THE HEAT CAPACITIES AT LOW–TEMPERATURES AND ENTROPIES AT 298.15 K OF NESQUEHONITE, MgCO₃·3H₂O, AND HYDROMAGNESITE[1]

RICHARD A. ROBIE, *U.S. Geological Survey, 8001 Newell Street, Silver Spring, Maryland 20910*

AND

BRUCE S. HEMINGWAY, *Department of Geology, University of Minnesota, Minneapolis, Minnesota 55455 and U.S. Geological Survey, Silver Spring, Maryland 20910*

ABSTRACT

The heat capacity of hydromagnesite, from Hindubagh, West Pakistan, and synthetic nesquehonite, MgCO₃·3H₂O, have been measured from approximately 18 to 309 and to 341 K, respectively.

The thermodynamic properties at 298.15K (25.0°C) $C°_p$, $(H°_{298.15} - H°_0)/T$, $(G°_{298.15} - H°_0)/T$, and $(S°_{298.15} - S°_0)$ for hydromagnesite, $5MgO·4CO_2·5H_2O$, are 125.86 ± 0.37, 67.35 ± 0.20, -53.03 ± 0.16, and 120.38 ± 0.37 cal mol⁻¹K⁻¹, and for nesquehonite, $MgCO_3·3H_2O$, are 56.81 ± 0.17, 26.11 ± 0.08, -20.65 ± 0.06, and 46.76 ± 0.14 cal mol⁻¹K⁻¹. The heat capacity of nesquehonite exhibits a λ–type transition between 280 and 320 K. Between 295 and 310K the heat capacity increases very rapidly from 55 to 64.7 cal mol⁻¹K⁻¹ and then drops precipitously to 57 cal mol⁻¹K⁻¹ with a maximum at 306.5K (33.35°C). The entropy change associated with this transistion is about 0.6 cal mol⁻¹K⁻¹.

INTRODUCTION

Hydromagnesite is a common product of the low–temperature alteration of serpentine rocks where it is found in association with artinite and brucite. It is also found, much less commonly, with magnesite and in this association the magnesite has apparently formed from the hydromagnesite (Christ and Hostetler, 1970).

Nesquehonite ($MgCO_3·3H_2O$) was originally found at the base of stalactites and as incrustations in an anthracite coal mine at Nesquehoning, Carbon County, Pennsylvania (Palache, Berman, and Frondel, 1951, p. 226). Nesquehonite has also been found as a fracture filling in serpentine and as deposits from mineral springs, and has recently been described from a carbonate scale in an air scrubber of an air conditioner by Marschner (1969) where it occurs with hydrocalcite ($CaCO_3·H_2O$). Nesquehonite is involved in numerous equilibria connected with the aqueous geochemistry of magnesium in natural waters (Kazakov, Tikhomirova, and Plotnikova, 1957, and Langmuir, 1965).

---

[1] Publication authorized by the Director, U.S. Geological Survey.

Several values for the standard Gibbs free energy of formation of $MgCO_3 \cdot 3H_2O$ are available based on the solubility studies of Kline (1929), Langmuir (1965), and P. B. Hostetler (written communication, April, 1970). Langmuir (1965) has summarized the aqueous solubility data for $MgCO_3 \cdot 3H_2O$ and estimated the entropy as 46.9 ± 2.1 cal mol^{-1}K^{-1}.

In his analysis of the equilibria in the system $MgO-CO_2-H_2O$ Langmuir (1965) suggested that the value of Stout and Robie (1962), (see also Robie, 1965) for the standard Gibbs free energy of formation of $MgCO_3$ (magnesite) was incorrect by 4 kcal. If true this would severely modify the calculated stable phase relations in the $MgO-CO_2-H_2O$ system. It therefore seemed worthwhile to determine the standard Gibbs free energy of formation of $MgCO_3 \cdot 3H_2O$ and $5MgO \cdot 4CO \cdot 5H_2O$ by calorimetric methods as an independent check on Langmuir's conclusions. While this work was in progress, Christ and Hostetler (1970) confirmed the value for the free energy of formation calculated by Stout and Robie (1963) on the basis of careful solubility measurements of $MgCO_3$ in H_2O at fixed CO_2 pressures at 90°C.

Table 1. Chemical analyses of hydromagnesite.

	1	2	3	4	5	6	7
MgO	43.10	43.76	43.37	44.02	44.01	43.29	44.14
CO_2	37.64	37.33	37.11	36.84	35.70	36.10	36.14
H_2O	19.26	19.63	19.38	19.60	19.53	20.25	19.72
FeO						0.16	
Fe_2O_3				0.30			
Insoluble						0.04	
	100.00	100.72	99.86	100.76	99.24	99.84	100.00

1. $5MgO \cdot 4CO_2 \cdot 5H_2O$

2. Hindubagh, West Pakistan. (Heat of solution sample.) Analyst Ellen Gray, U.S. Geological Survey (W-169044).

3. Hindubagh, West Pakistan. (Heat capacity sample.) Analyst Ellen Gray, U.S. Geological Survey (W-169045).

4. Coalinga, California. Analyst Ellen Gray, U.S. Geological Survey (W-169043).

5. Hindubagh, West Pakistan. (Shams, 1965).

6. Rockville, Maryland. Analyst J.J. Fahey, U.S. Geological Survey (Larrabee, 1969).

7. $4MgO \cdot 3CO_2 \cdot 4H_2O$

A second reason for a calorimetric determination of $\Delta G^{\circ}{}_f$ of $MgCO_3 \cdot 3H_2O$ and $5MgO \cdot 4CO_2 \cdot 5H_2O$ (hydromagnesite) is to obtain an independent value of the standard free energy of formation of Mg^{2+} by combining the calorimetric data with precise solubility results.

In this paper we report measurements of the heat capacities of hydromagnesite and nesquehonite and calculated values of the entropy change, $S^{\circ}{}_{298.15} - S^{\circ}{}_0$, for these phases.

<div align="center">MATERIALS</div>

Hydromagnesite

The sample of hydromagnesite used for our low–temperature heat capacity measurements was kindly supplied by Dr. S. A. Bilgrami who collected it from the Zhob Valley, Hindubagh, West Pakistan, (Bilgrami, 1964), and who supplied the following information: "the mineral occurs as veins in fractured serpentine on the eastern slope of Jungtoghar about 900 yards east of mine 88. The veins vary in thickness from a fraction of a centimeter to 15 centimeters, are several meters long and follow no definite direction" (S. A. Bilgrami, written communication to B. S. Hemingway, December 8, 1966). The material was in the form of small twinned crystals of between 1 and 6 mm on a side. Chemical analyses of this sample of hydromagnesite together with one from Coalinga,

Table 2. Chemical analyses of nesquehonite, $MgCO_3 \cdot 3H_2O$.

	1	2	3	4	5	6
MgO	*28.40	29.96	27.7	33.40	36.68	29.13
CO_2	30.44	30.72	30.4	32.45	34.44	31.81
H_2O^-	39.27	38.62	24.3	34.39	28.12	39.06
H_2O^+			15.2			
SiO_2			0.26			
Al_2O_3			1.80			
K_2O		0.01	0.42			
MgO By difference	28.40					
	98.11	99.31	100.08	100.24	99.24	100.00
Elapsed time (days) after synthesis	8	21	63	312	665	

* Residue after ignition.

1. Sample NBH-4 Analyst Ellen Gray, U.S. Geological Survey (W-171159).

2. Sample NBH-2 Analysts D.B. Heck, J.R. Schleicher, Illinois Geological Survey (R-6534).

3. Sample NBH-4 Analyst Leonard Shapiro, U.S. Geological Survey (W-171159).

4. Sample NBH-3 Analyst Ellen Gray, U.S. Geological Survey (W-169042).

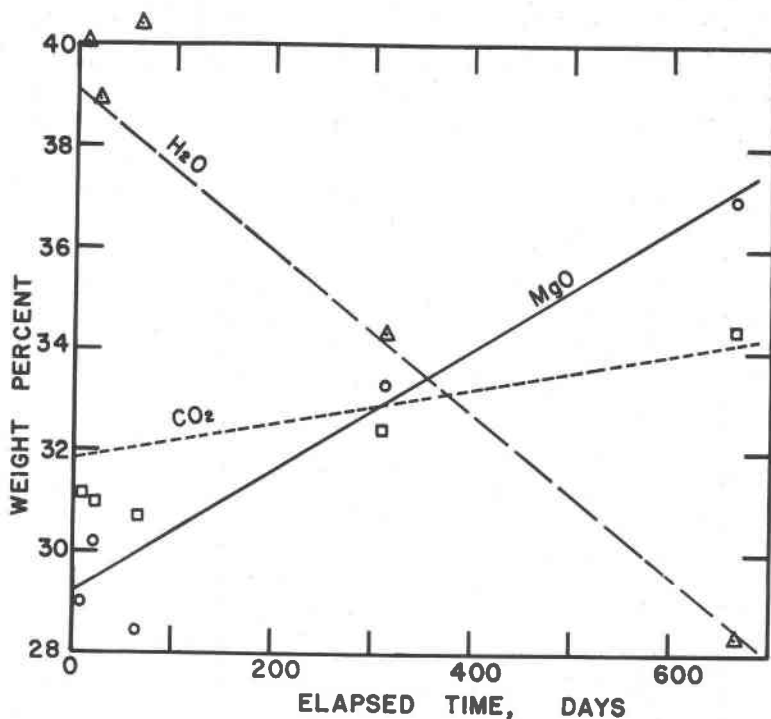5. Sample NBH-1 Analyst Ellen Gray, U.S. Geological Survey (W-169041).

6. $MgCO_3 \cdot 3H_2O$

FIG. 1. Change of the chemical composition of $MgCO_3 \cdot 3H_2O$ as a function of elapsed time after preparation.

California (which we used for some preliminary heat of solution measurements), and two recent analyses from the literature are given in Table 1.

The crystal structure of hydromagnesite has not been determined and the basic geometry of the unit cell is still questionable (Murdock, 1954). Consequently, the correct chemical formula for hydromagnesite is in doubt. Palache, Berman, and Frondel (1951, p. 272) accepted the formula $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, whereas the Strukturbericht (1940, Band V, 1937, p. 81) and Donnay *et al.* (1963) adopted the formula $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$. White (1971) has studied the infrared spectra of hydromagnesite and interpreted his data as indicating distinct kinds of carbonate groups with no evidence for hydrogen bonding between the CO_3^{2-} groups and water molecules. He suggested that most of the H_2O occurred as OH^- rather than H_2O. The chemical analyses listed in Table 1 are inadequate to resolve this discrepancy between chemical formulas. The measured specific gravities of hydromagnesite range from 2.14 to 2.3 g ml^{-1}. Palache, Berman, and Frondel (1951) gave 2.236 g ml^{-1} as the most likely value. Fahey, in Larrabee (1969), got 2.171 g ml^{-1} for the material of analysis 6, Table 1.

The most complete published X–ray data are those of Murdock (1954) who showed that hydromagnesite was orthorhombic or possibly monoclinic with $a = 9.06$, $b = 18.58$, $c = 8.42$. If monoclinic, $\beta \approx 90°$ or $114°1'$. We have measured the specific gravity of the hydromagnesite sample from West Pakistan using the

Table 3. Experimental heat capacity measurements for 467.638 grams of hydromagnesite from Hindubagh, West Pakistan.

TEMP.	HEAT CAPACITY	ΔT	TEMP.	HEAT CAPACITY	ΔT
KELVIN	CAL/MOL-K	KELVINS	KELVIN	CAL/MOL-K	KELVINS
	SERIES I			SERIES III	
53.06	17.33	1.202	217.72	101.4	5.705
55.38	18.77	3.443	223.41	103.5	5.690
59.35	21.33	4.510	229.07	105.4	5.654
64.33	24.58	5.455	234.71	107.2	5.643
69.47	27.97	4.836	240.32	109.1	5.602
74.53	31.31	5.278	245.92	110.8	5.615
79.79	34.77	5.239	251.52	112.5	5.623
85.03	38.19	5.248	257.17	114.3	5.705
90.30	41.56	5.293	262.93	116.0	5.853
95.79	45.00	5.694		SERIES IV	
	SERIES II		262.35	115.8	5.828
101.34	48.38	5.344	267.91	117.5	5.334
106.65	51.55	5.286	273.27	119.1	5.481
111.90	54.60	5.244	279.09	120.6	6.192
117.27	57.63	5.514	285.23	122.4	6.114
122.78	60.64	5.528	291.28	124.0	6.042
128.30	63.57	5.517	297.23	125.6	5.967
133.91	66.46	5.722	303.14	127.4	5.900
139.62	69.30	5.714	308.98	129.9	5.835
145.32	72.07	5.698			
150.97	74.75	5.622		SERIES V	
156.65	77.39	5.743	20.48	2.030	3.138
162.31	79.87	5.592	23.42	2.793	2.248
	SERIES III		26.29	3.674	1.653
			28.39	4.478	1.968
163.77	80.50	5.534	30.49	5.618	1.841
169.24	82.87	5.403	32.64	6.382	2.054
174.56	85.11	5.282	35.78	7.536	2.270
179.83	87.27	5.264	38.81	9.092	3.338
185.12	89.27	5.322	42.61	11.01	4.473
190.47	91.45	5.408	47.21	13.68	4.722
195.90	93.60	5.469	51.85	16.52	4.572
201.32	95.62	5.373	56.37	19.40	4.472
206.72	97.59	5.448	61.07	22.41	4.940
212.16	99.50	5.446			

method described by Fahey (1961). Our results are 2.25, 2.22, and 2.25 g ml^{-1}. Howard T. Evans, Jr., Daniel Appleman, and Mary Mrose (written communication, April 7, 1972) have determined the unit cell parameters for the hydromagnesite from West Pakistan. They find that hydromagnesite is monoclinic with $a = 10.106$ Å, $b = 8.951$ (1) Å, $c = 8.368$ (1) Å, and $\beta = 114.61$ (1)°.

The X-ray density corresponding to the formula $5MgO \cdot 4CO_2 \cdot 5H_2O$ is 2.215 g cm^{-3}.

The best fit to the chemical, specific gravity, and X-ray data indicate that the correct formula for hydromagnesite is $5MgO \cdot 4CO_2 \cdot 5H_2O$ and we have assumed this formula in tabulating our heat capacity measurements.

Nesquehonite

$MgCO_3 \cdot 3H_2O$ (synthetic nesquehonite) was prepared by a method suggested by Professor D. L. Graf, of the Department of Geology, University of Illinois, Urbana, Illinois. A 1.8 molar solution of K_2CO_3 was prepared from Baker Analyzed Reagent (3012) potassium carbonate. A 1.8 molar solution of $MgCl_2$ was prepared from Fisher Certified Reagent $MgCl_2 \cdot 6H_2O$ (M–33). Two hundred milliliters of the K_2CO_3 solution was poured into a 500 ml beaker containing 200 ml of 1.8 molar $MgCl_2$ solution and the beaker covered with a watch glass. The gel which formed immediately upon mixing of the two solutions was allowed to stand about 3 to 5 days while the crystals of nesquehonite grew from the gel. The crystals were mechanically separated from the residual gel and solution. They were washed successively in distilled water, 0.1 N HCl (this removed any remaining uncrystallized gel), distilled water, and finally in methanol.
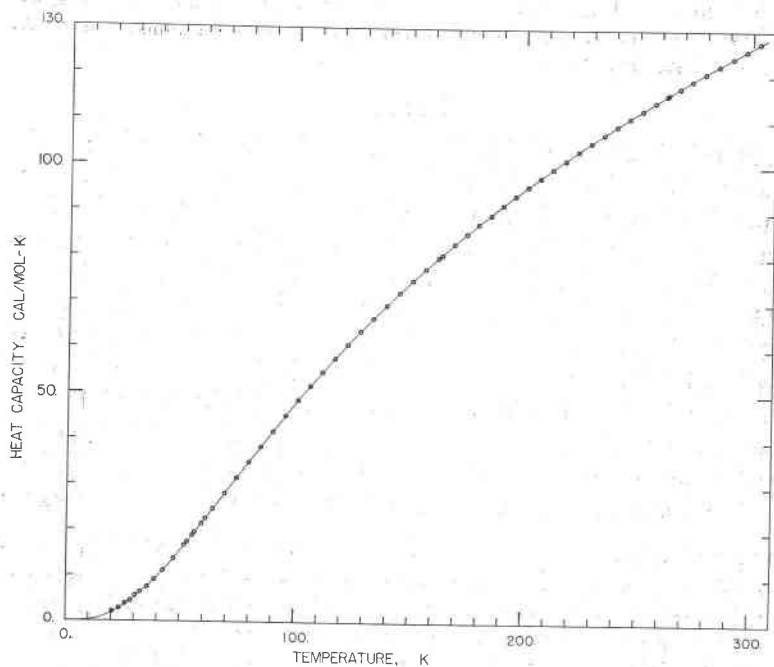

Fig. 2. Observed low–temperature heat capacity of hydromagnesite from Hindubagh, West Pakistan. Solid line is the least squares fit to the experimental points.

At room temperature and ambient CO_2 pressure, $MgCO_3 \cdot 3H_2O$ is apparently unstable and after three to four weeks it begins to lose water and CO_2.[1]

The samples were examined periodically with an X-ray diffractometer to determine whether any change had occurred in the material. The first sign of alteration detected by diffractometer is a poorly developed reflection with $d \approx 10.6$ Å which may appear as early as two weeks after preparation. Additional reflections with $d \approx 4.48, 4.41, 2.91, 2.86,$ and 2.21 Å were noted on one sample after four weeks. All of the heat capacity measurements were made on material prepared within two weeks of the date the measurements were made.

Four samples of synthetic nesquehonite were analyzed chemically at varying elapsed times after preparation and the results are given in Table 2. The quantities of SiO_2, K_2O, and Al_2O_3 reported in analysis 3 are suspect. Spectroscopic analysis of samples 2 and 5 which were prepared from the same source of K_2CO_3 and $MgCl_2 \cdot 6H_2O$ showed less than one-tenth the amount of SiO_2, and no Al_2O_3 as compared to analysis 3.

The change in the weight percentage of MgO, CO_2, and H_2O as a function of the elapsed time after preparation of $MgCO_3 \cdot 3H_2O$ are shown in Figure 1. It is readily seen that $MgCO_3 \cdot 3H_2O$ loses both H_2O and CO_2 as a function of time after preparation under ambient conditions.

Kinsolving, MacGillvary, and Pepinsky (1950) have determined the unit cell parameters and White (1971) has examined the infrared spectra of $MgCO_3 \cdot 3H_2O$. Very recently, Stephan and MacGillvary (1972) determined the crystal structure of nesquehonite.

RESULTS

The calorimeter used in this investigation has been described by Robie and Hemingway (1972). The data are reported on the basis of the International Practical Temperature Scale of 1968 (Comité International des Poids et Mesures, 1969), with one calorie equal to 4.1840 joules, and using the formula weight of $MgCO_3 \cdot 3H_2O = 138.360$ grams and for $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O = 467.638$ grams based on the 1969 table of atomic weights (Commission on Atomic Weights, 1970). For the measurements on hydromagnesite the calorimeter was filled with 118.781 grams, *in vacuo*, of the Hindubagh, West Pakistan, crystals. The empty calorimeter contributed 53 percent of the total heat capacity measured at 40 K and 30 percent at 300 K. The sample of nesquehonite used for the heat capacity studies weighed

---

[1] In this connection we report the following observation which bears upon the stability of $MgCO_3 \cdot 3H_2O$. The 43.3–gram heat–capacity sample was removed from the calorimeter and stored in a 250 ml erlenmeyer flask which was tightly sealed with a rubber stopper. Approximately four months later, the flask was opened to obtain a sample for X-ray analysis. The removal of the stopper was accompanied by a violent expulsion of gas and some sample, much like that of a bottle of warm champagne which had been shaken before opening. The flask was restoppered and opened again several months later with similar but slightly less violent expulsion of gas.

TABLE 4.   EXPERIMENTAL HEAT CAPACITY MEASUREMENTS FOR 138.360 GRAMS OF SYNTHETIC $MgCO_3 \cdot 3H_2O$.

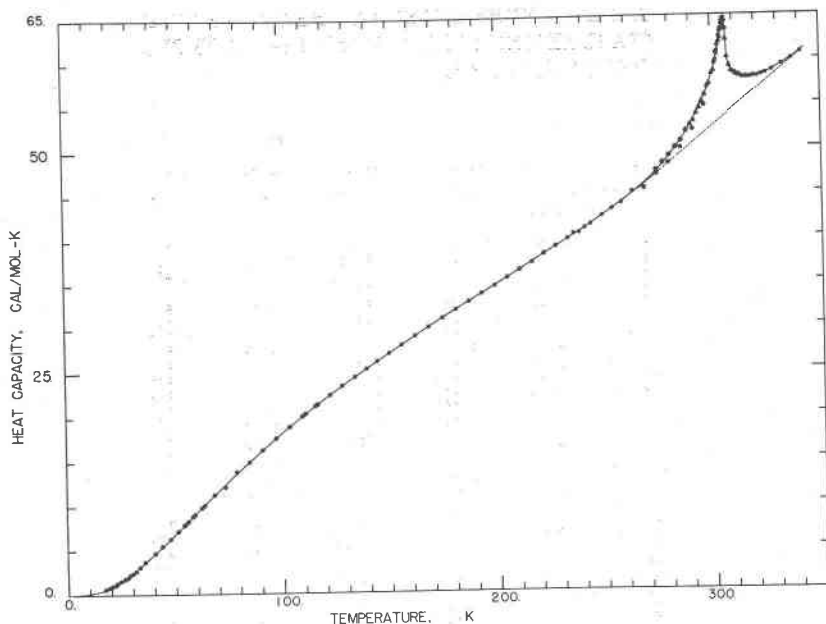| TEMP.	HEAT CAPACITY	ΔT	TEMP.	HEAT CAPACITY	ΔT
KELVIN	CAL/MOL-K	KELVINS	KELVIN	CAL/MOL-K	KELVINS
SERIES I			SERIES III		
54.02	7.869	1.220	235.17	40.55	5.325
55.76	8.285	2.251	240.43	41.18	5.263
58.93	9.033	4.108	237.68	40.64	5.455
63.38	10.10	4.791	243.13	41.58	5.375
68.21	11.29	4.884	248.51	42.55	5.295
73.26	12.40	5.254	253.16	43.29	3.999
78.68	13.61	5.588	257.50	43.96	4.698
84.64	14.93	6.210	262.56	45.16	5.430
90.87	16.32	6.291	268.16	45.51	5.813
97.20	17.61	6.408	273.88	47.09	5.694
103.42	18.88	6.044	279.48	48.32	5.600
109.41	20.05	5.944	285.19	50.02	5.934
115.21	21.17	5.686	290.99	52.06	5.786
			296.61	54.79	5.608
SERIES II			301.99	59.55	5.338
			307.13	61.08	5.270
110.82	20.33	5.845			
116.54	21.40	5.607	SERIES IV		
122.04	22.42	5.403			
127.70	23.43	5.916	17.14	0.602	1.681
133.73	24.47	6.177	18.72	0.781	1.568
139.08	25.39	4.542	20.37	0.902	1.319
144.00	26.21	5.307	21.92	1.055	1.345
149.57	27.13	5.832	22.62	1.278	1.176
155.46	28.10	5.969	24.26	1.501	1.138
161.58	29.07	6.288	25.90	1.753	0.951
167.93	30.09	6.431	27.38	1.849	0.846
174.28	31.08	6.284	28.61	2.268	1.130
180.49	32.00	6.155	29.86	2.425	1.116
186.57	32.94	6.028	31.23	2.697	1.410
192.53	33.88	5.912	33.12	3.134	2.136
198.46	34.76	5.975	35.56	3.728	2.288
204.37	35.65	5.868	40.33	4.665	2.620
210.17	36.53	5.767	43.71	5.470	3.557
215.87	37.40	5.671	47.46	6.287	3.934
221.47	38.32	5.576	51.13	7.163	3.421
226.98	39.15	5.489	54.36	7.937	3.068
232.41	40.00	5.404	58.04	8.819	4.322
			62.13	9.793	3.878
SERIES V			SERIES VII		
301.17	58.65	1.606	287.88	51.90	2.138
302.75	60.57	1.575	289.81	52.58	1.766
304.31	62.34	1.548	291.35	53.07	1.403
305.84	63.59	1.528	292.74	53.88	1.391
307.54	60.21	1.891	294.12	54.48	1.381
309.43	58.57	1.921	295.48	55.17	1.371
311.18	58.32	1.603	296.83	55.97	1.359
312.77	58.14	1.605	298.17	56.96	1.345
SERIES VI			SERIES VIII		
305.33	63.35	1.530	298.97	57.25	1.332
306.87	62.16	1.547	300.26	58.35	1.317
308.43	59.21	1.591	301.54	59.59	1.300
310.02	58.55	1.600	302.24	59.94	0.360
311.61	58.21	1.604	302.57	60.72	0.357
313.21	58.05	1.606	302.89	60.92	0.356
314.78	57.88	1.606	303.22	61.52	0.354
316.38	57.89	1.604	303.54	61.82	0.352
317.97	57.91	1.603	303.81	61.92	0.352
319.56	58.04	1.600	304.14	62.58	0.349
321.27	58.03	1.918	304.47	63.10	0.347
323.17	58.20	1.914	304.79	63.33	0.347
325.07	58.36	1.909	305.11	63.93	0.344
328.19	58.71	4.432	305.43	64.19	0.344
332.58	59.35	4.400	305.68	64.14	0.343
336.93	59.96	4.366	306.00	64.53	0.342
341.24	60.68	4.331	306.32	64.63	0.341
			306.64	64.27	0.342
SERIES VII			306.97	63.40	0.345
273.78	47.56	3.063			
276.79	48.39	3.031			
279.77	49.20	2.998			
282.69	50.10	2.965			
285.40	50.83	2.886			

Fɪɢ. 3. Observed low–temperature heat capacity of $MgCO_3 \cdot 3H_2O$, (synthetic nesquehonite). Solid line is the least squares fit to the data. The dashed line represents our estimate for the normal heat capacity. The area between the two curves corresponds to an enthalpy of transition of 176 cal mol⁻¹.

43.396 grams *in vacuo*. The empty calorimeter was approximately 60 percent of the observed total heat capacity between 40 and 300 K. In correcting the weights of the calorimetric samples for buoyancy, we used the densities 2.24 and 1.85 grams cm⁻³ for hydromagnesite and nesquehonite, respectively.

Our heat capacity data for hydromagnesite are listed in Table 3, assuming a formula $5MgO \cdot 4CO_2 \cdot 5H_2O$. The data are shown graphically in Figure 2.

The experimental heat capacity data for $MgCO_3 \cdot 3H_2O$ are listed in chronological order of measurement in Table 4 and are shown in Figure 3. The solid line is the least squares fit to the data. After the data of series IV had been completed the calorimeter was disassembled and the data were reduced. It was then found that there was an anomaly in the heat capacity of $MgCO_3 \cdot 3H_2O$. A new sample of $MgCO_3 \cdot 3H_2O$ was prepared and the measurements of series V through VIII were made in order to examine the nature of the heat capacity anomaly in detail.

Between about 280 and 320 K the heat capacity of $MgCO_3 \cdot 3H_2O$

increases rapidly from approximately 58 cal mol⁻¹K⁻¹ to a maximum of 64.7 cal mol⁻¹K⁻¹ at 306.5 K (λ-point) and then decreases precipitously to about 57 cal mol⁻¹K⁻¹ at 320 K. Three sets of measurements of the heat capacity of $MgCO_3 \cdot 3H_2O$ were made between 280 and 320 K with temperature increments as small as 0.3 K. The results are shown in Figure 4.

Apparently no thermal hysteresis is associated with the transition. We do not know the structural cause for the transition but it may be related to partial rotation of the H_2O groups. The enthalpy of transition is 176 ± 1 cal mol⁻¹. The entropy change associated with the transition is 0.58 ± 0.02 cal mol⁻¹K⁻¹.

The experimental heat capacities were extrapolated to 0 K by means of a C_p/T^2 versus T plot, and smoothed by computer. From the smoothed heat capacities, tables of the thermodynamic functions $C°_p$, $(H°_T - H°_0)/T$, $S°_T - S°_0$, and $(G°_T - H°_0)/T$ were generated and are listed for $5MgO \cdot 4CO_2 \cdot 5H_2O$ and $MgCO_3 \cdot 3H_2O$, in Tables 5 and 6 respectively.

For the reasons mentioned by Hemingway and Robie (1972) we

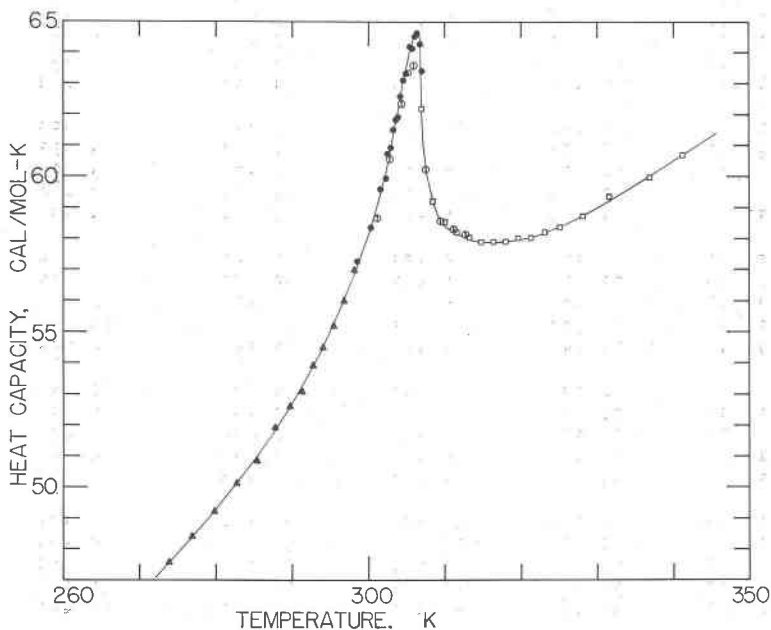FIG. 4. The λ-type transition in the heat capacity of $MgCO_3 \cdot 3H_2O$. The circles with the vertical bar are the data of series V, Table 4. The squares represent the results of series VI. The triangles are the data of series VII and the solid circles are those of series VIII.

Table 5. Thermodynamic properties of hydromagnesite,
          $5MgO \cdot 4CO_2 \cdot 5H_2O$

TEMPERATURE	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^{\circ} - S_0^{\circ})$	$(H_T^{\circ} - H_0^{\circ})/T$	$-(G_T^{\circ} - H_0^{\circ})/T$
KELVINS		CALORIES/MOL-KELVIN		
5.00	0.035	0.009	0.004	0.005
10.00	0.275	0.087	0.061	0.026
15.00	0.877	0.296	0.215	0.081
20.00	1.894	0.677	0.495	0.182
25.00	3.300	1.244	0.906	0.338
30.00	5.085	1.997	1.445	0.552
35.00	7.234	2.938	2.112	0.826
40.00	9.672	4.061	2.901	1.160
45.00	12.449	5.361	3.808	1.553
50.00	15.392	6.823	4.818	2.006
60.00	21.719	10.182	7.101	3.081
70.00	28.324	14.025	9.660	4.365
80.00	34.931	18.239	12.407	5.833
90.00	41.375	22.728	15.269	7.458
100.00	47.575	27.410	18.192	9.218
110.00	53.494	32.225	21.135	11.090
120.00	59.121	37.123	24.068	13.055
130.00	64.458	42.067	26.971	15.096
140.00	69.513	47.031	29.831	17.200
150.00	74.302	51.992	32.638	19.354
160.00	78.850	56.933	35.385	21.548
170.00	83.180	61.845	38.070	23.775
180.00	87.317	66.717	40.692	26.025
190.00	91.282	71.545	43.251	28.294
200.00	95.091	76.325	45.748	30.576
210.00	98.756	81.053	48.186	32.868
220.00	102.282	85.729	50.565	35.164
230.00	105.675	90.351	52.888	37.463
240.00	108.940	94.918	55.156	39.762
250.00	112.085	99.430	57.370	42.059
260.00	115.128	103.885	59.534	44.352
270.00	118.084	108.286	61.648	46.638
280.00	120.939	112.632	63.715	48.918
290.00	123.657	116.924	65.735	51.189
300.00	126.396	121.161	67.711	53.451
273.15	118.996	109.661	62.304	47.357
298.15	125.857	120.381	67.348	53.033
	±.37	±.37	±.20	±.16

Table 6. Thermodynamic properties of nesquehonite, $MgCO_3 \cdot 3H_2O$

TEMPERATURE	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_P°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVINS		CALORIES/MOL-KELVIN		
5.00	0.016	0.006	0.005	0.001
10.00	0.139	0.045	0.034	0.011
15.00	0.422	0.148	0.112	0.036
20.00	0.918	0.330	0.244	0.086
25.00	1.601	0.606	0.447	0.159
30.00	2.461	0.973	0.708	0.265
35.00	3.463	1.427	1.031	0.396
40.00	4.575	1.960	1.401	0.559
45.00	5.735	2.566	1.819	0.748
50.00	6.912	3.231	2.269	0.962
60.00	9.297	4.702	3.242	1.461
70.00	11.650	6.313	4.275	2.037
80.00	13.924	8.018	5.340	2.678
90.00	16.105	9.785	6.416	3.369
100.00	18.189	11.590	7.490	4.100
110.00	20.171	13.418	8.554	4.864
120.00	22.046	15.254	9.601	5.654
130.00	23.827	17.090	10.627	6.463
140.00	25.537	18.918	11.631	7.287
150.00	27.201	20.737	12.614	8.123
160.00	28.828	22.545	13.577	8.968
170.00	30.411	24.340	14.521	9.820
180.00	31.950	26.122	15.446	10.676
190.00	33.462	27.890	16.355	11.535
200.00	34.982	29.645	17.248	12.397
210.00	36.524	31.389	18.129	13.260
220.00	38.073	33.124	19.001	14.124
230.00	39.604	34.850	19.863	14.987
240.00	41.143	36.568	20.718	15.851
250.00	42.729	38.280	21.566	16.714
260.00	44.517	39.989	22.413	17.576
270.00	46.305	41.698	23.478	18.220
280.00	49.217	43.432	24.350	19.082
290.00	52.662	45.216	25.272	19.944
300.00	57.976	47.107	26.297	20.810
273.15	47.118	42.241	23.749	18.492
298.15	56.808	46.756	26.106	20.650
	±.17	±.14	±.08	±.06

have reported values for the entropy change $S°_{298.15} - S°_0$ rather than an absolute value for the entropy of hydromagnesite and nesquehonite. Until the crystal structure of hydromagnesite is determined, its absolute entropy will remain in doubt. We shall, however, tentatively assume that hydromagnesite is an ordered compound and thus $S_{298.15}$ is 120.38 $\pm$ 0.37 cal mol^{-1} K^{-1}. We have also measured (Robie and Hemingway, unpublished data) the enthalpy of formation of $MgCO_3 \cdot 3H_2O$ by solution calorimetry. The agreement between the Gibbs free energy of formation obtained from the measured enthalpy and entropy data and that obtained from the solubility studies of Kline (1929) and P. B. Hostetler (written communication, April 1970) indicated that $S°_0$ for $MgCO_3 \cdot 3H_2O$ is zero. Accordingly the correct value for the entropy, $S°_{298.15}$, for use in thermodynamic calculations is 46.76 $\pm$ 0.14 cal mol^{-1}K^{-1}.

REFERENCES

BILGRAMI, S. A. (1964) Mineralogy and petrology of the central part of the Hindubagh igneous complex, Hindubagh mining district, Zhob Valley, West Pakistan. *Rec. Geol. Surv. Pakistan* 10, Part 2G, 28 p.

CHRIST, C. L., AND P. B. HOSTETLER (1970) Studies in the system MgO–SiO₂–CO₂–H₂). II: The activity product constant of magnesite. *Amer. J. Sci.* 268, 439–453.

COMITÉ INTERNATIONAL DES POIDS ET MESURES (1969) The International Practical Temperature Scale of 1968. *Metrologia*, 5, 35–44.

COMMISSION ON ATOMIC WEIGHTS (1970) Atomic weights of the elements, 1969. *Pure Appl. Chem.* 21, 95–108.

DONNAY, J. D. H., G. DONNAY, E. G. COX, O. KENNARD, AND M. V. KING (1963) *Crystal data determinative tables, 2nd ed. Amer. Crystallogr. Assoc. Monogr.* 5, 1302 p.

FAHEY, J. J. (1961) A method for determining the specific gravity of sand and ground rock or minerals. *U.S. Geol. Surv. Prof. Pap.* 424–C, 372 p.

HEMINGWAY, B. S., AND R. A. ROBIE (1972) The heat capacities at low temperatures and entropies at 298.15 K of huntite, CaMg₃(CO₃)₄, artinite, Mg₂(OH)₂ CO₃·3H₂O. *Amer. Mineral.* 57, 1754–1767.

KAZAKOV, A. V., M. M. TIKHOMIROVA, AND V. I. PLOTNIKOVA (1957) The system

of carbonate equilibria. *Akad. Nauk SSSR, Inst. Geol. Nauk, Tr. Geol. Ser.* 64, 13–58. [transl. *Int. Geol. Rev.* 1, 1–39 (1959)]

KINSOLVING, M. R., C. MACGILLVARY, AND R. PEPINSKY (1950) Twinning in nesquehonite MgCO₃·3H₂O [abstr.]. *Amer. Mineral.* 35, 127.

KLINE, W. D. (1929) The solubility of magnesium carbonate (nesquehonite) in water at 25°C and pressures of carbon dioxide up to one atmosphere. *J. Amer. Chem. Soc.* 51, 2093–2097.

LANGMUIR, D. (1965) Stability of carbonates in the system MgO–CO₂–H₂O. *J. Geol.* 73, 730–754.

LARRABEE, D. M. (1969) Serpentine and rodingite in the Hunting Hill quarry, Montgomery County, Maryland. *U.S. Geol. Surv. Bull.* 1283, 34 p.

MARSCHNER, H. (1969) Hydrocalcite (CaCO₃·H₂O) and nesquehonite (MgCO₃·3H₂O) in carbonate scales. *Science,* 165, 1119–1121.

MURDOCK, J. (1954) Unit cell of hydromagnesite. *Amer. Mineral.* 39, 24–29.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *Dana's system of mineralogy, 7th ed.* John Wiley and Sons, New York. 1124 p.

ROBIE, R. A. (1965) Heat and free energy of formation of herzenbergite, troilite, magnesite, and rhodochrosite calculated from equilibrium data. *U.S. Geol. Surv. Prof. Pap.* 525–D, 65–72.

———, AND B. S. HEMINGWAY (1972) Calorimeters for heat of solution and low–temperature heat capacity measurements. *U.S. Geol. Surv. Prof. Pap.* 755, 32 p.

SHAMS, F. A. (1965) Hydromagnesite from Hindubagh, Zhob Valley, West Pakistan. *Mineral. Mag.* 35, 236–237.

STEPHAN, G. W., AND C. H. MACGILLVARY (1972) The crystal structure of nesquehonite, MgCO₃·3H₂O. *Acta Crystallogr.* B28, 1031–1033.

STOUT, J. W., AND R. A. ROBIE (1963) Heat capacity from 11 to 300°K. Entropy and heat of formation of dolomite. *J. Phys. Chem.* 67, 2248–2252.

WHITE, W. B. (1971) Infrared characterization of water and hydroxyl ion in the basic magnesium carbonate minerals. *Amer. Mineral.* 56, 46–53.