

SHORT  
COMMUNICATIONS

## Heat Capacity and Thermodynamic Functions of Epsomite $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ at 0–303 K

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Received April 14, 2006

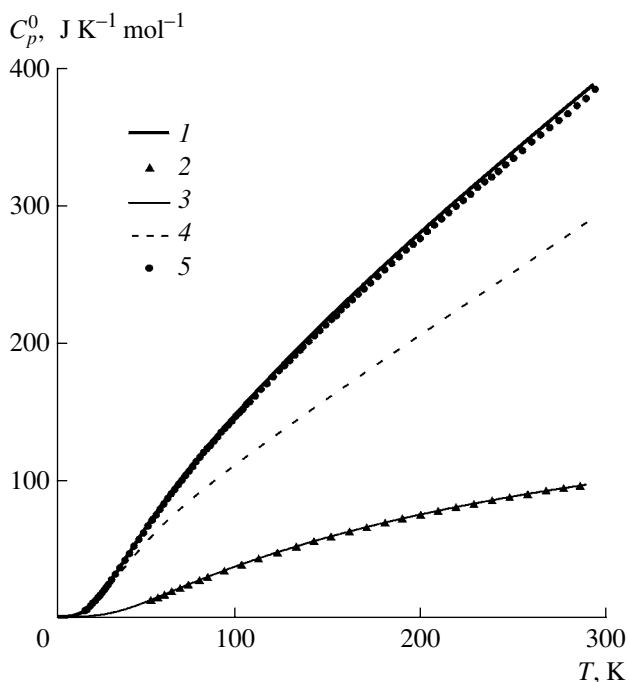
DOI: 10.1134/S0016702907020103

Geological–geophysical data obtained by the Galileo spacecraft during its traveling around Jupiter’s satellites suggest the presence of a water layer (in terrestrial terms, marine or oceanic water) from tens (Europe) to a few hundred (Ganymede and Callisto) kilometers thick beneath an outer solid ice shell [1–2]. The oceans of Europa, Ganymede, and Callisto are supposedly high-pressure electrolytic solutions. The presence of water supports the hypotheses of the existence of primitive extraterrestrial life forms in the surface ocean. The outer shells of Jupiter’s icy satellites consist mainly of  $\text{H}_2\text{O}$  ice contaminated with dark non-ice component (carbonaceous chondrite-type matter). The data obtained by the Galileo probe point out the presence of mixtures of salt crystal hydrates ( $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ , and others) on the ice surface of the satellites [3].

To develop a compositional model of the modern ocean, thermodynamic and thermal physical data are required on crystal hydrates of Mg and Na sulfates and carbonates, whose presence on the ice surface was indicated by spectral imaging. For this purpose, the low-temperature heat capacity of epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (c) was obtained from experimentally measured values.

**Heat capacity determination.** The studied sample consisted of magnesium sulfate heptahydrate of analytical grade purity (total admixture  $< 5 \times 10^{-3}\%$ ) in the form of white crystalline powder with grain sizes from a few tenths of a millimeter to 1 mm. X-ray and differential thermal analyses confirmed the composition of epsomite within the detection limit. Preparatory to the measurements, the epsomite was stored over a saturated NaCl solution in an exsiccator until a constant weight. As follows from its chemical analysis ( $\text{MgO}$ , 16.50;  $\text{SO}_3$ , 32.78;  $\text{H}_2\text{O}^-$ , 36.58; and  $\text{H}_2\text{O}^+$ , 14.14%), the mineral has a lower water content ( $6.868\text{H}_2\text{O}$ ) than that in the theoretical composition ( $7\text{H}_2\text{O}$ ). The molecular weight of the sample ( $\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O}$ ) is  $244.091 \text{ g mol}^{-1}$ .

The heat capacity of epsomite from 16.09 to 303.90 K was measured by adiabatic calorimetry [4] (Table 1, figure). Helium at a pressure of  $\sim 1$  bar was used as the heat exchanger. The sample weight was 1.5749 g.



Heat capacity of epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , magnesium sulfate  $\text{MgSO}_4$ , and crystal hydrate water in epsomite  $7\text{H}_2\text{O}$  at 0–303 K. (1)  $C_p^0(T)$   $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; (2) Moore and Kelley, experimental data [7]; (3)  $C_p^0(T)$   $\text{MgSO}_4$ , calculated using Eq. (4); (4)  $C_p^0(T)$   $7\text{H}_2\text{O}(\text{cr})$  calculated using Eq. (5); (5)  $C_p^0(T)$   $\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O}$ , our experimental data.

**Table 1.** Experimental values of the heat capacity of epsomite  $\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O}(\text{cr})$ 

$T, \text{K}$	$C_p^0$ $\text{J K}^{-1} \text{mol}^{-1}$	$T, \text{K}$	$C_p^0$ $\text{J K}^{-1} \text{mol}^{-1}$	$T, \text{K}$	$C_p^0$ $\text{J K}^{-1} \text{mol}^{-1}$	$T, \text{K}$	$C_p^0$ $\text{J K}^{-1} \text{mol}^{-1}$
16.09	4.661	62.66	86.26	118.77	170.18	205.13	276.04
17.04	5.237	64.71	89.84	122.23	175.13	209.19	281.20
19.12	7.966	66.75	92.98	125.61	179.72	213.22	285.87
20.49	10.12	68.79	96.50	128.58	183.31	217.25	290.34
21.95	11.99	70.82	99.75	131.56	187.08	221.32	294.98
23.42	14.19	72.83	103.19	134.54	191.01	225.39	299.68
24.64	15.90	74.84	106.37	137.53	194.67	229.47	303.90
25.80	17.83	76.84	109.64	139.08	197.18	233.56	308.46
26.83	19.49	78.85	113.45	142.43	201.18	237.65	313.32
28.01	21.67	80.96	116.56	145.55	205.20	241.63	317.48
29.34	23.81	82.96	119.94	148.60	208.90	245.49	320.96
31.11	27.22	84.96	122.81	151.86	213.04	249.37	325.05
33.31	31.29	86.96	125.25	155.13	217.11	253.37	329.85
35.82	35.93	88.96	128.43	158.00	219.87	257.84	334.70
38.66	41.34	90.96	131.49	160.62	224.01	262.93	340.24
41.28	46.35	92.97	134.85	163.66	227.77	268.03	346.62
43.82	51.72	94.99	137.54	166.95	231.53	273.15	351.66
46.50	56.45	97.00	140.23	170.24	235.61	278.25	357.03
49.16	61.37	99.05	143.05	173.55	239.30	283.36	362.30
51.59	66.47	101.11	146.26	177.20	243.71	288.47	367.18
51.73	66.36	103.13	148.84	181.35	248.46	293.61	373.00
53.97	70.57	105.16	151.60	185.19	253.21	298.76	378.21
54.21	71.19	107.18	155.08	189.21	257.94	303.90	385.06
56.26	74.47	109.09	157.00	193.24	262.83		
58.44	78.57	112.13	161.11	197.27	267.67		
60.57	82.40	115.36	166.12	201.20	271.85		

**The determination of heat capacity of epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ .** Experimental data on  $C_p^0(T)$   $\text{MgSO}_4 \cdot 6.868 \text{H}_2\text{O}$  were fitted by the following polynomial algorithm [5–6]:

$$C_p^0(T)\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O} = \sum_{j=0}^m A_j [1 - \exp(-0.001T)]^j \quad (1)$$

The values of coefficients  $A_j$  are shown in Table 2.

To convert the actual heat capacity to theoretical epsomite, we have assumed that

**Table 2.** Coefficient of polynomial (1)  $C_p^0(T) = \sum_{j=0}^m A_j [1 - \exp(-0.001T)]^j$  (epsomite  $\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O}(\text{cr})$ ; temperature interval: 16.09–303.90 K)

$j$	$A_j$ $\text{J K}^{-1} \text{mol}^{-1}$	$j$	$A_j$ $\text{J K}^{-1} \text{mol}^{-1}$
0	$0.4727 \times 10^1$	5	$-0.1288354 \times 10^9$
1	$-0.151449 \times 10^4$	6	$0.453751783 \times 10^9$
2	$0.1236951 \times 10^6$	7	$-0.87802457 \times 10^9$
3	$-0.219984126 \times 10^7$	8	$0.7191021 \times 10^9$
4	$0.217693393 \times 10^8$		

**Table 3.** Parameters of Eqs. (4) and (5)

Parameters	Values of parameters	
	Equation (4)	Equation (5)
$a_0, \text{J}^{-1} \text{mol}$	–	$1.4689 \times 10^{-5}$
$a_1$	0.98533	0.33333
$a_2$	0.98383	0.33333
$a_3$	0.98933	0.33333
$a_4$	0.01583	0.33333
$a_5$	–	0.33333
$\theta_1, \text{K}$	343	171
$\theta_2, \text{K}$	837	287
$\theta_3, \text{K}$	1712	671
$\theta_E, \text{K}$	472	2047
$\theta_L, \text{K}$	–	484
$\theta_U, \text{K}$	–	1444

1. If the nonstoichiometry is insignificant (in our case, 0.132 H<sub>2</sub>O), the following equation is valid:

$$C_p^0(T)\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = C_p^0(T)\text{MgSO}_4 \cdot 6.868\text{H}_2\text{O} + 0.132C_p^0(T)\text{H}_2\text{O}(\text{cr}), \quad (2)$$

where  $C_p^0(T)\text{H}_2\text{O}$  is the heat capacity of one mole of crystal hydrate water in epsomite.

2. Heat capacity of one mole of crystal hydrate water in epsomite can be expressed by the equation

$$C_p^0(T)\text{H}_2\text{O}(\text{cr}) = [C_p^0(T)\text{MgSO}_4 \cdot x\text{H}_2\text{O} - C_p^0(T)\text{MgSO}_4]/x, \quad (3)$$

where  $x$  is the number of water molecules in epsomite; for our sample,  $x = 6.868$ .

Data on the heat capacity of Mg sulfate were taken from [7], in which  $C_p^0(T)\text{MgSO}_4$  was measured in the range of 53.30–295.40 K. To obtain a dependence for  $C_p^0(T)\text{MgSO}_4$  within 0–303 K, experimental data [7] were approximated by equation DE [8]

$$C_p^0(T)\text{MgSO}_4(\text{cr}) = n \left[ (1/3) \sum_{j=0}^3 a_j D(\theta_j/T) + a_4 E(\theta_E/T) \right], \quad (4)$$

where  $n$  is the number of atoms in one molecule of the compound ( $n = 6$  for MgSO<sub>4</sub>);  $D$  and  $E$  are the Debye and Einstein functions;  $\theta_1, \theta_2, \theta_3,$  and  $\theta_E$  are the characteristic temperatures; and  $a_1, a_2, a_3,$  and  $a_4$  are linear

coefficients. The values of parameters  $a_1, \dots, a_4, \theta_1, \dots, \theta_E$  determined by nonlinear LSM are shown in Table 3. The method of calculations is described in detail in [8]. Equation (4) was applied to calculate the heat capacity of MgSO<sub>4</sub> at 0–303 K, while Eq. (3) was used to determine  $C_p^0(T)\text{H}_2\text{O}(\text{cr})$  at 16.09–303.90 K.

The dependence obtained for  $C_p^0(T)\text{H}_2\text{O}(\text{cr})$  was approximated by the ADEK equation

$$C_p^0(T)\text{H}_2\text{O}(\text{cr}) = a_0 T (C_v)^2 + n \left[ (1/3) \sum_{j=1}^3 a_j D_j(\theta_j/T) + a_4 E(\theta_E/T) + a_5 K \left( \theta_L/T, \theta_U/T \right) \right], \quad (5)$$

where  $n = 3$ ;  $K$  is the Kieffer function [9];  $\theta_L$  and  $\theta_U$  are the characteristic temperatures of the  $K$ -function; ( $a_5$ ) is a linear coefficient; function  $C_v(T)$  has the following form:

$$C_v = n \left[ (1/3) \sum_{j=1}^3 a_j D_j(\theta_j/T) + a_4 E(\theta_E/T) + a_5 K(\theta_L/T, \theta_U/T) \right].$$

The abbreviation ADEK means that dependence (5) is the sum consisting of term  $a_0 T (C_v)^2$  (the contribution of the expansion work of the crystal lattice), three Debye, one Einstein, and one  $K$ -functions. The combination of functions  $D, E,$  and  $K$  in Eq. (5) and its application to the approximation of the dependence  $C_p^0(T)$  is described in [10].

As for Eq. (4), the values of parameters  $a_0, \dots, a_5, \theta_1, \dots, \theta_U$  were determined by nonlinear LSM; the values are listed in Table 3. Equation (5) was applied to estimate the heat capacity of crystal hydrate water in epsomite H<sub>2</sub>O(cr) in the subsequent calculations.

The heat capacity was determined with Eq. (2), and entropy and enthalpy changes were then defined for MgSO<sub>4</sub> · 7H<sub>2</sub>O (cr) in the temperature range of 0–303 K (Table 4). At 298.15 K, these functions have the following form:

$$C_p^0(T)(298.15 \text{ K}) = 383.43 \pm 0.29 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$S^0(298.15 \text{ K}) = 375.47 \pm 0.18 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$H^0(298.15 \text{ K}) - H^0(0 \text{ K}) = 60.098 \pm 0.017 \text{ J K}^{-1} \text{ mol}^{-1}.$$

The uncertainties correspond to random errors.

The value obtained for  $S^0(298.15 \text{ K}) = 375.47 \pm 0.18 \text{ J K}^{-1} \text{ mol}^{-1}$  is well consistent with the tabulated data [11]:  $S^0(298.15 \text{ K}) = 372.0 \pm 4.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . The heat capacity of epsomite  $C_p^0(298.15, \text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = 383.43 \pm 0.29 \text{ J K}^{-1} \text{ mol}^{-1}$  is in reasonable agreement

**Table 4.** Heat capacity and thermodynamic functions of epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$  in a range of 0–303 K; MM = 246.469 g mol<sup>-1</sup>

$T, \text{K}$	$C_p^0(T)$ J K <sup>-1</sup> mol <sup>-1</sup>	$S^0(T)$ J K <sup>-1</sup> mol <sup>-1</sup>	$H^0(T) - H^0(0)$ J mol <sup>-1</sup>	$T, \text{K}$	$C_p^0(T)$ J K <sup>-1</sup> mol <sup>-1</sup>	$S^0(T)$ J K <sup>-1</sup> mol <sup>-1</sup>	$H^0(T) - H^0(0)$ J mol <sup>-1</sup>
1	0.0012	0.00040	0.00030	90	131.85	88.38	5094.31
2	0.0097	0.0035	0.0058	95	139.22	95.70	5772.04
4	0.078	0.027	0.083	100	146.47	103.03	6486.33
6	0.26	0.089	0.40	110	160.59	117.65	8022.05
8	0.624	0.209	1.27	120	174.34	132.22	9697.1
10	1.22	0.408	3.07	130	187.75	146.71	11508
12	2.10	0.703	6.35	140	200.85	161.10	13451
14	3.32	1.114	11.73	150	213.70	175.40	15524
16	4.92	1.659	19.93	160	226.28	189.59	17724
18	6.90	2.349	31.70	170	238.62	203.69	20049
20	9.25	3.194	47.80	180	250.75	217.66	22496
25	16.52	6.005	111.5	190	262.67	231.54	25063
30	25.24	9.771	215.5	200	274.31	245.31	27748
35	34.78	14.37	365.3	210	285.97	258.98	30550
40	44.69	19.66	563.9	220	297.39	272.55	33467
45	54.62	25.50	812.2	230	308.69	286.02	36498
50	64.39	31.76	1189.8	240	319.92	299.40	39641
55	73.88	38.34	1455.7	250	330.94	312.68	42895
60	83.05	45.17	1848.1	260	341.96	325.87	46259
65	91.87	52.17	2285.5	270	352.89	338.98	49734
70	100.37	59.29	2766.3	280	363.78	352.01	53317
75	108.59	66.49	3288.8	290	374.63	364.97	57009
80	116.55	73.76	3851.7	300	385.43	377.85	60809
85	124.29	81.06	4453.9	303	388.66	381.70	61971

with  $C_p^0(298.15, \text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = 394.3 \text{ J K}^{-1} \text{ mol}^{-1}$  obtained by differential scanning calorimetry in the range of 123–873 K in [12].

#### ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project nos. 03-05-64413 and 06-05-64308) and Programs 9 and 18 of the Department of Earth Sciences, Russian Academy of Sciences.

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