

THE HEAT CAPACITIES AT LOW TEMPERATURES AND  
ENTROPIES AT 298.15 K OF HUNTITE,  $\text{CaMg}_3(\text{CO}_3)_4$ ,  
AND ARTINITE,  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}^1$

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ABSTRACT

The heat capacities of huntite,  $\text{CaMg}_3(\text{CO}_3)_4$ , and artinite,  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , have been measured from 18 to above 306K using an adiabatic calorimeter. Tables of the thermodynamic functions  $C_p$ ,  $(H^\circ_T - H^\circ_0)/T$ ,  $(G^\circ_T - H^\circ_0)/T$ , and  $(S^\circ_T - S^\circ_0)$  are presented for these two phases, at integral temperatures, from 0 to 300K. At 298.15K (25.0°C) the values of  $C_p$ ,  $(H^\circ_T - H^\circ_0)/T$ ,  $(G^\circ_T - H^\circ_0)/T$ , and  $(S^\circ_T - S^\circ_0)$  for  $\text{CaMg}_3(\text{CO}_3)_4$  are  $74.11 \pm 0.22$ ,  $40.40 \pm 0.12$ ,  $-31.19 \pm 0.03$ , and  $71.59 \pm 0.21$  cal mol<sup>-1</sup>K<sup>-1</sup> and for  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ ,  $53.18 \pm 0.18$ ,  $30.68 \pm 0.09$ ,  $-23.61 \pm 0.07$ , and  $54.29 \pm 0.16$  cal mol<sup>-1</sup>K<sup>-1</sup>, respectively.

INTRODUCTION

The system  $\text{MgO}-\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$  is of particular interest in the study of the chemical equilibria of surface waters and the hydrothermal alteration of serpentine bodies. The solid phases of mineralogical importance in this system are  $\text{CaCO}_3$  (calcite, aragonite, vaterite),  $\text{CaO}$  (lime),  $\text{Ca}(\text{OH})_2$  (portlandite),  $\text{MgO}$  (periclase),  $\text{Mg}(\text{OH})_2$  (brucite),  $\text{MgCO}_3$  (magnesite),  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  (nesquehonite),  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$  (lansfordite),  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$  (artinite),  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$  (hydromagnesite),  $\text{CaMg}(\text{CO}_3)_2$  (dolomite), and  $\text{CaMg}_3(\text{CO}_3)_4$  (huntite).

Huntite is an example (as is dolomite) of an ordered double carbonate (Graf and Bradley, 1962) on the join  $\text{CaCO}_3-\text{MgCO}_3$ . Faust (1953) in his original description of huntite indicated that it formed during the late stages of the hydrothermal alteration of volcanic tuffs by magnesium-rich aqueous solutions. Skinner (1958) has found huntite as a weathering product of a shaly dolomite where it occurred as nodules in a brecciated shale associated with the dolomite. Huntite has also been described as a vein-filling mineral in a serpentine body by Larrabee (1969), and it has been found in recent evaporite deposits

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in Arabia and Turkey by Kinsman (1967) and Irion and Muller (1968).

Artinite commonly occurs as fracture fillings in and encrustations upon serpentine rocks (Hurlbut, 1946) and is presumably a low-temperature alteration product caused by the reaction of  $\text{CO}_2$ -charged waters with the serpentine. Artinite is usually found in association with brucite and hydromagnesite. deWolff (1952) and Jagodzinski (1965) have determined the crystal structure of artinite and Jagodzinski (1965) has shown that an interesting type of disorder exists in the structure of artinite involving the position of the carbonate group and one of the three  $\text{H}_2\text{O}$  groups. White (1971) has studied the infrared spectra of artinite.

Previous studies of the thermodynamic properties of huntite and artinite include a value for the Gibbs free energy of formation,  $\Delta G^\circ_{f,298.15}$ , of huntite by Garrels, Thompson, and Siever (1960) based on solubility measurements, and Langmuir's (1965) summary of the aqueous solubility data for artinite and nesquehonite, hydromagnesite, lansfordite, and magnesite.

As part of a continuing calorimetric study of the thermodynamic properties of minerals in the  $\text{MgO-CaO-CO}_2\text{-H}_2\text{O}$  system, Stout and Robie (1963), Robie and Hemingway (unpub. measurements on  $\Delta H^\circ_f$  of dolomite), we have measured the heat capacities of huntite and artinite between 18 and 306 K in order to determine their standard entropies,  $S^\circ_{298.15}$ . We have also measured the low-temperature heat capacities of hydromagnesite and nesquehonite (Robie and Hemingway, 1972a).

#### MATERIALS

##### *Huntite*

The sample of huntite used for our heat capacity measurements was provided by Professor D. L. Graf of the University of Illinois. It was a mineral specimen from Tea Tree Gully, South Australia, (Skinner, 1958) and was in the form of nodules composed of very finely divided ( $<2$  micron diameter) crystals. The nodules were crushed and handpicked free of visible clay particles under a binocular microscope. A wet chemical analysis of the purified material is listed in Table 1 together with several previous analyses of huntite. The material gave a sharp diffractometer pattern for huntite and showed no evidence of any other phase.

##### *Artinite*

The sample of artinite used was also kindly provided by Professor Graf. It was from Coalinga, California, and was in the form of radiate aggregates or sheaths of needle-like crystals about one centimeter long. The principal

Table 1. Chemical analyses of huntite

	1	2	2a	3	4	5
MgO	34.26	33.4		34.4	33.2	34.09
CaO	15.88	15.3		16.0	15.6	15.42
CO <sub>2</sub>	49.86	48.5	48.49	50.4	48.9	48.85
SiO <sub>2</sub>		0.08				0.06
H <sub>2</sub> O <sup>-</sup>		0.16	0.79			0.47
H <sub>2</sub> O <sup>+</sup>		1.4				
Na <sub>2</sub> O		0.22				
Ignition residue			49.78			
	100.00	99.06	99.06	100.8	97.7	99.75

1 CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub>

2 Tea Tree Gully, South Australia. Heat capacity sample. Analyst Leonard Shapiro, U.S. Geological Survey (W 171160)

2a Tea Tree Gully, South Australia. Heat capacity sample. Analyst Ellen Gray, U.S. Geological Survey (W 171160)

3 Skinner (1958), Tea Tree Gully, South Australia. Analyzed in the Department of Geology, University of Adelaide, Australia

4 Skinner (1958), Tea Tree Gully, South Australia. Analyst J. H. Hutton, C. S. I. R. O.

5 Faust (1953), Currant Creek, Nevada. Analyst R. E. Stevens, U.S. Geological Survey

impurity was serpentine. The aggregates were crushed in a Diamonite (aluminum oxide) mortar to -20+100 mesh and the serpentine removed by handpicking under a binocular microscope. Chemical analyses of the purified material are given in Table 2. Because of the uncertainties in the chemical analyses we have made no attempt to correct our measurements for the impurities in the calorimetric samples. This is not as serious a source of error as it might at first seem. The mean atomic weights of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O are not too different from the mean atomic weight of huntite and artinite and as a first approximation the specific heats (*i.e.*, cal deg<sup>-1</sup> gram<sup>-1</sup>) of the impurities can be assumed to be the same as that of the huntite or artinite.

## APPARATUS AND PROCEDURES

The adiabatically shielded low-temperature heat capacity calorimeter used in this investigation together with the methods of data reduction have been described by Robie and Hemingway (1972b). The platinum resistance thermometer used with our calorimeter was calibrated in terms of the International Practical Temperature Scale of 1968 (Comité International des Poids et Mesures, 1969). It had an ice point resistance,  $R_0$ , of 34.94 ohms and the temperature derivative of the resistance at 0°C was 0.14 ohms deg<sup>-1</sup>. The temperature measurements had a sensitivity of  $\pm 0.0002$  Kelvins at 300 K and  $\pm 0.001$  Kelvins at 20 K. The atomic weights for 1969 (Commission on Atomic Weights, 1970) were used to calculate the gram-formula weights for  $\text{CaMg}_2(\text{CO}_3)_4 =$

Table 2. Chemical analyses of artinite

	1	2	2a	3	3a	4
MgO	40.99	40.5	*41.85	40.3	*41.75	41.84
CO <sub>2</sub>	22.37	22.0	22.52	22.3	22.36	22.82
H <sub>2</sub> O <sup>-</sup>	--	0.16	36.22	0.22	36.09	35.46
H <sub>2</sub> O <sup>+</sup>	36.64	36.5		36.3		
SiO <sub>2</sub>		0.08				
Al <sub>2</sub> O <sub>3</sub>		0.81		0.85		
	100.00	100.05	100.59	99.97	100.20	100.09

\* Ignition residue

1  $\text{Mg}_2(\text{OH})_2 \cdot \text{CO}_3 \cdot 3\text{H}_2\text{O}$

2 Coalinga, California. Analyst Leonard Shapiro, U.S. Geological Survey (W 171161)

2a Coalinga, California. Analyst Ellen Gray, U.S. Geological Survey (W 171161)

3 Coalinga, California. Analyst Leonard Shapiro, U.S. Geological Survey (W 171162)

3a Coalinga, California. Analyst Ellen Gray, U.S. Geological Survey (W 171162). Samples 2 and 3 are separate splits of the material used in the calorimetric measurements.

4 Luning, Nevada. Analyst Forest Gonyer. (Hurlbut, 1946)

TABLE 3. EXPERIMENTAL HEAT CAPACITY MEASUREMENTS FOR 353.032 GRAMS OF HUNTITE FROM TEA TREE GULLY, SOUTH AUSTRALIA.

TEMP.	HEAT CAPACITY	$\Delta T$	TEMP.	HEAT CAPACITY	$\Delta T$
KELVIN	CAL/MOL-K	KELVINS	KELVIN	CAL/MOL-K	KELVINS
	SERIES I			SERIES III	
55.87	10.48	4.168	221.28	61.76	5.547
60.30	12.28	4.730	226.78	62.78	5.473
65.11	14.25	4.918	232.21	63.76	5.402
70.67	16.59	6.209	237.61	64.74	5.416
76.51	19.10	5.507	243.01	65.67	5.423
82.00	21.53	5.473	248.39	66.54	5.363
87.49	23.77	5.509	253.80	67.39	5.492
93.01	26.11	5.536	259.29	68.35	5.518
98.60	28.34	5.639	264.80	69.28	5.528
104.72	30.73	6.602	270.34	70.14	5.551
110.87	33.02	5.699	275.90	70.94	5.587
			281.56	71.77	5.775
	SERIES II		287.66	72.65	6.458
			293.89	73.57	6.061
			299.90	74.30	6.008
112.96	33.85	3.906		SERIES IV	
117.39	35.39	4.963			
122.47	37.12	5.190			
128.05	39.00	5.987			
134.40	41.00	6.709	274.10	70.54	6.245
140.98	43.01	6.455	280.72	71.62	7.024
147.32	44.83	6.242	287.86	72.79	7.379
153.47	46.53	6.058	295.39	73.76	7.727
159.44	48.14	5.896	303.29	74.95	8.120
165.26	49.62	5.755	309.00	76.50	3.357
170.95	51.01	5.628			
176.51	52.36	5.512		SERIES	
181.96	53.68	5.404			
187.40	54.95	5.479	18.75	0.787	2.745
192.88	56.07	5.488	19.27	0.812	2.611
198.37	57.24	5.497	32.64	3.151	0.595
203.85	58.36	5.492	39.99	4.833	0.807
209.34	59.51	5.492	40.87	5.092	1.023
			42.54	5.623	2.369
	SERIES III		44.76	6.370	2.107
			47.26	7.232	2.949
204.78	58.48	5.541	51.15	8.666	4.859
210.27	59.67	5.452	55.74	10.45	4.330
215.76	60.81	5.539	60.23	12.26	4.649
			65.08	14.26	5.056

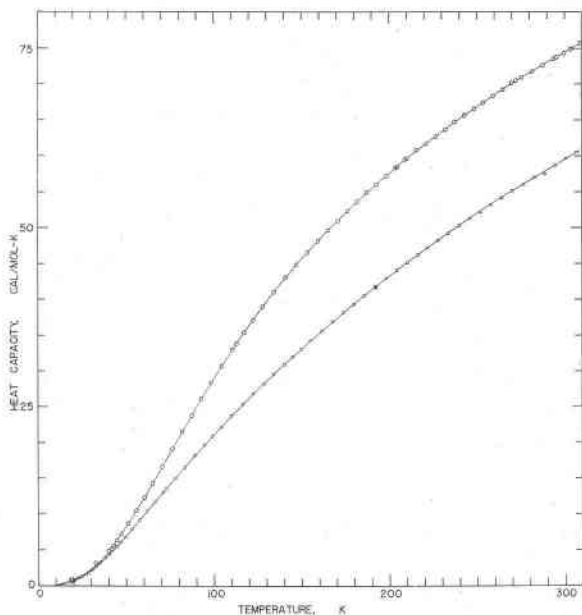


Fig. 1. Molar heat capacities of artinite,  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , squares, and huntite,  $\text{CaMg}_3(\text{CO}_3)_4$ , circles.

353.032, and for  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O} = 196.680$ . The densities used to correct the sample weights for buoyancy were 2.880 and 2.03  $\text{gm cm}^{-3}$  for  $\text{CaMg}_3(\text{CO}_3)_4$  and  $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , respectively.

During the measurements on huntite the calorimeter was filled with 112.150 grams, *in vacuo*, of material; for artinite, 88.807 grams. The contribution of the calorimeter to the total observed heat capacity (sample + calorimeter) was 55 percent at 40 K and approximately 30 percent at 300 K. The observed heat capacities were corrected for slight differences in the quantity of helium, solder, and Teflon tape between the measurements on the empty and filled calorimeter. The results are reported in terms of the defined thermochemical calorie (one calorie = 4.1840 joules).

## RESULTS

The experimental heat capacity data for huntite are listed in Table 3 in the chronological order of measurement, and are shown graphically in Figure 1. The absence of measurements between 20 and 32 K is due to a failure of the power supply used to provide the heater current. The right hand column of the table gives the temperature rise ( $\Delta T$ ) for the individual measurement. The heat capacity was extrapolated to 0 K by means of a  $C_p^\circ/T^2$  versus  $T$  plot for the observed data between 18 and 50 K. The heat capacities were analytically smoothed

TABLE 4. THERMODYNAMIC PROPERTIES OF HUNTITE,  $\text{CaMg}_3(\text{CO}_3)_4$ .

TEMPERATURE	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	$C_P^\circ$	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVINS		CALORIES/MOL-KELVIN		
5.00	0.020	0.005	0.003	0.002
10.00	0.144	0.049	0.034	0.015
15.00	0.427	0.154	0.110	0.044
20.00	0.893	0.336	0.242	0.094
25.00	1.552	0.602	0.433	0.169
30.00	2.417	0.958	0.687	0.271
35.00	3.507	1.409	1.008	0.401
40.00	4.835	1.961	1.399	0.562
45.00	6.431	2.623	1.870	0.753
50.00	8.193	3.390	2.412	0.978
60.00	12.143	5.226	3.699	1.527
70.00	16.368	7.414	5.205	2.208
80.00	20.635	9.878	6.868	3.011
90.00	24.828	12.552	8.631	3.920
100.00	28.877	15.379	10.455	4.924
110.00	32.723	18.313	12.306	6.007
120.00	36.315	21.317	14.159	7.157
130.00	39.636	24.356	15.993	8.363
140.00	42.705	27.408	17.793	9.615
150.00	45.566	30.452	19.550	10.902
160.00	48.260	33.480	21.261	12.219
170.00	50.808	36.483	22.925	13.558
180.00	53.212	39.456	24.541	14.914
190.00	55.470	42.394	26.110	16.284
200.00	57.591	45.294	27.632	17.662
210.00	59.601	48.153	29.107	19.046
220.00	61.527	50.970	30.537	20.433
230.00	63.380	53.746	31.925	21.821
240.00	65.152	56.481	33.273	23.209
250.00	66.832	59.175	34.582	24.593
260.00	68.436	61.828	35.853	25.975
270.00	70.008	64.440	37.089	27.351
280.00	71.561	67.014	38.293	28.722
290.00	73.012	69.551	39.465	30.086
300.00	74.377	72.049	40.606	31.443
273.15	70.501	65.255	37.472	27.783
298.15	74.107	71.590	40.397	31.193
	$\pm .22$	$\pm .21$	$\pm .12$	$\pm .09$

by computer using orthogonal polynomials for curve fitting (Justice, 1969). Based on our results for the heat capacity of the Calorimetry Conference sample of benzoic acid, (Robie and Hemingway, 1972b) using the same calorimeter, we believe that our measurements on huntite and artinite between 30 and 305 K are accurate to  $\pm 0.15$  percent. Below 30 K the precision of the measurements decreases to  $\pm 3$  percent because of the greatly increased heat leak and rapid decrease in the sensitivity of the platinum resistance thermometer. The entropy is determined from the heat capacity data, extrapolated to 0 K by means of the third law of thermodynamics,

$$S^{\circ}_T = S^{\circ}_0 + \int_0^T C^{\circ}_p/T dT \quad (1)$$

where  $S^{\circ}_0$  is the entropy at 0K and is zero for an ordered phase. The enthalpy and Gibbs free energy functions are calculated from

$$(H^{\circ}_T - H^{\circ}_0)/T = \frac{1}{T} \int_0^T C^{\circ}_p dT \quad (2)$$

and

$$(G^{\circ}_T - H^{\circ}_0)/T = (H^{\circ}_T - H^{\circ}_0)/T - S^{\circ}_T \quad (3)$$

In evaluating the final uncertainties of the thermodynamic properties

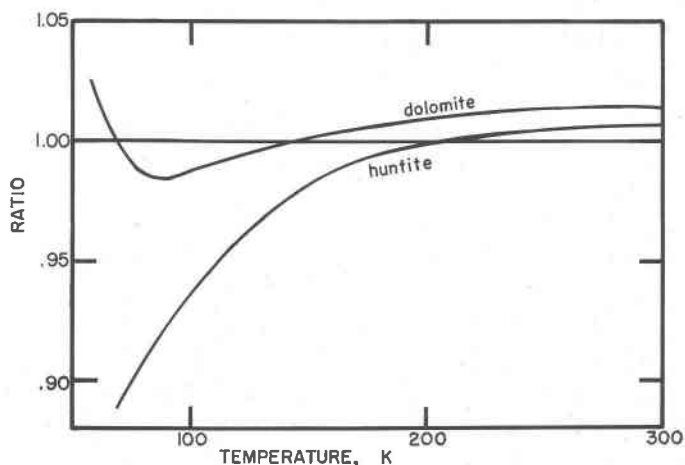


Fig. 2. Comparison of the heat capacity of  $\text{CaMg}(\text{CO}_3)_2$  (dolomite), and  $\text{CaMg}_3(\text{CO}_3)_4$  (huntite) with that of a 1:1 and 3:1 molar mixture of magnesite and calcite. The ordinate is the ratio  $[C^{\circ}_p(\text{C}) + C^{\circ}_p(\text{M})]/C^{\circ}_p(\text{D})$  for dolomite or  $[C^{\circ}_p(\text{C}) + 3C^{\circ}_p(\text{M})]/C^{\circ}_p(\text{H})$  for huntite, where D, C, M, and H indicate dolomite, calcite, magnesite, and huntite, respectively.



at 298.15 K we have made an allowance of  $\pm 0.05$  percent for deviations from stoichiometry,  $\pm 0.15$  percent for the scatter of the experimental data about the least-squares curve and  $\pm 0.1$  percent to allow for errors in the extrapolation of  $C_p^\circ$  to 0 K. For both artinite and huntite, the contribution to the entropy at 298.15 K due to the extrapolation of the heat capacities below 20 K is less than  $0.3 \text{ cal mol}^{-1}\text{K}^{-1}$ .

Smoothed values for the thermodynamic functions  $C_p^\circ$ ,  $(S_T^\circ - S_0^\circ)$ ,  $(H_T^\circ - H_0^\circ)/T$ , and  $-(G_T^\circ - H_0^\circ)/T$  for  $\text{CaMg}_3(\text{CO}_3)_4$  are listed in Table 4 at integral temperatures. The superscript  $^\circ$  indicates that the thermodynamic properties refer to the standard state for the phase, that is, for solids, one atmosphere pressure at any temperature.

The molar heat capacity,  $C_p^\circ$ , of huntite and that of dolomite (Stout and Robie, 1963) were compared with that of a 1:3 and a 1:1 mechanical mixture of calcite (Stavely and Linford, 1969, Anderson, 1934a, Nernst and Schwers, 1914, Simon and Swain, 1935) and magnesite (Anderson, 1934b). The results are shown graphically in Figure 2. Above 150 K the molar heat capacities of dolomite and huntite are equal to the sums  $[C_p^\circ(C) + C_p^\circ(M)]$  and  $[C_p^\circ(C) + 3C_p^\circ(M)]$  to within about 2 percent. In the absence of heat capacity measurements above 305 K, the additivity approximation should be accurate to better than 5 percent.

The measured entropy of huntite was also compared with the sum of the entropies of  $3\text{MgCO}_3 + \text{CaCO}_3$ . It is well known that the entropies of polymorphs of a given composition vary inversely with their density or directly with the molar volume. Therefore, in comparing the entropy of huntite with that of a 1:3 molar mixture of calcite and magnesite, we must also allow for the difference between the molar volume of huntite and that of  $\text{CaCO}_3 + 3\text{MgCO}_3$ . The entropy at 298.15 K of calcite is  $21.92 \pm 0.04 \text{ cal mol}^{-1}\text{K}^{-1}$  (Stavely and Linford, 1969) and of magnesite,  $15.7 \pm 0.2 \text{ cal mol}^{-1}\text{K}^{-1}$  (Anderson, 1934b). The molar volumes of calcite, magnesite, and huntite are  $36.93 \pm 0.02$ ,  $28.02 \pm 0.01$ , and  $122.58 \pm 0.10 \text{ cm}^3$ , respectively (Robie, Bethke, and Beardsley, 1967). We therefore approximate the entropy of huntite by the relation

$$S_H = [S_C + 3S_M]V_H/(V_C + 3V_M) \quad (4)$$

or at 298.15 K.

$$\begin{aligned} S_H &= [21.92 + 3(15.7)] \cdot 122.58 / [36.93 + 3(28.02)] \\ &= 69.9 \pm 0.7 \text{ cal mol}^{-1} \text{ K}^{-1} \end{aligned}$$

TABLE 5. EXPERIMENTAL HEAT CAPACITY MEASUREMENTS FOR 196.680 GRAMS OF ARTINITE FROM COALINGA, CALIFORNIA.

TEMP.	HEAT CAPACITY	$\Delta T$	TEMP.	HEAT CAPACITY	$\Delta T$
KELVIN	CAL/MOL-K	KELVINS	KELVIN	CAL/MOL-K	KELVINS
SERIES I			SERIES II		
18.72	0.538	0.605	149.80	33.10	5.092
20.07	0.668	0.840	155.25	34.28	5.811
21.52	0.834	0.930	161.41	35.59	6.534
23.17	1.076	1.183	167.85	36.94	6.345
25.01	1.300	1.509	174.10	38.22	6.175
26.88	1.567	1.673	180.00	39.39	5.623
28.77	1.887	1.815	186.01	40.57	6.416
30.69	2.255	1.919	192.34	41.83	6.263
32.85	2.739	2.271	198.53	42.97	6.128
35.21	3.253	2.087			
38.23	3.948	1.712			
40.32	4.400	1.902			
42.38	4.937	2.042	192.26	41.76	6.235
44.52	5.493	2.191	198.43	42.94	6.101
46.82	6.089	2.385	204.46	44.06	5.977
49.41	6.792	2.808	210.58	45.16	6.280
53.24	7.862	4.862	216.50	46.23	5.618
57.87	9.177	4.410	222.06	47.22	5.521
62.19	10.41	4.229	227.78	48.20	5.924
66.54	11.66	4.489	233.89	49.24	6.324
71.30	13.03	5.041	240.14	50.31	6.210
			246.22	51.31	5.979
			252.20	52.25	6.014
			258.25	53.21	6.117
			264.37	54.19	6.160
			270.56	55.19	6.244
			276.83	56.06	6.335
			282.81	57.01	5.784
			288.79	57.52	6.219
			294.88	58.72	6.015
			300.83	59.66	5.936
			306.71	60.80	5.863
SERIES II					
73.05	13.52	5.024			
78.19	14.99	5.250			
83.58	16.52	5.547			
89.34	18.13	5.965			
94.57	19.58	4.536			
99.22	20.83	4.750			
104.29	22.18	5.398			
110.25	23.73	6.542			
116.62	25.33	6.197			
122.67	26.82	5.912			
128.46	28.21	5.676			
134.23	29.58	5.878			
140.22	30.95	6.092			
145.26	32.09	3.998			

TABLE 6. THERMODYNAMIC PROPERTIES OF ARTINITE,  $Mg_2(OH)_2CO_3 \cdot H_2O$ 

TEMPERATURE	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	$C_P^{\circ}$	$(S_T^{\circ} - S_0^{\circ})$	$(H_T^{\circ} - H_0^{\circ})/T$	$-(G_T^{\circ} - H_0^{\circ})/T$
KELVINS		CALORIES/MOL-KELVIN		
5.00	0.011	0.004	0.003	0.001
10.00	0.085	0.028	0.021	0.007
15.00	0.282	0.096	0.072	0.024
20.00	0.659	0.224	0.116	0.108
25.00	1.269	0.426	0.284	0.142
30.00	2.126	0.728	0.514	0.214
35.00	3.187	1.135	0.821	0.314
40.00	4.362	1.634	1.186	0.448
45.00	5.623	2.219	1.607	0.611
50.00	6.970	2.880	2.076	0.805
60.00	9.778	4.398	3.124	1.274
70.00	12.645	6.120	4.279	1.841
80.00	15.507	7.996	5.504	2.492
90.00	18.319	9.985	6.773	3.213
100.00	21.045	12.058	8.064	3.993
110.00	23.662	14.187	9.364	4.823
120.00	26.169	16.354	10.661	5.693
130.00	28.576	18.544	11.947	6.597
140.00	30.898	20.748	13.218	7.529
150.00	33.140	22.956	14.472	8.484
160.00	35.304	25.165	15.707	9.458
170.00	37.387	27.368	16.921	10.447
180.00	39.395	29.562	18.114	11.448
190.00	41.340	31.744	19.286	12.459
200.00	43.234	33.913	20.436	13.477
210.00	45.076	36.067	21.566	14.502
220.00	46.862	38.206	22.675	15.531
230.00	48.585	40.327	23.765	16.563
240.00	50.257	42.430	24.834	17.597
250.00	51.901	44.515	25.884	18.632
260.00	53.525	46.583	26.916	19.667
270.00	55.083	48.632	27.930	20.702
280.00	56.507	50.662	28.926	21.736
290.00	57.871	52.668	29.900	22.768
300.00	59.527	54.657	30.859	23.798
273.15	55.548	49.274	28.246	21.028
298.15	59.183	54.289	30.682	23.607
	$\pm .18$	$\pm .16$	$\pm .09$	$\pm .07$

The estimated entropy of huntite,  $69.9 \pm 0.7$  cal mol<sup>-1</sup>K<sup>-1</sup> compares moderately well with the observed value,  $71.59 \pm 0.21$  cal mol<sup>-1</sup>K<sup>-1</sup>.

The experimental heat capacity data for artinite from Coalinga, California, are listed in Table 5 and are shown graphically in Figure 1. Tables of the thermodynamic properties of Mg<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>·3H<sub>2</sub>O are listed in Table 6.

In Tables 4 and 6 we have tabulated the entropy function  $S^\circ_T - S^\circ_0$  rather than  $S^\circ_T$  in order to allow for the possibility that either huntite or artinite might retain some residual disorder, and entropy, at 0 K.

#### DISCUSSION

Graf and Bradley (1962) determined the crystal structure of huntite and showed that it is an ordered double carbonate similar to dolomite. On this basis we believe that there is no *frozen-in* disorder at low temperatures and accordingly,  $S_0$  (equation 1) is zero. The entropy of CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub> at 298.15 K to be used in chemical thermodynamic calculations is therefore  $71.59 \pm 0.21$  cal mol<sup>-1</sup>K<sup>-1</sup>.

Jagodzinski (1965) has shown that the crystal structure of artinite, Mg<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>·3H<sub>2</sub>O, is disordered with respect to the position of the CO<sub>3</sub><sup>2-</sup> group and one of the H<sub>2</sub>O groups. For a disordered phase,  $S^\circ_0$ , equation (1) is not 0 and an additional term, related to the number of possible distinct configurations of the structure, must be added to the tabulated values of  $S^\circ_T - S^\circ_0$  in order to obtain the correct value of the entropy to be used in thermodynamic calculations. On the basis of the artinite structure given by Jagodzinski (1965) the configurational contribution to the entropy of artinite is apparently  $R \ln 2 = 1.38$  cal mol<sup>-1</sup>K<sup>-1</sup> where  $R$  is the gas constant  $1.98718 \pm 0.00008$  cal mol<sup>-1</sup>K<sup>-1</sup> (U.S. National Bureau of Standards, 1971). The correct value of  $S^\circ_{298.15}$  for use in thermodynamic calculations is thus  $54.29 + 1.38 = 55.67 \pm 0.16$  cal mol<sup>-1</sup>K<sup>-1</sup>. This, of course, assumes that there is no decrease in the configurational disorder as  $T$  approaches 0 K.

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