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HEAT CAPACITIES AND ENTROPIES FROM 8 TO 1000 K OF LANGBEINITE ($K_2Mg_2(SO_4)_3$), ANHYDRITE ($CaSO_4$) AND OF GYPSUM ($CaSO_4 \cdot 2H_2O$) TO 325 K *

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ABSTRACT

Heat capacities of $K_2Mg_2(SO_4)_3$ (langbeinite) and $CaSO_4$ (anhydrite) were measured from approximately 8 to 1000 K by combined adiabatic shield calorimetry (8–365 K) and differential scanning calorimetry (350–1000 K). Heat capacities were also measured on natural crystals of gypsum ($CaSO_4 \cdot 2H_2O$) between 8.1 and 323.5 K. The molar entropies at 298.15 K, $S^\circ_m(298.15\ \mathrm{K})$, are 378.8 ± 0.6, 107.4 ± 0.2 and 193.8 ± 0.3 J K^{-1} mol^{-1} for langbeinite, anhydrite and gypsum, respectively. The heat capacity in J K^{-1} mol^{-1} of langbeinite can be represented by the equation

$$C^\circ_{p,m}(K_2Mg_2(SO_4)_3, T) = 535.9 + 0.11011T - 1.0200 \times 10^6/T^2 - 4.909 \times 10^{-5}T^2 - 4040.2/T^{0.5}$$

between 300 and 1000 K with an average deviation of $\pm 0.4\%$. For anhydrite the heat capacity between 300 and 1000 K is given by

$$C^\circ_{p,m}(CaSO_4, T) = 372.8 - 0.1574T + 1.695 \times 10^6/T^2 + 7.993 \times 10^{-5}T^2 - 4330.8/T^{0.5}$$

with an average deviation of $\pm 0.4\%$.

Combining our heat-capacity and entropy data with the solution calorimetric results of Kelley et al. (U.S. Bur. Mines Tech. Paper, 625, 1941) yields an equilibrium temperature for the reaction gypsum $\rightarrow$ anhydrite + 2 water of 314.7 K (41.5 °C).

Our observations are in agreement with the conclusions of Speer and Salje (Phys. Chem. Miner., 13 (1986) 17); we see no evidence in our heat capacity measurements for the transformation of cubic langbeinite ($P2_13$) to a low temperature orthorhombic ($P2_12_12_1$) form as is seen in the isostructural Co, Zn, Ca, Mn and Cd langbeinites.

Although Bond (Bell Sys. Tech. J., 22 (1943) 145) reported that langbeinite was piezoelectric at room temperature, we found no evidence in our C°_p measurements for a Curie temperature above which langbeinite would no longer be piezoelectric.

INTRODUCTION

The sulfate minerals langbeinite, anhydrite and gypsum are major components of many commercial salt deposits. Langbeinite ($K_2Mg_2(SO_4)_3$) is a

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honor of his contributions to calorimetry and thermal analysis.

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major source of potash for agricultural use. In 1982, for example, 16 million tonnes of mixed $K_2Mg_2(SO_4)_3$–KCl ore were mined near Carlsbad, NM. The major coexisting phase in these potash-rich salt deposits is anhydrite, $CaSO_4$.

One of the locations selected by the Waste Isolation Pilot Plant (WIPP) which is designed to demonstrate the safe storage of high-level radioactive waste is sited in these same Permian salt deposits near Carlsbad, NM. Engineering calculations of the heat buildup in the surrounding rocks as a consequence of this radioactive waste storage require data for the heat capacities of the several mineral phases which comprise the salt deposits. Accurate heat capacity data exist for two of the principal phases which make up the salt deposits, sylvite (KCl), and halite (NaCl). There are, however, no C_p^o data available for langbeinite, while those for anhydrite were obtained on a somewhat impure mineral sample, and those for gypsum are over 55 years old and extend upwards in temperature only to 302 K. Modern heat capacity data on these sulfate minerals would therefore be of considerable engineering use for nuclear waste repository modeling.

At room temperature langbeinite is cubic (point group 23 (tetratoidal), space group $P2_13$ (198)) and is reported by Bond [3] to be piezoelectric. One would suspect that at some higher temperature (i.e. the Curie temperature) langbeinite would transform to the normal (non-piezoelectric) state and that this transformation would be accompanied by an anomaly in the heat capacity such as that exhibited, for example, by quartz or $BaTiO_3$.

The heat capacity of $CaSO_4$ was previously measured by Kelley et al. [1] at 23 temperatures between 53.5 and 295.7 K using as a sample anhydrite crystals from Arden, NV which contained some gypsum. Kelley [4] also derived values for the heat capacity at higher temperatures based upon the heat-content measurements of Lastschenko and Kompanski [5] between 293 and 1393 K. Lastschenko and Kompanski's sample was also a mineral sample and contained 0.23% SiO_2 and 1.23% H_2O.

The heat capacity of gypsum was previously determined by Latimer et al. [6] between 18.7 and 302.1 K. Heat capacity data are apparently not available for langbeinite.

SAMPLE PREPARATION

Coarse crystals of $K_2Mg_2(SO_4)_3$ were prepared by crystallization from a melt of an equimolar mixture of K_2SO_4 and $MgSO_4$. Because of its very fine grain size and hygroscopic nature, reagent grade $MgSO_4$ (Fisher M-65) was first heated at 1150 K for 2 h in a 100 cm^3 platinum crucible immedately prior to weighing. The appropriate number of moles of reagent K_2SO_4 (Fisher P-304) which had been heated at 400 K before weighing was added to the crucible containing the $MgSO_4$, mixed well, and placed in an electric furnace at 1225 ± 10 K in which it was held for 4 h. The furnace controller was then turned off and the crucible and its contents allowed to cool to room temperature overnight. This procedure yielded crystals which measured 2 mm on edge.

The sample was freed from the crucible, crushed to pass through a 10 mesh screen (1.68 mm), washed with cold distilled water to remove possible excess K_2SO_4, and vacuum dried. It was then sieved and the material passing a 35 mesh screen was discarded. The sample was heated in an oven at 385 K for 1 h before loading in the calorimeter.

An X-ray diffractometer tracing using Cu K_α showed only those lines for langbeinite given in the National Bureau of Standards (NBS) pattern (Swanson et al. [7]). The unit cell edge of the calorimetric sample was 0.99196 ± 0.00015 nm and was obtained using NBS Standard Reference Material 640 silicon ($a = 0.543088$ nm, Hubbard et al. [8]) as an internal standard, Cu $K_{\alpha 1}$ radiation ($\lambda = 0.1540598$ nm), and 12 lines for which $2\theta \geq 49°$. Our value agrees with that of Swanson et al. [7] to within ± 0.014%. The molar volume V_m^o (298.15 K) of langbeinite calculated from our cell edge and using Cohen and Taylor's [9] value for Avogradro's number ($6.022137(4) \times 10^{23}$ mol^{-1}) is 146.95 ± 0.04 cm^3.

Anhydrous $CaSO_4$ was prepared using the procedure described by Manross [10]. Reagent grade $CaCl_2 \cdot 2H_2O$ (Fisher C-79) was heated in a resistance furnace in a 100 cm^3 platinum crucible to 1123 K and held for 3 h. It was removed from the furnace while still molten and quenched in air. Reagent grade K_2SO_4 (Fisher P-304) was then added to the crucible. A typical charge was 40 g of $CaCl_2$ (anhydrous) and 8.5 g of K_2SO_4. The crucible was returned to the furnace and held at 1150 K for 3 h. The furnace controller was then reset to 950 K and the crucible and its contents cooled over approximately 1 h to 950 K and then held at 950 K for 16 h. The crucible was removed from the furnace and cooled to room temperature. The salt pellet was broken free of the crucible, crushed coarsely in an alumina mortar and washed with copious quantities of hot water to remove the residual $CaCl_2$ and KCl.

Tabular crystals of $CaSO_4$ up to 1.2 cm in length were grown in this fashion. For the calorimetric measurements the material was sieved and the crystals passing a 35 mesh sieve (0.42 mm) were discarded. Spectrographic analysis indicated the presence of 0.09% K_2O in the $CaSO_4$ sample.

Unit cell parameters for our sample were measured using NBS Standard Reference Material 640 (silicon) as an internal standard. Our values are $a = (0.69893 \pm 0.00038)$, $b = (0.69964 \pm 0.00030)$ and $c = (0.62409 \pm 0.00028)$ nm and agree to within 0.04% with those of McMurdie et al. [11]. Our data lead to a molar volume V_m^o(298.15 K) of 45.96 ± 0.03 cm^3. McMurdie et al.'s [11] cell parameters yield a value for $V_m^o(298.15\ K) = 46.008 \pm 0.006$ cm^3.

The gypsum sample was part of a large, 15 cm long, glass-clear crystal of selenite from Brazil. Semi-quantitative spectroscopic analysis indicated the presence of 300 p.p.m. strontium, i.e. 0.35 wt.% SrO, as the only significant impurity.

EXPERIMENTAL METHODS AND RESULTS

Our heat capacity measurements were made by the intermittent heating method under quasi-adiabatic conditions using the calorimeter–cryostat and automatic data-acquisition system described by Robie [12]. Temperatures were determined with a Minco model S 1059-1 platinum resistance thermometer ($R_0 = 100.02\ \Omega$) that had been calibrated by the Temperature Measurements Section of the National Bureau of Standards on IPTS-68 between 13.8 and 505 K, and on a provisional scale used in this laboratory between 4.2 and 13.8 K [12]. The samples were sealed in the calorimeter under purified helium gas at a pressure of 5 kPa (approximately 4×10^{-5} mol of He). The langbeinite sample had a mass of 35.713 g, that of anhydrite was 33.748 g and the mass of the gypsum sample was 30.014 g.

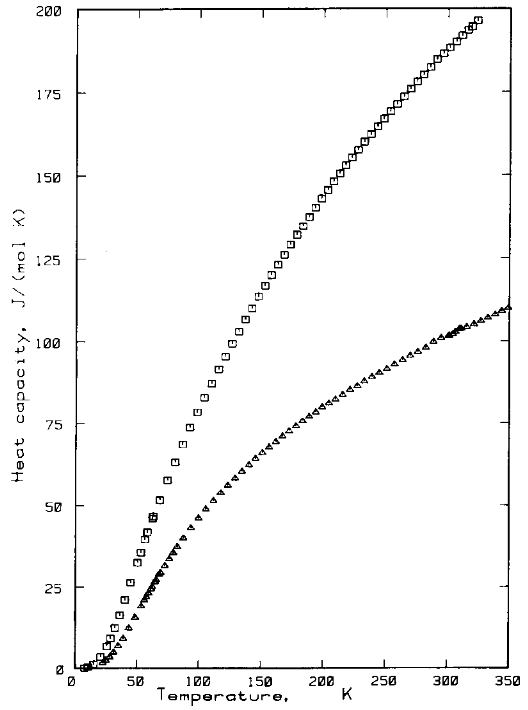

Fig. 1. Experimental heat capacities of synthetic anhydrite ($CaSO_4$) crystals (△) and natural gypsum crystals from Brazil (□).

TABLE 1

Experimental heat capacities (J mol^{-1} K^{-1}) of $K_2Mg_2(SO_4)_3$ measured with an adiabatic calorimeter; formula weight 414.9794 g mol^{-1}

Temp. (K)	Heat capacity	Temp. (K)	Heat capacity	Temp. (K)	Heat capacity
Series 1		124.09	187.2	144.12	208.2
302.22	321.2	128.53	192.0	148.28	212.1
306.73	323.4	132.92	196.8	152.48	216.0
311.29	326.3	137.28	201.4	156.66	220.1
315.87	328.2			160.83	223.8
320.31	330.8	Series 5		164.99	227.6
324.75	333.5	8.24	0.836	169.13	231.1
329.18	335.9	8.89	1.117	173.26	234.5
333.62	337.1	9.78	1.580	177.39	238.0
338.05	339.9	10.85	2.197	181.50	241.8
		12.11	2.969		
Series 3		13.55	4.109	Series 7	
338.77	339.9	15.11	5.580	191.93	250.3
344.09	342.6	16.84	7.397	196.83	253.7
349.51	344.8	18.75	9.761	201.77	257.5
354.91	347.2	20.88	12.90	206.77	261.4
360.18	349.5	23.24	16.78	211.56	264.7
365.43	351.4	25.88	21.67	216.43	268.2
370.66	353.6	28.84	27.76	221.35	271.8
		32.17	35.34	226.35	275.1
Series 4		35.91	44.38	231.46	278.8
51.76	84.60	40.11	54.96	236.69	282.0
56.41	93.74	44.77	67.70	242.03	285.4
66.04	110.1	49.91	81.31	247.45	288.7
71.49	118.6	54.89	90.64	252.94	292.0
76.67	126.6	66.43	110.6	258.47	295.1
81.67	133.9	68.81	114.4	264.08	298.4
86.53	140.9	71.12	117.9	269.76	302.0
91.39	147.7	73.40	121.4	275.43	305.6
96.30	154.2			281.08	308.8
101.12	160.4	Series 6		286.72	312.4
105.84	166.2	131.24	195.2	292.33	316.1
110.49	171.7	135.40	199.4	297.93	319.2
115.08	177.1	139.72	203.8	303.52	321.8
119.61	182.3				

Our experimental heat capacities, measured with the adiabatic calorimeter, are listed in their chronological order of measurement in Tables 1, 2 and 3 for synthetic langbeinite, synthetic anhydrite and natural gypsum, respectively. The data for anhydrite and gypsum are shown graphically in Fig. 1. The C_p^o data were extrapolated graphically to 0 K using a plot of $C_{p,m}^o/T$ against T^2. Above 25 K the data were smoothed by splines.

TABLE 2

Experimental heat capacities (J mol^{-1} K^{-1}) of $CaSO_4$ measured with an adiabatic calorimeter; formula weight: 136.138 g mol^{-1}

Temp. (K)	Heat capacity	Temp. (K)	Heat capacity	Temp. (K)	Heat capacity
Series 1		43.66	12.46	167.27	71.08
304.26	102.1	48.69	15.80	172.63	72.62
309.87	103.7	53.63	19.23	177.97	74.08
315.58	104.2	57.79	22.10	183.31	75.68
321.29	105.1	61.40	24.52	188.63	77.11
326.98	106.1	64.74	26.67	193.96	78.48
332.64	107.0	67.91	29.09	199.28	79.96
338.28	108.0				
		Series 4		Series 5	
Series 2		56.21	21.06	204.40	81.17
343.71	109.1	59.44	23.27	209.91	82.40
349.08	110.1	62.42	25.27	215.75	83.87
354.73	110.9	65.60	27.34	221.67	85.32
360.42	111.5	69.18	29.61	227.34	86.48
366.04	112.6	72.67	31.78	233.12	87.85
		76.11	33.85	239.02	89.22
Series 3		79.49	35.77	245.02	90.45
8.65	0.0299	82.80	37.64	251.16	91.65
9.89	0.0925	87.53	40.20	257.42	93.00
10.87	0.1247	93.62	43.33	263.70	94.24
12.03	0.1700	99.64	46.26	269.98	95.59
13.46	0.2734	105.66	48.99	276.24	96.74
14.95	0.4122	111.60	51.58	282.49	97.99
16.63	0.6012	117.45	54.03	288.74	99.74
18.50	0.8760	123.22	56.26	294.97	100.9
20.56	1.273	128.91	58.39	301.19	101.7
22.85	1.827	134.52	60.47		
25.41	2.612	140.08	62.45	Series 6	
28.27	3.693	145.59	64.33	301.50	101.5
31.48	5.164	151.06	66.13	306.30	102.7
35.08	7.095	156.49	67.79	311.19	103.7
39.14	9.344	161.89	69.42		

The extrapolation of the data for anhydrite below 10 K corresponds to a Debye temperature of 502 K which is in only fair agreement with the value 435 K which one calculates from the room temperature elastic constant data of Schwerdtner et al. [13]. For langbeinite our extrapolation below 10 K corresponds to an apparent Debye temperature of 282 ± 10 K which is completely out of line with the θ_D calculated from the elastic constants of Haussuhl [14] and of Liebertz and Quadflieg [15], whose data yield θ_D of 500 and 505 K, respectively.

TABLE 3

Experimental heat capacities (J $\mathrm{mol^{-1}\ K^{-1}}$) of gypsum ($CaSO_4 \cdot 2H_2O$) measured with adiabatic calorimeter; formula weight 172.168 g $\mathrm{mol^{-1}}$

Temp. (K)	Heat capacity	Temp. (K)	Heat capacity	Temp. (K)	Heat capacity
Series 1		188.35	137.5	9.04	0.2052
53.16	35.77	193.34	140.3	9.98	0.3100
58.47	41.93	198.37	143.0	11.05	0.4419
63.21	46.70	203.22	145.6	12.37	0.6414
68.52	51.73	208.07	148.1	13.80	0.9336
74.74	57.76	212.93	150.5	15.35	1.327
80.72	63.28	217.82	152.9	17.07	1.868
86.64	68.51	222.75	155.3	18.99	2.659
92.56	73.64	227.75	157.6	21.10	3.712
98.43	78.41	232.84	160.0	23.44	5.092
104.20	82.95	237.99	162.3	26.10	6.929
109.86	87.20	243.17	164.7	29.06	9.348
115.44	91.37	248.37	167.0	32.39	12.45
120.94	95.35	253.63	169.2	36.16	16.30
126.38	99.20	258.96	171.4	40.40	21.07
131.76	102.9	264.29	173.6	45.18	26.37
137.09	106.5	269.61	176.0	50.52	32.61
142.36	110.0	274.92	178.1	56.41	39.66
147.59	113.5	280.21	180.2	62.57	46.09
152.78	116.7	285.49	182.4		
157.93	119.9	290.74	184.9	Series 4	
163.06	123.0	295.98	186.5	311.00	192.0
168.15	126.0	301.20	188.4	315.83	193.7
173.22	129.1	306.41	190.3		
178.27	132.0				
				Series 5	
Series 2		Series 3		319.05	194.7
183.30	134.7	8.09	0.1402	323.51	196.4

Smooth values for $C^{\circ}_{p,m}$, $S^{\circ}_{m}(T) - S^{\circ}_{m}(0)$, $[H^{\circ}_{m}(T) - H^{\circ}_{m}(0)]/T$, and $-[G^{\circ}_{m}(T) - H^{\circ}_{m}(0)]/T$ are listed in Tables 4, 5 and 6 for langbeinite, anhydrite and gypsum respectively.

Our $C^{\circ}_{p,m}$ values for anhydrite are systematically greater than those given by Kelley et al. [3] by 1.4% at 50 K decreasing to 0.4% at 200 K and rising again to 1.4% at 300 K. For gypsum our results are significantly lower (up to 14% at 20 K) than the values of Latimer et al. [6] up to 50 K above which our values are consistently larger by 0.2–0.6% to 300 K.

The heat capacities of langbeinite and anhydrite were also measured between 350 and 990 K using a differential scanning calorimeter (Perkin-Elmer DSC-2 *). The sample weights for langbeinite and anhydrite were

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* Reference to specific manufacturers and model numbers is made to facilitate understanding and does not imply endorsement by the U.S. Geological Survey.

TABLE 4

Standard molar thermodynamic functions for $K_2Mg_2(SO_4)_3$ between 0 and 370 K

Temp. T (K)	Heat capacity C_p^o	Entropy $S_T^o - S_0^o$	Enthalpy function $(H_T^o - H_0^o)/T$ ($J\ mol^{-1}\ K^{-1}$)	Gibbs energy function $-(G_T^o - H_0^o)/T$
5	0.22	0.07	0.05	0.02
10	1.69	0.56	0.42	0.14
15	5.46	1.87	1.40	0.47
20	11.55	4.21	3.12	1.09
25	19.99	7.65	5.61	2.04
30	30.33	12.18	8.84	3.34
35	42.15	17.73	12.74	4.99
40	54.96	24.19	17.21	6.98
45	68.14	31.42	22.14	9.28
50	80.47	39.25	27.37	11.88
60	100.2	55.76	37.94	17.81
70	116.3	72.44	48.02	24.42
80	131.5	88.97	57.51	31.46
90	145.7	105.3	66.53	38.76
100	158.9	121.3	75.12	46.22
110	171.2	137.1	83.30	53.76
120	182.7	152.5	91.11	61.35
130	193.7	167.5	98.59	68.94
140	204.1	182.3	105.8	76.51
150	213.8	196.7	112.6	84.04
160	223.0	210.8	119.3	91.52
170	231.8	224.6	125.6	98.95
180	240.4	238.1	131.8	106.3
190	248.5	251.3	137.7	113.6
200	256.3	264.2	143.4	120.8
210	263.7	276.9	149.0	127.9
220	270.8	289.3	154.4	135.0
230	277.6	301.5	159.6	142.0
240	284.1	313.5	164.6	148.9
250	290.2	325.2	169.5	155.7
260	296.2	336.7	174.3	162.4
270	302.2	348.0	178.9	169.1
280	308.3	359.1	183.4	175.7
290	314.3	370.0	187.8	182.2
300	320.0	380.8	192.1	188.6
310	325.5	391.4	196.4	195.0
320	330.7	401.8	200.5	201.3
330	335.8	412.0	204.5	207.5
340	340.6	422.1	208.4	213.7
350	345.1	432.1	212.3	219.8
360	349.3	441.8	216.0	225.8
370	353.4	451.5	219.7	231.8
273.15	304.2	351.5	180.3	171.2
298.15	319.0	378.8	191.4	187.4

TABLE 5

Standard molar thermodynamic functions for $CaSO_4$ between 0 and 360 K

Temp. T (K)	Heat capacity C_p°	Entropy $S_T^\circ - S_0^\circ$	Enthalpy function $(H_T^\circ - H_0^\circ)/T$ (J mol^{-1} K^{-1})	Gibbs energy function $-(G_T^\circ - H_0^\circ)/T$
5	0.010	0.003	0.002	0.001
10	0.094	0.029	0.022	0.007
15	0.419	0.115	0.089	0.026
20	1.167	0.325	0.254	0.071
25	2.476	0.712	0.555	0.158
30	4.457	1.328	1.031	0.298
35	7.017	2.202	1.698	0.504
40	9.956	3.326	2.542	0.784
45	13.29	4.689	3.549	1.140
50	16.72	6.266	4.694	1.572
60	23.62	9.927	7.276	2.652
70	30.17	14.07	10.08	3.982
80	36.08	18.49	12.97	5.517
90	41.48	23.05	15.84	7.211
100	46.41	27.68	18.66	9.027
110	50.90	32.32	21.39	10.93
120	55.02	36.93	24.02	12.91
130	58.83	41.49	26.55	14.93
140	62.41	45.98	28.99	16.99
150	65.76	50.40	31.33	19.07
160	68.88	54.75	33.58	21.16
170	71.86	59.01	35.75	23.27
180	74.72	63.20	37.83	25.37
190	77.46	67.31	39.85	27.47
200	80.06	71.35	41.79	29.56
210	82.51	75.32	43.67	31.65
220	84.87	79.21	45.49	33.72
230	87.15	83.04	47.25	35.78
240	89.35	86.79	48.96	37.83
250	91.46	90.48	50.62	39.86
260	93.52	94.11	52.23	41.88
270	95.57	97.68	53.80	43.88
280	97.64	101.2	55.33	45.86
290	99.67	104.7	56.82	47.83
300	101.5	108.1	58.28	49.78
310	103.3	111.4	59.71	51.72
320	105.0	114.7	61.10	53.63
330	106.7	118.0	62.45	55.54
340	108.4	121.2	63.78	57.42
350	110.1	124.4	65.08	59.29
360	111.6	127.5	66.35	61.14
273.15	96.22	98.79	54.28	44.51
298.15	101.2	107.4	58.01	49.42

TABLE 6

Standard molar thermodynamic functions for $CaSO_4 \cdot 2H_2O$ between 0 and 320 K

Temp. T (K)	Heat capacity C_p°	Entropy $S_T^\circ - S_0^\circ$	Enthalpy function $(H_T^\circ - H_0^\circ)/T$ ($J\ mol^{-1}\ K^{-1}$)	Gibbs energy function $-(G_T^\circ - H_0^\circ)/T$
5	0.040	0.016	0.011	0.005
10	0.309	0.102	0.074	0.028
15	1.23	0.370	0.280	0.090
20	3.17	0.959	0.733	0.226
25	6.15	1.96	1.50	0.460
30	10.19	3.43	2.60	0.830
35	15.07	5.36	4.02	1.34
40	20.50	7.72	5.74	1.98
45	26.21	10.46	7.69	2.77
50	32.03	13.52	9.84	3.68
60	43.26	20.37	14.48	5.89
70	53.39	27.81	19.33	8.48
80	62.71	35.56	24.18	11.38
90	71.43	43.45	28.95	14.50
100	79.63	51.40	33.61	17.79
110	87.36	59.36	38.15	21.21
120	94.71	67.28	42.56	24.72
130	101.7	75.14	46.84	28.30
140	108.5	82.93	51.01	31.92
150	114.9	90.63	55.05	35.58
160	121.2	98.25	58.99	39.26
170	127.2	105.8	62.83	42.95
180	132.9	113.2	66.56	46.65
190	138.5	120.5	70.20	50.35
200	143.9	127.8	73.75	54.04
210	149.0	134.9	77.22	57.72
220	154.0	142.0	80.59	61.39
230	158.7	148.9	83.89	65.05
240	163.2	155.8	87.10	68.68
250	167.7	162.5	90.23	72.30
260	171.9	169.2	93.29	75.90
270	176.1	175.8	96.28	79.48
280	180.2	182.2	99.21	83.03
290	184.1	188.6	102.1	86.57
300	187.9	194.9	104.9	90.07
310	191.6	201.2	107.6	93.56
320	195.3	207.3	110.3	97.02
273.15	177.4	177.8	97.21	80.60
298.15	187.2	193.8	104.4	89.43

30.203 and 30.010 mg, respectively. The calorimeter was operated at a rate of 10 K min^{-1} and the sensitivity was set at 0.021 W. The results are listed in Tables 7 and 8 for langbeinite and anhydrite, respectively. Our $C^\circ_{p,m}$

TABLE 7

Experimental molar heat capacities (J K^{-1} mol^{-1}) of $K_2Mg_2(SO_4)_3$ measured with a differential scanning calorimeter

Temp. (K)	Heat capacity	Temp. (K)	Heat capacity	Temp. (K)	Heat capacity
Series 1		Series 3		815.0	451.6
338.9	339.9	567.5	412.2		
348.8	344.2	577.5	413.0	Series 6	
358.8	348.3	587.4	413.9	806.0	450.2
368.7	353.0	597.3	416.0	816.0	451.1
378.7	355.6	607.3	417.6	825.9	451.7
388.6	358.4	617.2	418.0	835.9	453.1
398.6	361.6	627.2	419.8	845.7	453.6
408.5	365.3	637.1	421.5	855.4	454.4
418.4	365.4	647.0	423.1	865.1	456.2
428.4	372.7	657.0	425.2	874.8	459.3
438.3	376.2	666.9	427.8	883.5	463.8
448.3	379.5	676.8	431.9		
458.3	383.8	686.8	436.6	Series 7	
468.2	387.2	695.7	439.4	913.6	461.2
478.1	390.3			923.3	465.2
488.0	393.7	Series 4		933.0	462.8
497.0	397.4	666.9	425.0	941.7	464.7
		676.8	428.5		
Series 2		686.8	428.7	Series 8	
468.1	386.2	696.7	432.1	962.0	460.1
478.1	388.2	706.7	434.3	971.7	460.6
488.0	390.5	716.6	434.8	981.4	465.5
498.0	393.5	726.5	435.9	990.0	468.4
507.9	395.7	736.5	436.8		
517.8	398.2	745.4	437.3	Series 9	
527.8	401.0			835.9	455.9
537.7	403.8	Series 5		845.7	454.5
547.6	406.2	736.5	439.9	855.4	453.2
557.6	408.6	746.4	441.8	865.1	455.4
567.5	410.8	756.3	442.0	874.8	459.5
577.5	413.5	766.3	444.1	884.5	455.8
587.4	416.5	776.2	445.7	894.2	460.4
596.3	419.4	786.2	447.4	903.9	458.8
		796.1	448.0	912.6	460.1
		806.0	449.9		

measurements for langbeinite form a smooth, monotonic sigmoidal curve between 9 and 990 K with no indication of either a low temperature transition to a less symmetric (orthorhombic) form or of a Curie point above room temperature.

The C_p^o data obtained with the scanning calorimeter were combined with those measured with the low temperature adiabatic calorimeter to generate

TABLE 8

Experimental molar heat capacities (J K^{-1} mol^{-1}) of $CaSO_4$ measured with a differential scanning calorimeter

Temp. (K)	Heat capacity	Temp. (K)	Heat capacity	Temp. (K)	Heat capacity
Series 1		587.4	136.4	746.4	144.6
338.9	107.3	596.3	137.8	756.3	144.9
348.8	108.7			766.3	145.3
358.8	110.2	Series 3		776.2	145.7
368.7	111.4	567.5	132.3	786.2	146.8
378.7	112.7	577.5	132.7	796.1	147.3
388.6	114.2	587.4	134.0	806.0	148.0
398.6	115.6	597.3	134.9	815.0	148.5
408.5	116.8	607.3	135.7		
418.4	118.1	617.2	136.4	Series 6	
428.4	119.2	627.2	137.1	806.0	147.9
438.3	120.6	637.1	137.7	816.0	148.3
448.3	121.6	647.0	138.3	825.9	149.0
458.3	122.5	657.0	138.5	835.9	149.8
468.2	123.7	666.9	139.2	845.9	149.8
478.1	124.8	676.8	140.9	855.4	150.1
488.0	126.0	686.8	140.5	865.1	151.4
497.0	126.7	695.7	140.9	874.8	152.3
				883.5	152.4
Series 2		Series 4			
468.1	124.8	666.9	138.3	Series 7	
478.1	125.5	676.8	139.6	913.6	155.3
488.0	126.2	686.8	140.3	923.3	155.7
498.0	127.0	696.7	140.9	933.0	156.3
507.9	127.8	706.7	141.2	941.7	157.3
517.8	128.5	716.6	141.8		
527.8	129.5	726.5	142.3	Series 8	
537.7	130.6	736.5	143.0	962.0	156.9
547.6	131.6	745.4	143.6	971.7	158.0
557.6	133.0			981.4	159.5
567.5	133.8	Series 5		990.0	158.5
577.5	135.4	736.5	144.2		

the following equations in J K^{-1} mol^{-1} valid from 300 to 1000 K

$$C^{\circ}_{p,m}(K_2Mg_2(SO_4)_3,\ T) = 535.9 + 0.11011T - 1.0200 \times 10^6/T^2$$
$$-4.909 \times 10^{-5}T^2 - 4040.2/T^{0.5}$$

$$C^{\circ}_{p,m}(CaSO_4,\ T) = 372.8 - 0.1574T + 1.695 \times 10^6/T^2$$
$$+7.993 \times 10^{-5}T^2 - 4330.8/T^{0.5}$$

The average deviation of each data set from the fitted equation was 0.4%.

THE GYPSUM-ANHYDRITE REACTION

The dehydration of gypsum to form anhydrite apparently occurs readily in nature. Replacement of anhydrite crystals by gypsum is also common. In several localities bedded deposits of alternating layers of gypsum and anhydrite exist. There have been a number of studies of the equilibrium temperature of the reaction

$$\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} = \underset{\text{anhydrite}}{CaSO_4} + \underset{\text{water}}{2H_2O} \qquad (1)$$

Three of the more recent studies are Zen [16], Hardie [17] and Blount and Dickson [18]. The last two papers take issue with the previously accepted value of 314 K (42 °C) for the equilibrium temperatures of reaction (1) based principally on the work of Posnjak [19] and opt for a higher temperature of 330 ± 2 K (57 °C).

Our heat capacity data for anhydrite and gypsum between 300 and 325 K were fitted to linear equations yielding

$$C^{\circ}_{p,m}(\text{anhydrite}) = 49.9 + 0.172T \qquad (2)$$

and

$$C^{\circ}_{p,m}(\text{gypsum}) = 76.9 + 0.37T \qquad (3)$$

For water we used the value 75.345 J K^{-1} mol^{-1} from the CODATA tables (Garvin et al., [20]). For reaction (1) we get

$$\Delta C^{\circ}_{p} = 123.69 - 0.198T \qquad (300\text{–}325\ K) \qquad (4)$$

Using Kelley et al.'s [3] value for $\Delta_r H^{\circ}(298.15\ K)$ for this reaction, 16 862 ± 84 J, we can write

$$\Delta_r H^{\circ}(T) = -11\,216 + 123.69T - 0.099T^2 \qquad (300\text{–}325\ K) \qquad (5)$$

Combining our entropy data with the equation for ΔC°_{p} we get

$$\Delta_r S^{\circ} = 123.69 - 0.198T + 123.69 \times \ln T - 715.9 \qquad (6)$$

and

$$\Delta_r G^{\circ} = -11\,216 + 0.099T^2 - 123.69 \times T \times \ln T + 715.9T \qquad (7)$$

From this expression $\Delta_r G^{\circ}$ is 0 at 314.7 K (41.5 °C). The uncertainties in $\Delta_r G^{\circ}$ arising from the ± 84 J uncertainty in $\Delta_r H^{\circ}$ correspond to ± 1.4 K at this temperature, whereas the ± 0.39 J K^{-1} uncertainty in $\Delta_r S^{\circ}(298.15\ K)$ yields an uncertainty of ± 2.1 K at the equilibrium temperature. Thus, in the extreme case the calorimetric uncertainties result in a possible spread of ± 3.5 K in the calculated equilibrium temperature. Blount and Dickson's [18] assertion that "the 40 °C value calculated from thermochemical data by Kelley et al. [4] must be regarded as fortuitous" is unwarranted. The solution calorimetric results of Kelley et al. [4] for $\Delta_r H^{\circ}(298.15\ K)$ when combined with the present more accurate entropies support Posnjak's [19] value for the equilibrium temperature (~ 41° C). It is well known from the work of Weiser et al. [21] that gypsum crystals in the absence of an aqueous solution can persist metastabily up to ~ 333 K.

The pressure effect on this equilibrium can be obtained as follows. From the X-ray unit cell parameters (Morris et al. [22]) and using $6.022137(4) \times 10^{23}$ mol^{-1} for Avogadro's number, we calculate 74.58 ± 0.02 cm^3 for the molar volume of gypsum. Using our value for the molar volume of anhydrite 45.96 ± 0.03 cm^3 and 18.167 ± 0.005 cm^3 for $V^{\circ}_{\text{m}}(\text{H}_2\text{O}, 314.7\ \text{K})$ we get $\Delta_{\text{r}}V^{\circ}(314.7\ \text{K}) = 7.714 \pm 0.029\ \text{cm}^3$ or $0.7714\ \text{J bar}^{-1}$. From our equation for $\Delta_{\text{r}}S^{\circ}$ we calculate $\Delta_{\text{r}}S^{\circ}(314.7\ \text{K}) = 56.89\ \text{K} \pm 0.39\ \text{J K}^{-1}$, and thus $\text{d}p/\text{d}T = (56.89 \pm 0.39)/(0.7714 \pm 0.003) = 73.7 \pm 0.5\ \text{bar K}^{-1}$.

CONCLUSIONS

Combination of our entropy and heat capacity data for gypsum and anhydrite with the enthalpy of reaction measured by Kelley et al. [1] leads to 314.7 ± 3.5 K for the temperature at which gypsum and anhydrite are in equilibrium in aqueous solution. This temperature is in excellent agreement with that determined by Posnjak [19] from solubility measurements and does not support the higher temperatures obtained by Hardie [17] and Blount and Dickson [18]. Our low temperature $C^{\circ}_{\text{p,m}}$ measurements on $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, down to 9 K, show no suggestion of a transition and therefore support Speer and Salje [2], who concluded from their structural investigations that the cubic to orthorhombic phase transition exhibited by Ca, Cd, Co, Mn and Zn "langbeinites" would not occur in $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$. However, the excessively high $C^{\circ}_{\text{p,m}}$ of langbeinite below 20 K might possibly be indicative of a transition occurring at a temperature below 9 K. We believe that this is most unlikely.

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Note added in proof

Professor Juliana Boerio-Goates (Brigham Young University) has independently measured the heat capacity of $K_2Mg_2(SO_4)_3$. She has found that, by using very low heating rates and small temperature rises, she was able to show the existence of three small transitions in C_p^o between 50 and 70 K.

Our measurements on $K_2Mg_2(SO_4)_3$ in this temperature range (see Table 1, series 4 and 5) were made with heating rates of 0.006 to 0.025 K s^{-1} and temperature rises of between 2.3 and 5.6 K, and it is quite possible that our much larger temperature rises caused us to miss these transitions.