	(45.60)	0
1000	6.46	6.55	(19680)
1500	3.47	3.73	22140
2000	2.10	2.38	23640
3000	0.92	1.13	25310
4000	.49	0.53	26100
5000	.30	.23	26450
6000	.20	.10	26600
7000	...	.04	26670
8000	...	.02	26690
0	38.30	(38.30)	0
1000	6.36	6.52	(18160)
1500	3.41	3.67	20610
2000	2.07	2.32	22080
3000	0.92	1.02	23640
4000	.48	0.46	24340
5000	.30	.21	24650
6000	...	.09	24780
7000	...	.04	24850
8000	...	.02	24890
0	23.09	(23.09)	0
1000	5.64	6.07	(13460)
1500	3.07	3.33	15720
2000	1.87	1.99	17010
3000	0.83	0.81	18310
4000	...	.34	18860
5000	...	.15	19110
6000	...	.09	19230
7000	...	.07	19310
8000	...	.08	19390
0	16.06	(16.06)	0
1000	4.96	5.25	(10370)
1500	2.83	2.89	12340
2000	1.75	1.73	13460
3000	...	0.74	14610
4000	...	.34	15120
5000	...	.19	15380
6000	...	.15	15560
7000	...	.16	15700
8000	...	.19	15860
0	11.79	(11.79)	0
1000	4.37	4.44	(8240)
1500	2.54	2.47	9910
2000	1.60	1.52	10860
3000	...	0.72	11880
4000	...	.42	12410
5000	...	.30	12750
6000	...	.27	13000
7000	...	.28	13270
8000	...	.31	13550
0	9.81	(9.81)	0
1000	3.94	3.95	(7020)
1500	2.35	2.21	8520
2000	...	1.42	9400
3000	...	0.73	10400
4000	...	.48	10980
5000	...	.38	11400
6000	...	.35	11730
7000	...	.35	12090
8000	...	.38	12460

It is difficult to estimate the absolute accuracy of the differential susceptibility measurements. The susceptibility values depend on the difference between the values which the coil would have in the absence of the sample and the actual measurement. The precision of the inductance measurements was about 0.02% and an error of this amount in either value would lead to an error of nearly 0.1 unit in $(\partial I/\partial H)_S$.

Failure of the magnetic system to maintain equilibrium with the lattice energy[10] which becomes appreciable at the higher temperatures would make the measured values of $(\partial I/\partial H)_S$ too low. Any such effect as might exist in the present case is probably within the limit of accuracy.

In Table V we have compared experimental and theoretical values of the intensity of magnetization using the particular fields at which the temperature was recorded in the previous work.[1] The agreement is well within the limits of accuracy.

TABLE V

COMPARISON OF THE THEORETICAL AND MEASURED VALUES OF THE MOLAL INTENSITY OF MAGNETIZATION

T, °K.	H	I Theoretical	$\int_0^H (\partial I/\partial H)_S \, dH$
1.444	6420	26,060	26,640
1.451	5660	24,120	24,730
1.423	3750	18,380	18,750
1.430	2760	14,110	14,390
1.419	2040	10,830	10,920
1.429	1630	8,720	8,810

Summary

The heat capacity of gadolinium phosphomolyb-

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[10] *E. g.*, see de Haas and du Pre, *Physica*, **6**, 705 (1939).

date tridecahydrate has been measured from 0.17 to 4.7°K.

The sample was cooled by adiabatic demagnetization and energy was introduced by means of an amorphous carbon thermometer–heater.

Apparatus has been described for the measurement of adiabatic differential magnetic susceptibility $(\partial I/\partial H)_S$, while the sample is in a field with the usual fluctuations caused by a motor generator supply of current.

The differential susceptibility data for gadolinium phosphomolybdate tridecahydrate presented in a previous research by Giauque and MacDougall have been improved and extended at fields above 1000 gauss.

The intensity of magnetization along six adiabatic paths has been given as a function of magnetic field strength.

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[CONTRIBUTION NO. 205 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Apparent and Partial Molal Volumes of the Sodium Salts of Formic, Acetic, Propionic and *n*-Butyric Acids in Aqueous Solution

BY GEORGE M. WATSON WITH W. A. FELSING

Introduction

The object of this investigation was the determination of the apparent and partial molal volumes of the sodium salts of formic, acetic, propionic and *n*-butyric acids at different temperatures and concentrations from accurate density measurements in order to ascertain the effect of the increase in chain length upon the change in both the apparent and partial molal volumes. The literature affords but limited data on the densities of aqueous solutions of these salts; in some cases the methods of preparation and of purification are not given. These values are listed in "International Critical Tables,"[1] but the accuracy claimed is usually not better than about 1 part in 1000. Since this accuracy is not sufficient for the evaluation of reliable apparent and partial molal volumes, it was decided to re-determine the densities of solutions of the four salts.

Experimental

The experimental procedure consisted of determining 25, 30, 35 and 40° the densities of aqueous solutions of the salts in a specially designed pycnometer.

The Pycnometer.—Three separate pycnometers of Pyrex glass and of about 50 ml. capacity were employed. They were similar in design to those described by Kelso and Felsing.[2] The pycnometers were calibrated with distilled water (a) under each set of experimental conditions and at 0° and (b) by calibrating at 0° and employing the equation of Felsing and Thomas[3] for the thermal expansion of Pyrex glass:

$$V_{\mathrm{T}}\ (\text{Pyrex}) = V_0[0.998325 + 2.316 \times 10^{-7}T + 2.75 \times 10^{-9}T^2 - 2.2 \times 10^{-11}T^3] \quad (1)$$

The two calibrations agreed to at least 1 part in 15,000. The graduated capillaries of the pycnometers were calibrated with mercury; the volume per millimeter of capillary was 0.007 ml. at 0°. Volumes could be read correctly to within 1 part in 15,000.

The Thermostat.—Thermostat temperatures could be held constant to within 0.05° by means of a mercury-in-steel thermoregulator and a sensitive relay system controlling a 75-watt heater. Temperatures were determined by a long mercurial thermometer of short range calibrated by the National Bureau of Standards.

Weight Determinations.—Calibrated weights were employed; the balance had a Pregl sensitivity of better than 25 and weighings could be reproduced to better than 0.05 mg.; all weights were corrected to a vacuum.

Materials. (a) **Sodium Formate and Sodium Acetate.**—C. P. salts were recrystallized three times from conductivity water. (b) **Sodium Propionate.**—Weighed equivalent quantities of highly purified sodium carbonate and of propionic acid ($n^{19.9}_{\mathrm{D}}$, 1.3874; "I. C. T." value,[4] $n^{19.9}_{\mathrm{D}}$, 1.38736) were allowed to react in solution. The temperature was raised, after reaction, to 90° to expel the carbon dioxide from the solution. (c) **Sodium Butyrate.**—This salt was prepared by the interaction of pure sodium carbonate and butyric acid (m. p., −8.0°; Heilbron,[5] −8.0°). (d) Solutions.—Concentrated stock solutions of these salts were analyzed by treatment of a proper-sized sample with a slight excess of C. P. sulfuric acid in a platinum crucible. The sodium sulfate residue, after careful evaporation and heating to low red heat, had a weight of approximately 0.5 g. or over; analyses were made in triplicate and checked to better than 0.05%. All dilutions of this stock solution were made by weight. (e) **Water.**—All water used had a specific conductance of 1.0 × 10^{-6} reciprocal ohms.

The Experimental Data.—All solutions were introduced into the pycnometer by means of a long, thin capillary; the filled pycnometer was weighed at room temperature

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(1) "I. C. T.," Vol. 3, p. 83; *ibid.*, Vol. 7, p. 74.

(2) Kelso with Felsing, THIS JOURNAL, **60**, 1949 (1938).

(3) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

(4) "I. C. T.," Vol. 7, p. 35.

(5) Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1934, p. 222.