

Rossini and co-workers<sup>9</sup> list values leading to the following heats of formation from the oxides (kcal./mole):  $-24.7$  for strontium metasilicate,  $-33.0$  for strontium orthosilicate,  $-20.7$  for barium metasilicate, and  $-24.6$  for barium orthosilicate, based upon older thermochemical work. The present values are considered much superior. It is of interest to note that the new values become increasingly negative in going from magnesium to barium in both the meta- and ortho-series whereas the solder work indicated a reversal in this trend.

TABLE IV  
HEATS OF FORMATION FROM THE OXIDES AT 298.15°K.  
(KCAL./MOLE)

Substance	$\Delta H$	Substance	$\Delta H$
MgSiO <sub>3</sub> <sup>a</sup>	$-8.69 \pm 0.15$	Mg <sub>2</sub> SiO <sub>4</sub> <sup>c</sup>	$-15.12 \pm 0.21$
CaSiO <sub>3</sub> <sup>b</sup>	$-21.25 \pm .13$	Ca <sub>2</sub> SiO <sub>4</sub> ( $\beta$ )	$-30.19 \pm .23$
SrSiO <sub>3</sub>	$-31.24 \pm .16$	Ca <sub>2</sub> SiO <sub>4</sub> ( $\gamma$ )	$-32.7$
BaSiO <sub>3</sub>	$-38.03 \pm .17$	Sr <sub>2</sub> SiO <sub>4</sub>	$-50.04 \pm .24$
		Ba <sub>2</sub> SiO <sub>4</sub>	$-64.48 \pm .28$

<sup>a</sup> Clinoenstatite. <sup>b</sup> Wollastonite. <sup>c</sup> Forsterite.

The heats of formation of the silicates from the oxides may be converted to heats of formation from the elements by means of available data for the oxides. In this connection, the heat of formation of quartz ( $-210.26$  kcal./mole) obtained by

(9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circular 500, Feb. 1, 1952.

Humphrey and King<sup>10</sup> and the recent value of Huber and Holley<sup>11</sup> for calcium oxide ( $-151.79$  kcal./mole) are adopted. Shomate and Huffman<sup>12</sup> and Holley and Huber<sup>13</sup> have obtained values of the heat of formation of magnesium oxide that differ by only 140 cal./mole; the mean,  $-143.77$  kcal./mole, is adopted. Values for strontium oxide ( $-141.1$  kcal./mole) and barium oxide ( $-133.4$  kcal./mole) are from NBS Circular 500.<sup>9</sup> These values lead to the heats of formation from the elements listed in Table V, which also brings up-to-

TABLE V  
HEATS OF FORMATION FROM THE ELEMENTS AT 298.15°K.  
(KCAL./MOLE)

Substance	$\Delta H$	Substance	$\Delta H$
MgSiO <sub>3</sub>	$-362.7$	SrSiO <sub>3</sub>	$-382.6$
Mg <sub>2</sub> SiO <sub>4</sub>	$-512.9$	Sr <sub>2</sub> SiO <sub>4</sub>	$-542.5$
CaSiO <sub>3</sub>	$-383.3$	BaSi <sub>2</sub> O <sub>5</sub>	$-595.2$
Ca <sub>2</sub> SiO <sub>4</sub> ( $\beta$ )	$-544.0$	Ba <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	$-980.0$
Ca <sub>2</sub> SiO <sub>4</sub> ( $\gamma$ )	$-546.5$	BaSiO <sub>3</sub>	$-381.7$
Ca <sub>3</sub> SiO <sub>5</sub>	$-692.6$	Ba <sub>2</sub> SiO <sub>4</sub>	$-541.5$

date the values given by Torgeson and Sahama<sup>1</sup> and King.<sup>2</sup>

(10) G. L. Humphrey and E. G. King, THIS JOURNAL, **74**, 2041 (1952).

(11) E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, **60**, 498 (1956).

(12) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1627 (1943).

(13) C. E. Holley, Jr., and E. J. Huber, Jr., *ibid.*, **73**, 5577 (1951). BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

## Low Temperature Heat Capacities of Magnesium Diboride (MgB<sub>2</sub>) and Magnesium Tetraboride (MgB<sub>4</sub>)

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The heat capacities of magnesium diboride (MgB<sub>2</sub>) and magnesium tetraboride (MgB<sub>4</sub>) were measured in the temperature range 18 to 305°K. The values of heat capacity, entropy, enthalpy and free energy function have been tabulated at integral values of temperature. The entropy at 298.16°K. of MgB<sub>2</sub> is  $8.60 \pm 0.04$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, that of MgB<sub>4</sub> is  $12.41 \pm 0.06$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. The heat capacity of these compounds at the lowest temperatures measured do not exhibit at  $T^2$  relationship characteristic of some substances having a layer structure.

### Introduction

The existence of magnesium borides with formulas MgB<sub>2</sub><sup>2,3</sup> and MgBr<sub>4</sub><sup>2</sup> has been shown by X-ray diffraction studies and chemical analysis. The diboride has a layered structure in which hexagonal nets of boron atoms are separated by layers of magnesium atoms. The structure of the tetraboride is not known. Recent studies have shown that in crystalline substances with layer structures, such as graphite<sup>4</sup> and gallium,<sup>5</sup> the heat capacity at low temperatures follows a  $T^2$  law, rather than the Debye  $T^3$  law. However, for CdI<sub>4</sub>, a compound having a layered structure, it has been found that neither the  $T^2$  nor  $T^3$  relationship was followed

at low temperatures.<sup>6</sup> The pronounced anisotropy characteristic of the graphite and gallium structures does not prevail in CdI<sub>4</sub> which may account for the lack of a  $T^2$  relationship in the latter case.

The layer structure of MgB<sub>2</sub> is more closely related to that of CdI<sub>4</sub> than that of graphite from the standpoint of anisotropy. However, in the case of MgB<sub>4</sub>, if the hexagonal boron network is retained, the interactions between the layers may be sufficiently diminished so as to lead to a  $T^2$  dependence in the heat capacity at relatively low temperatures.

### Apparatus and Procedure

**Calorimeter.**—The Nernst type vacuum calorimeter which was used for the measurements was similar to that described by Johnston and Kerr<sup>7</sup> with only minor changes being made in the calorimeter assembly and vacuum system.

(1) Department of Chemistry, Ohio State University, Columbus, O.  
(2) V. Russell, R. Hirst, F. A. Kanda and A. J. King, *Acta Cryst.*, **6**, 870 (1953).

(3) M. E. Jones and R. E. Marsh, THIS JOURNAL, **76**, 1434 (1954).

(4) W. DeSorbo and W. W. Tyler, *Phys. Rev.*, **83**, 878 (1951); *J. Chem. Phys.*, **21**, 1660 (1953).

(5) W. DeSorbo, *ibid.*, **21**, 168 (1953).

(6) A. S. Dworkin, D. J. Sasmor and F. R. Van Artsdalen, THIS JOURNAL, **77**, 1304 (1955).

(7) H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).

The calorimeter itself had a capacity of about 60 ml. Its cylindrical surface was wound with AWG 40, formex-insulated gold-0.15% silver wire. This served as both resistance thermometer and heater and its resistance at room temperature was about 300 ohms. The winding was covered with gold foil cemented with General Electric Adhesive No. 7031. The calorimeter assembly was inserted directly into a Collins helium cryostat.

**Electrical Circuits.**—A White double potentiometer with a 100,000 microvolt range was used for the resistance thermometer and energy measurements together with suitable standard resistors calibrated by the National Bureau of Standards. A Wenner potentiometer with a 10,000 microvolt range was used to measure the thermocouple electromotive forces. A 30,000:100 ohm voltage divider was used in the energy circuit.

**Timing.**—The timing of the energy input was done by a clutch-operated Standard Electric Timing Company timing clock which read directly to 0.01 sec. This clock was driven by the amplified output of a General Radio Company precision fork and was actuated by a single master switch which also controlled the energy input.

**Temperature Scale.**—The thermodynamic temperature scale for this Laboratory was established by comparison of a copper-constantan thermocouple against a standard thermocouple obtained from the Ohio State University Cryogenic Laboratory, and calibrated there against a primary standard, No. 89.<sup>8</sup> Absolute temperatures are probably accurate to within  $\pm 0.05^\circ$ . The uncertainties in the measured temperature differences of the heat capacity runs are no greater than  $\pm 0.005^\circ$ .

**Data Computation.**—The calculations were made as outlined by Glauque<sup>9</sup> and Johnston.<sup>5</sup> Corrections were made to the measured heat capacities for the energy lost in the potential divider and leads, heat leaks, calorimeter surface superheating during energy input, drifts in block temperatures, radiation to the calorimeter from the blocks, potentiometer battery drifts, and heat generated in the leads connecting the calorimeter winding with the block terminals. The same corrections were applied to the empty calorimeter calculations. Helium gas was introduced into the calorimeter after filling with solid and before sealing to reduce superheating. Corrections were made for this and for the other impurities as listed in Table I, assuming that the heat capacities of the individual substances were completely independent and additive.

**Preparation of the Magnesium Borides.**—Magnesium diboride was prepared by heating together in a helium atmosphere at  $900 \pm 25^\circ$  for three hours stoichiometric quantities of the elements. The magnesium was a commercial grade analyzing 99.9%. The boron was obtained by vacuum sublimation at  $1500^\circ$  of Fisher Scientific Company "purified amorphous boron." After our further purification the residue analyzed  $99.70 \pm 0.25\%$  boron by sodium hydroxide-mannitol titration of the oxidized product. The  $MgB_2$  product included gross impurities as given in Table I and spectroscopic impurities totalling less than 0.1% and consisting principally of iron, aluminum, manganese, silicon and calcium.

The magnesium tetraboride was made by treating the magnesium diboride with somewhat more than two equivalents of purified boron at  $1050 \pm 25^\circ$  for four hours in an argon atmosphere. Higher temperatures favored production of a colored magnesium boride thought to be  $MgB_6$ ; lower temperatures and shorter times gave lower yields of  $MgB_4$  and larger amounts of unreacted  $MgB_2$ . The latter, together with other soluble impurities, was removed by treatment with warm dilute hydrochloric acid and subsequent washing with water. Considerable free boron remained with the  $MgB_4$ .

X-Ray diffraction studies identified the substances present and chemical analysis established the amounts in each of the two boride preparations. The analysis for each is given in Table I.

## Results and Discussion

The calculated molal heat capacity of magnesium diboride is shown in Table II and that of mag-

(8) T. Robin, H. L. Johnston and H. Altman, *THIS JOURNAL*, **73**, 3401 (1951).

(9) W. F. Glauque, "Heat Capacity Calculations," unpublished.

TABLE I

COMPOSITION OF SAMPLES OF MAGNESIUM BORIDES		
Substance	MgB <sub>2</sub> , wt. %	MgB <sub>4</sub> , wt. %
MgB <sub>2</sub>	93.90	...
MgB <sub>4</sub>	1.08	89.42
B	3.69	10.32
Mg	0.46	...
MgO	0.73	...
Spectroscopic impurity (as SiO <sub>2</sub> )	0.14	0.25
Wt. of sample in calorimeter (g.)	62.685	43.946

TABLE II

MOLAL HEAT CAPACITY OF MAGNESIUM DIBORIDE (MgB<sub>2</sub>)

Mol. wt. 45.96; 1.2808 moles			
Mean temp., °K.	C <sub>p</sub> , cal. deg. <sup>-1</sup>	Mean temp., °K.	C <sub>p</sub> , cal. deg.
18.28	...	140.35	5.070
21.12	0.010	154.92	5.911
23.05	.022	173.53	6.864
25.06	.034	194.73	7.973
27.19	.046	219.27	9.096
29.66	.053	236.77	9.857
32.41	.074	238.63	9.728
34.92	.103	246.14	10.111
37.75	.134	253.63	10.581
41.37	.163	259.61	10.694
45.43	.248	266.88	10.872
54.12	.450	274.04	11.134
57.42	.554	286.69	11.414
60.99	.661	298.81	11.492
65.42	.849		
70.26	1.108	26.44	0.058
75.60	1.355	128.41	4.398
81.29	1.684	145.03	5.366
85.52	1.871	160.29	6.266
91.29	2.188	183.37	7.414
97.04	2.485	208.21	8.593
102.83	2.786	248.39	10.196
108.58	3.155	279.19	11.251
114.13	3.421	300.14	11.410
119.20	3.767		
124.40	4.043	237.71	10.032
129.79	4.319	238.69	9.882
		254.87	10.409
203.42	11.419	287.69	11.370
		304.22	11.435
136.05	4.823	304.06	11.424

nesium tetraboride in Table III. These results have been corrected for the impurities listed in Table I.<sup>10</sup> They are listed in the order done. Temperature increments may be inferred from the mean temperatures. They never exceeded 10% of the temperature scale or  $10^\circ$ , whichever was smaller. Computed thermodynamic functions for these compounds are given in Tables IV and V. The ice point was taken as  $273.16^\circ K.$  and the results are expressed in calories equal to 4.1840 absolute joules.

The heat capacities of  $MgB_2$  and  $MgB_4$  do not follow the Debye  $T^3$  law at low temperatures; hence, a graphical extrapolation was made to absolute zero to determine the entropy and other

(10) R. S. Craig, C. A. Krier, L. W. Coffer, E. A. Bates and W. E. Wallace, *THIS JOURNAL*, **76**, 238 (1954); H. L. Johnston, H. N. Hersh and E. C. Kerr, *ibid.*, **73**, 1112 (1951); W. F. Glauque and R. C. Archibald, *ibid.*, **59**, 561 (1937); C. T. Anderson, *ibid.*, **58**, 568 (1936).

TABLE III  
MOLAL HEAT CAPACITY OF MAGNESIUM TETRABORIDE  
(MgB<sub>4</sub>)

Mean temp., °K.	Mol. wt. 67.60; C <sub>p</sub> , cal. deg. <sup>-1</sup>	0.5813 mole Mean temp., °K.	C <sub>p</sub> , cal. deg. <sup>-1</sup>
187.17	10.130	47.81	0.944
265.74	15.177	53.71	1.247
271.52	15.423	78.84	2.744
276.60	15.712	86.28	3.236
		94.01	3.750
20.29	0.071	103.08	4.288
25.83	.050	112.87	4.889
28.72	.243	121.84	5.553
31.45	.296	130.84	6.169
36.82	.449	139.20	6.740
149.05	7.430	188.99	10.215
155.81	7.971	201.24	11.161
162.66	8.438	212.85	11.995
169.74	8.873	225.01	12.647
177.27	9.320		
235.27	13.318	20.56	0.067
242.98	13.765	22.66	.028
251.01	14.298	24.38	.076
257.37	14.611	26.26	.155
267.17	15.215	29.82	.237
284.62	16.340	69.03	2.032
		75.69	2.489
17.34	0.110	154.62	7.799
52.96	1.175	179.64	9.298
58.32	1.509	220.17	11.902
62.81	1.717	225.11	13.044
68.65	2.011	281.27	16.536
75.11	2.522	283.39	15.017
		295.49	16.681
17.52	0.015	299.53	16.824
20.73	.033		
27.94	.167	280.31	15.939
34.55	.387	285.36	16.283
38.53	.502	290.41	16.438
42.77	.628		

TABLE IV  
THERMODYNAMIC FUNCTIONS FOR MAGNESIUM DIBORIDE  
(MgB<sub>2</sub>)

Temp., °K.	C <sub>p</sub> , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	S <sup>0</sup> , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	(H <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal. deg. <sup>-1</sup> mole <sup>-1</sup>	-(F <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal. deg. <sup>-1</sup> mole <sup>-1</sup>
20	0.014	0.005	0.0004	0.004
25	.036	.010	.005	.005
30	.060	.015	.008	.007
35	.095	.027	.019	.008
40	.150	.045	.033	.012
45	.222	.070	.053	.017
50	.337	.102	.076	.026
60	.630	.183	.141	.042
70	1.094	.318	.246	.072
80	1.595	.491	.379	.112
90	2.125	.711	.540	.171
100	2.670	.962	.729	.233
110	3.241	1.238	.938	.300
120	3.823	1.549	1.147	.402
130	4.43	1.872	1.372	.500
140	5.05	2.231	1.618	.613
150	5.63	2.65	1.859	.731
160	6.20	2.98	2.120	.862
170	6.72	3.37	2.365	1.001

180	7.24	3.77	2.632	1.141
190	7.74	4.18	2.876	1.300
200	8.22	4.59	3.126	1.462
210	8.68	4.99	3.382	1.612
220	9.11	5.41	3.645	1.768
230	9.53	5.82	3.90	1.92
240	9.95	6.24	4.15	2.09
250	10.34	6.65	4.38	2.27
260	10.71	7.07	4.61	2.46
270	11.01	7.48	4.84	2.64
280	11.26	7.89	5.07	2.82
290	11.39	8.27	5.28	2.99
298.16	11.43	8.60	5.45	3.15
300	11.44	8.67	5.49	3.18

TABLE V  
THERMODYNAMIC FUNCTIONS FOR MAGNESIUM TETRA-  
BORIDE (MgB<sub>4</sub>)

Temp., °K.	C <sub>p</sub> , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	S <sup>0</sup> , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	(H <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal. deg. <sup>-1</sup> mole <sup>-1</sup>	-(F <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal. deg. <sup>-1</sup> mole <sup>-1</sup>
20	0.030	0.022	0.018	0.004
25	.107	.046	.037	.009
30	.225	.077	.063	.014
35	.370	.119	.093	.026
40	.540	.175	.130	.045
45	.746	.242	.184	.058
50	.978	.339	.259	.080
60	1.520	.559	.413	.146
70	2.15	.831	.622	.209
80	2.80	1.155	.852	.303
90	3.45	1.52	1.111	.413
100	4.12	1.92	1.370	.546
110	4.88	2.34	1.648	.688
120	5.45	2.79	1.93	.856
130	6.12	3.26	2.23	1.031
140	6.80	3.73	2.53	1.202
150	7.49	4.23	2.84	1.39
160	8.20	4.73	3.15	1.58
170	8.90	5.25	3.47	1.78
180	9.61	5.78	3.80	1.98
190	10.33	6.32	4.13	2.19
200	11.06	6.86	4.46	2.40
210	11.74	7.42	4.79	2.63
220	12.40	7.98	5.12	2.86
230	13.01	8.55	5.45	3.10
240	13.61	9.12	5.78	3.34
250	14.20	9.68	6.10	3.58
260	14.78	10.75	6.42	3.83
270	15.34	10.82	6.74	4.08
280	15.88	11.39	7.06	4.33
290	16.40	11.95	7.37	4.58
298.16	16.81	12.41	7.63	4.78
300	16.90	12.52	7.68	4.84

thermodynamic functions. The entropy of the MgB<sub>2</sub> at 298.16°K. is 8.60 ± 0.04 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, with 0.013 (0.15%) being obtained by the extrapolation. For MgB<sub>4</sub>, the entropy at 298.16°K. is 12.41 ± 0.06 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, with 0.062 (0.50%) being obtained by the extrapolation.

Since the X-ray diffraction studies<sup>1,2</sup> had shown layered structures for at least one of these compounds, MgB<sub>2</sub> plots of log C<sub>p</sub> versus log T were made to determine whether a region of T<sup>2</sup> dependency existed. A linear relationship was found for MgB<sub>2</sub> from 20 to 80°K. with slope of 3.5 and for MgB<sub>4</sub> from 30 to 70°K. with slope of 2.6.

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## Heat Capacity and Magnetic Susceptibility of Copper(II) Tetrammine Sulfate Monohydrate from 1.3 to 24°K.

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The heat capacity and magnetic susceptibility of copper tetrammine sulfate have been investigated between 1.3 and 29°K. The results indicate strong interactions between copper ions, leading to a transition, of order higher than the second, with a maximum in the heat capacity of 0.75 cal. mole<sup>-1</sup> deg.<sup>-1</sup> at 3.0°K. The magnetic susceptibility is nearly constant between 1 and 4°K., and thereafter falls gradually; the maximum value of the molar susceptibility is 0.04. It is believed that the interaction is directly related to the coordination with ammonia.

### Introduction

The magnetic behavior of crystalline salts of cupric ion varies considerably from salt to salt. The Tutton salt, CuSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O, is one of the most ideal of all paramagnetic salts, and has been used in the attainment of temperatures far below 1°K.<sup>1</sup> The ordinary hydrated sulfate, CuSO<sub>4</sub>·5H<sub>2</sub>O, has a magnetic transition<sup>2</sup> in the vicinity of 1°K., the exact nature of which is not clear. The hydrated chloride, CuCl<sub>2</sub>·2H<sub>2</sub>O, has a lambda-type transition at about 4.2°K. below which the salt becomes anti-ferromagnetic.<sup>3</sup> The acetate, Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O, becomes diamagnetic at about 50°K.<sup>4</sup>

With the exception of the acetate, the properties of all the salts described above may be explained in terms of the effect of crystalline environment on a substantially free copper ion. The ground state of free cupric ion is <sup>2</sup>D<sub>5/2</sub>. At temperatures above the magnetic transitions, the typical copper salts behave almost as <sup>2</sup>S states; their magnetic susceptibilities are but slightly higher than the "spin-only" values.

Copper tetrammine sulfate differs formally from CuSO<sub>4</sub>·5H<sub>2</sub>O only in the replacement of four of the water molecules by ammonia molecules. In the crystal the basic unit is Cu(NH<sub>3</sub>)<sub>4</sub><sup>++</sup>, rather than Cu(H<sub>2</sub>O)<sub>4</sub><sup>++</sup>; due to differences in crystal structure, the less near neighbors of the copper ion are different in the two salts. At the outset of this research, it was expected that the ammine salt would behave in the same general fashion as the hydrate, so that comparison of the two would show the effect of the ammonia and in addition shed further light on the behavior of the ordinary hydrate.

### Experimental

The experimental procedures were substantially the same as those employed by Fritz and Pinch in the investigation

- (1) J. Ashmead, *Nature*, **143**, 853 (1939).
- (2) T. H. Geballe and W. F. Gianque, *THIS JOURNAL*, **74**, 3515 (1952).
- (3) S. Friedberg, *Physica*, **18**, 714 (1952); J. van den Handel, H. M. Gijssman and N. S. Poulis, *ibid.*, **18**, 862 (1952).
- (4) B. C. Guha, *Proc. Roy. Soc. (London)*, **A206**, 353 (1951).

of vanadium ammonium alum,<sup>5</sup> and will not be described in detail. The ellipsoidal sample container had an internal volume of 31.13 cm.<sup>3</sup>, and contained 32.64 g. of the salt. The weight of the container was 19.56 g. The carbon thermometer had a resistance at room temperature of about 6000 ohms. At low temperatures its sensitivity was decidedly higher than that of the thermometer previously described,<sup>6</sup> but it was also considerably less stable.

The specimen used in the investigation was prepared by addition of C.P. ammonium hydroxide to a solution of C.P. copper sulfate according to the method of Walton.<sup>6</sup> The crystalline salt was obtained by cooling of the resulting hot solution. The crystals used were ground to a powder; the portion selected for use passed through a 20-mesh screen, but failed to pass through a 100-mesh screen. The irregular particles were stored for a time under a saturated solution of the salt and then dried manually.

A sample for analysis was withdrawn during the filling of the sample tube. Its copper content was determined electrolytically to be 25.92% (theoretical 25.87%); the ammonia-copper ratio was determined by titration to be 3.92 to 1.

Measurements of heat capacity and magnetic susceptibility were made in the manner previously described.<sup>5</sup> For the low temperature susceptibility measurements, the coil constants were obtained with the specimen near 70°K., after the coils had been cooled by liquid helium or hydrogen. The effect of the sample at 70°K., upon the coils was determined in a separate experiment in which the specimen was cooled from room temperature to 70°K. The susceptibilities were thus based upon the room temperature susceptibility of the salt. The molar susceptibility at 290°K. is 1.40 × 10<sup>-3</sup>, according to Bhatnage, Lessheim and Khanna.<sup>7</sup> An independent check on our specimen by the Gouy method gave a result of 1.35 × 10<sup>-3</sup>. (For the purpose of the correction this susceptibility is required only to about 20%.)

### Results

The heat capacity of the salt was measured between 1.3 and 24°K. The observed measurements were corrected for the heat capacity of 19.56 g. of Pyrex as previously described.<sup>5</sup> At the highest temperatures, this represented 1/4 of the observed heat capacity. In view of the unusual behavior of the heat capacity between 12 and 20°K., this region was investigated in three separate sets of experiments; the results of the several sets were consistent. The heat capacity measurements are given

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- (7) S. S. Bhatnage, H. Lessheim and M. L. Khanna, *J. Ind. Chem. Soc.*, 445 (1937).