HEAT CAPACITIES OF KAOLINITE FROM 7 TO 380 K AND OF DMSO-INTERCALATED KAOLINITE FROM 20 TO 310 K. THE ENTROPY OF KAOLINITE $Al_2Si_2O_5(OH)_4$

RICHARD A. ROBIE AND BRUCE S. HEMINGWAY

MS 959, National Center U.S. Geological Survey, Reston, Virginia 22092

Abstract—The heat capacities of kaolinite (7 to 380 K) and of dimethyl sulfoxide (DMSO) intercalated kaolinite (20 to 310 K) were measured by adiabatically shielded calorimetry. The third law entropy of kaolinite, S°_{298}, is 200.9 ± 0.5 $J \cdot mol^{-1} \cdot K^{-1}$.

The "melting point" of the DMSO in the intercalate, 288.0 ± 0.2 K, is 3.7 K lower than that of pure DMSO, 291.67 K. The heat capacity of DMSO in the intercalate above 290 K is approximately 5.2 $J \cdot mol^{-1} \cdot K^{-1}$ smaller than that of pure liquid DMSO at the same temperature.

Key Words—Kaolinite, Heat capacity, Entropy, Specific heat, DMSO:kaolinite.

INTRODUCTION

We have measured the low-temperature heat capacity of kaolinite in order to obtain a more precise value for the entropy, S°_{298}, than has been previously available. This is part of an ongoing study of the thermochemistry of minerals and aqueous species in the system Al_2O_3-SiO_2-H_2O as related to the formation of bauxite deposits (Hemingway and Sposito, 1989; Hemingway *et al.*, 1977, 1978, 1991; Robie *et al.*, 1976). Kaolinite commonly forms as one product of weathering or hydrothermal alteration of feldspar-rich rocks. Under favorable conditions this leads to the formation of large scale deposits of kaolinite of enormous commercial value. Desilication of the kaolinite under conditions of tropical weathering yields the "bauxite" minerals, diaspore, gibbsite, and boehmite. A knowledge of the thermodynamic properties of kaolinite is thus desirable for the quantitative modeling of the chemical equilibria involved in the weathering or hydrothermal alteration processes leading to these deposits.

Kaolinite has the ability to incorporate many different organic molecules between lamellae thus forming an intercalate. This property makes it possible to use kaolinite as a "clay catalyst" (Thomas, 1982). Dimethyl sulfoxide (DMSO) $(CH_3)_2SO$ is one of the best studied of these organic intercalates. Specific heat measurements on the intercalate in the region of the melting temperature of pure DMSO may provide useful information concerning the structural behavior of the intercalated organic molecule. For this reason we have also measured the heat capacity of a kaolinite:DMSO intercalate between 20 and 310 K.

The heat capacity of kaolinite has been studied previously by King and Weller (1961) between 53 and 296 K and by Hemingway *et al.* (1978) between 340 and 600 K. Lipsicas *et al.* (1986) present a graph of the heat capacities of Georgia kaolinite, the kaolinite:

DMSO intercalate and of deintercalated kaolinite between 110 and 280 K.

EXPERIMENTAL

Materials

The kaolinite sample was obtained from the Source Clay Repository of the Clay Minerals Society and is well-crystallized Georgia kaolinite, KGa-1. Van Olphen and Fripiat (1979) give details on the location of the sample source, method of collection, processing and chemical analysis of these source clays. Part of this sample was run in the "as received" condition, except for vacuum drying at room temperature. A second aliquot of KGa-1 was intercalated with DMSO as described by Lipsicas *et al.* (1986).

After loading the kaolinite sample into the calorimeter the calorimeter was placed in the vacuum sealing jig described by Robie *et al.* (1976) and evacuated. After two hours evacuation at 6.6 Pa the valve separating the bell jar from the vacuum pump was closed and the bell jar and calorimeter were back filled with helium gas to a pressure of approximately 5 kPa. The calorimeter was then sealed. For our heat capacity measurements the kaolinite mass was 16.465 g.

From preliminary experiments it was known that the as-received kaolinite:DMSO sample suffered an approximate 20% weight loss after being pumped under vacuum. This loss was accompanied by a change in color from beige to light cream, presumably because of the removal of the excess surface adsorbed DMSO. Accordingly, after loading the kaolinite:DMSO sample into the calorimeter, it was evacuated to a terminal vacuum of ~23 Pa for six hours before back filling with He gas at 5 kPa and sealing the calorimeter. After completion of the heat capacity measurements the sample was analyzed for total sulfur using a Leco SC 132 sulfur analyzer to calculate the amount of inter-
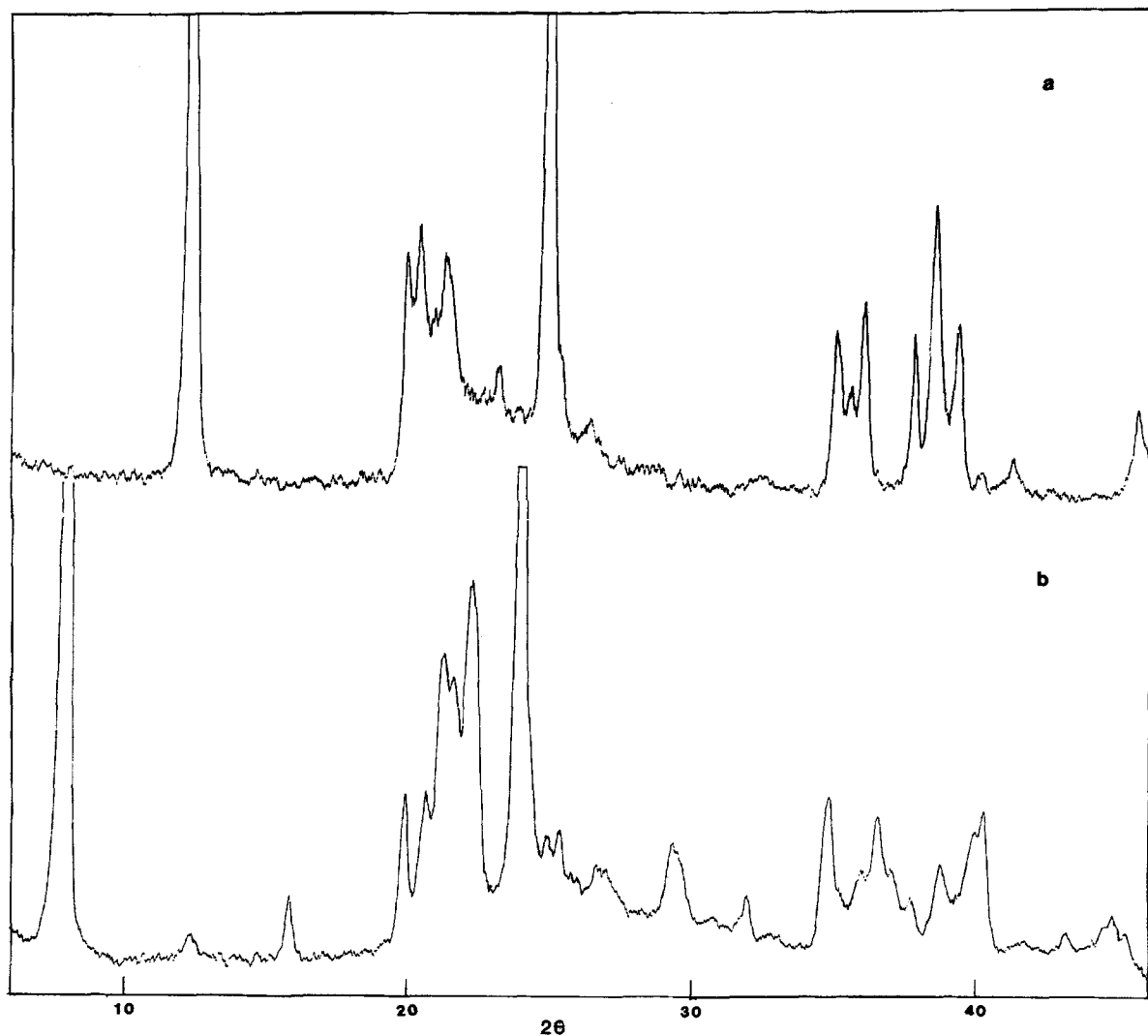
Figure 1. X-ray diffractometer profiles, using CuKα radiation. a. KGa-1 kaolinite, b. DMSO-intercalated kaolinite. Both *after* removal from the calorimeter.

calated DMSO. The result, 9.1 wt. % sulfur, leads to a weight fraction of 0.78 for kaolinite and 0.22 for DMSO, or a formula of $Al_2Si_2O_5(OH)_4 \cdot 0.94$ DMSO. Figure 1 shows X-ray diffractometer profiles for well-crystallized Georgia kaolinite KGa-1, and for the DMSO intercalated kaolinite. The small peak at 12.3° 2θ, Figure 1a, corresponds to the (001) reflection of kaolinite and indicates the presence of a minor amount of unintercalated material. Based upon the ratio of the peak heights, we estimate less than 5% unintercalated kaolinite. For the measurements on the kaolinite:DMSO intercalate the calorimeter contained 23.649 g of sample.

Measurements

The calorimeter-cryostat assembly and the automatic data acquisition system used for our heat ca-

pacity measurements have been previously described (Robie, 1987). The measurements have an accuracy of ±10% below 10 K, 0.5% between 10 and 50 K and ±0.2% above 50 K.

RESULTS AND DISCUSSION

Kaolinite

Our experimental results for kaolinite are listed in their chronological order of measurement in Table 1 and are shown graphically in Figure 2. The heat capacity of kaolinite follows a normal sigmoidal shaped curve. The data are not corrected for the presence of impurities or deviations from stoichiometry.

The results of two chemical analyses of kaolinite KGa-1 are listed in van Olphen and Fripiat (1979) and show the presence of 1.39 to 1.58 wt. % TiO_2 as the

Table 1. Experimental specific heats of well-crystallized Georgia kaolinite (KGa-1), uncorrected for the presence of $\sim$1.5 wt. % TiO_2.

Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$	Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$	Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$
Series 1		Series 2		Series 3	
51.86	0.0701	224.55	0.7159	6.70	0.00044
56.09	0.0840	229.62	0.7677	8.08	0.00062
60.58	0.1007	234.57	0.7825	8.95	0.00069
65.60	0.1208	239.56	0.7968	9.92	0.00092
71.63	0.1474	244.57	0.8138	11.14	0.0014
77.61	0.1753	249.54	0.8255	12.41	0.0020
83.62	0.2032	254.50	0.8394	13.84	0.0029
89.59	0.2301	259.46	0.8533	15.44	0.0041
95.50	0.2557	264.45	0.8681	17.22	0.0053
101.38	0.2806	269.45	0.8801	19.17	0.0064
107.17	0.3051	274.44	0.8940	21.31	0.0084
112.90	0.3294	279.42	0.9068	23.70	0.0109
118.56	0.3540	284.37	0.9188	26.34	0.0143
124.18	0.3794	289.30	0.9320	29.29	0.0190
129.74	0.4028	294.22	0.9428	32.58	0.0253
135.26	0.4265	299.12	0.9537	36.25	0.0334
140.73	0.4493	304.01	0.9649	44.96	0.0537
146.18	0.4726	308.87	0.9765	50.13	0.0648
151.59	0.4943	313.72	0.9897	55.87	0.0832
156.97	0.5148	318.55	0.9994	62.05	0.1061
162.31	0.5357	323.37	1.0067	68.38	0.1326
167.62	0.5559	328.17	1.0184	74.69	0.1614
172.91	0.5760	332.95	1.0273	80.91	0.1907
178.17	0.5946	337.71	1.0346	87.01	0.2186
183.42	0.6143	342.48	1.0459	93.03	0.2467
188.64	0.6345	347.27	1.0563	98.98	0.2706
193.85	0.6523	352.05	1.0641		
199.04	0.6690	356.80	1.0722		
204.22	0.6856	361.53	1.0826		
209.37	0.7019	366.24	1.0904		
214.51	0.7201	370.94	1.1005		
219.64	0.7367	375.61	1.1129		
		380.28	1.1210		

principal impurity. Nagelschmidt *et al.* (1949) have shown that the ubiquitous TiO_2 present in the sedimentary kaolinites of Georgia is in the form of anatase. We therefore corrected our results for the presence of $\sim$1.5 wt. % TiO_2 using the heat capacity data for anatase of Shomate (1947) and Dugdale *et al.* (1954). This correction ranges from 0.0 to +0.5% between 50 and 350 K.

Below 17 K the C_p data behave approximately as a Debye solid and can be fitted with a Debye function for which $\theta_D = 500$ K. We used this value to extrapolate our heat capacity values below 10 K after correcting for TiO_2. Above 10 K our data were fitted by smoothing splines to generate smoothed values (Table 2) for the molar thermodynamic properties of kaolinite. The extrapolation below 10 K contributed 0.1 $J \cdot mol^{-1} \cdot K^{-1}$ to S°_{298}.

Our values for the molar heat capacities of kaolinite between 100 and 300 K are in good agreement with the previous results of King and Weller (1961), on a kaolinite sample from Gordon, Georgia. The values range from 0.2% greater at 300 K to 0.3% smaller at 100 K. Below 100 K, however, our values become increasingly smaller than those of King and Weller (1961). The difference is -4.7% at 75 K and -19% at 50 K. We can provide no explanation for this discrepancy, in particular since for other compounds studied by both laboratories the difference has never been greater than 2%. It may represent a real difference between the two different kaolinite samples.

At 298.15 K our value for the standard molar entropy of $Al_2Si_2O_5(OH)_4$ (kaolinite) is 200.9 $\pm$ 0.5 $J \cdot mol^{-1} \cdot K^{-1}$ and is 2.65 $J \cdot mol^{-1} \cdot K^{-1}$ smaller than the value obtained by King and Weller (1961). Their value included a contribution to S°_{298} of 8.5 $J \cdot mol^{-1} \cdot K^{-1}$ based upon their *estimated* values for C_p at temperatures below 51 K. Lipsicas *et al.* (1986) published a graph of C_p versus temperature for "untreated" KGa-1 kaolinite, measured by differential scanning calorimetry. After multiplying by 4.184 we get 71.5 and 184.5 $J \cdot mol^{-1} \cdot K^{-1}$ at 120 and 280 K, respectively, using their graph. On the other hand our measurements and those of King and Weller (1961) yield 93.3 and 235.3 $J \cdot mol^{-1} \cdot K^{-1}$ at 120 and 280 K. With respect to this 30% difference
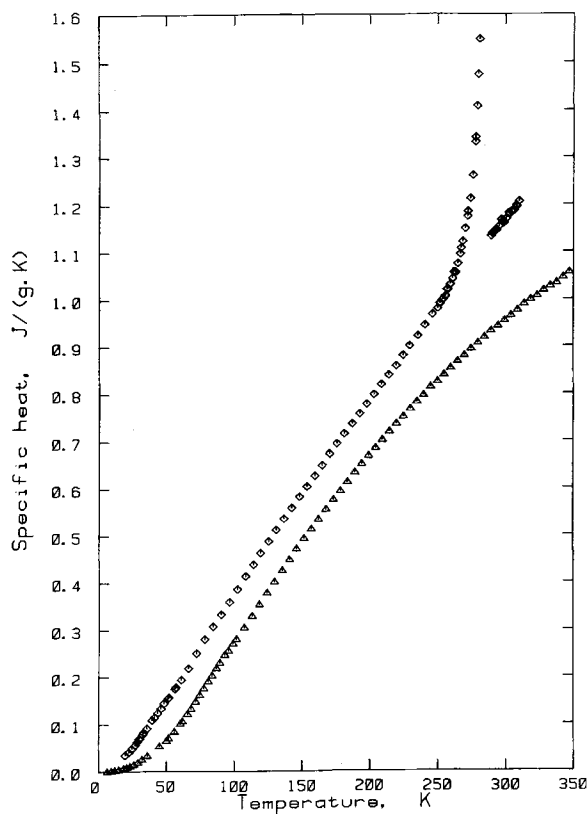
Figure 2. Specific heats of kaolinite (triangles) and kaolinite: DMSO intercalate (diamonds) measured by adiabatic calorimetry.

Table 2. Smoothed values of the standard molar thermodynamic properties of kaolinite, $Al_2Si_2O_5(OH)_4$. Formula weight 258.162 g·mol^{-1}.

Temp., T Kelvin	Heat capacity, C_P°	Entropy, $S_T^\circ - S_O^\circ$	Enthalpy function, $(H_T^\circ - H_O^\circ)/T$ J/(mol·K)	Gibbs energy function, $-(G_T^\circ - H_O^\circ)/T$
5	0.033	0.011	0.008	0.003
10	0.264	0.088	0.066	0.022
15	0.892	0.297	0.223	0.074
20	1.895	0.700	0.523	0.177
25	3.238	1.255	0.921	0.334
30	5.257	2.013	1.465	0.548
35	7.887	3.016	2.189	0.826
40	10.76	4.255	3.080	1.175
45	13.72	5.692	4.097	1.596
50	16.88	7.297	5.213	2.084
60	25.36	11.08	7.822	3.256
70	36.17	15.78	11.08	4.698
80	48.08	21.38	14.95	6.425
90	59.90	27.73	19.30	8.433
100	71.19	34.63	23.93	10.70
110	82.24	41.93	28.72	13.21
120	93.33	49.56	33.65	15.92
130	104.5	57.47	38.66	18.81
140	115.4	65.62	43.76	21.86
150	126.1	73.95	48.89	25.05
160	136.4	82.41	54.04	28.37
170	146.3	90.98	59.18	31.80
180	155.9	99.62	64.29	35.33
190	165.2	108.3	69.35	38.94
200	174.1	117.0	74.37	42.63
210	182.7	125.7	79.32	46.38
220	191.0	134.4	84.21	50.18
230	199.1	143.1	89.03	54.03
240	206.9	151.7	93.78	57.92
250	214.4	160.3	98.46	61.84
260	221.6	168.9	103.1	65.79
270	228.6	177.3	107.6	69.77
280	235.3	185.8	112.0	73.76
290	241.7	194.2	116.4	77.77
300	247.9	202.5	120.7	81.79
310	253.7	210.7	124.9	85.81
320	259.3	218.8	129.0	89.84
330	264.6	226.9	133.0	93.87
340	269.8	234.9	137.0	97.90
350	274.8	242.8	140.8	101.9
360	279.9	250.6	144.6	105.9
370	284.9	258.3	148.3	110.0
380	290.0	266.0	152.0	114.0
273.15	230.8	180.0	109.0	71.02
298.15	246.8	200.9	119.9	81.04

between our results and those of Lipsicas *et al.* (1986) for the heat capacity of kaolinite, we make the following observations:

Three independent sets of measurements [present study, King and Weller (1961), and Hemingway *et al.* (1978)], using three different types of calorimeter and kaolinite samples from three different localities give values for C_p in the region of overlapping measurements that agree within 3%, whereas the values of Lipsicas *et al.* (1986) are systematically about 30% *smaller.*

Secondly, the C_p values for DMSO measured by Lipsicas *et al.* (1986) and shown in their Figure 6 are *greater* than the precise adiabatic calorimetric measurements for DMSO of Clever and Westrum (1970) by 23% at 240 K, by 52% at 260 K and by approximately 63% at 270 K!

Furthermore, the heat capacity of benzoic acid, which was used by Lipsicas *et al.* (1986) to calibrate their calorimeter, has also been measured in our laboratory on two different occasions. Robie and Hemingway (1972) and Hemingway *et al.* (1977) produced results, above 40 K, that agree with those of Ginnings and Furukawa (1953) to ±0.1%. Lipsicas *et al.* (1986) used the C_p values for benzoic acid of Ginnings and Furukawa (1953) for their calibration. Therefore, it seems

likely that there may be a procedural error in the data reduction scheme used by Lipsicas *et al.* (1986).

Kaolinite:DMSO intercalate

Our specific heat measurements on the DMSO-intercalated sample are listed in Table 3. The sample was measured through the "melting" or transition region twice. The initial measurements, series 1 and 2 of Table 3, were made in 5 K steps, up to 308 K. The calorimeter was then cooled to 249 K and a new set of measurements was made using temperature increments of 1 to

Table 3. Experimental specific heats of a kaolinite:DMSO intercalate of approximate composition $Al_2Si_2O_5(OH)_4 \cdot 0.94$ DMSO.

Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$	Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$	Temp., K	Specific heat, $J \cdot g^{-1} \cdot K^{-1}$
Series 1		Series 1		Series 3	
51.98	0.1564	272.41	1.1846	288.27	1.8250
56.44	0.1747	277.61	1.3418	289.46	1.1332
61.01	0.1946	282.52	1.7692	290.38	1.1384
66.08	0.2188	287.26	2.2434	291.07	1.1402
72.14	0.2501			291.90	1.1428
78.15	0.2806	Series 2		293.30	1.1451
84.20	0.3081	292.39	1.1449	295.15	1.1528
90.26	0.3334	297.92	1.1632	297.00	1.1674
96.28	0.3593	303.00	1.1783	298.86	1.1602
102.24	0.3867	308.05	1.1975	300.72	1.1687
108.14	0.4142			302.57	1.1810
113.98	0.4388	Series 3		304.42	1.1843
119.77	0.4633	249.72	0.9801	306.27	1.1869
125.52	0.4882	251.66	0.9907	308.12	1.1942
131.23	0.5128	253.47	0.9995	309.96	1.2063
136.91	0.5364	255.30	1.0072		
142.56	0.5594	257.18	1.0212	Series 4	
148.17	0.5830	259.06	1.0314	20.14	0.0347
153.76	0.6058	260.94	1.0439	22.80	0.0409
159.32	0.6281	262.81	1.0561	24.79	0.0478
164.85	0.6506	264.68	1.0749	27.24	0.0562
170.36	0.6730	266.54	1.0954	30.28	0.0687
175.85	0.6944	268.40	1.1211	33.60	0.0822
181.33	0.7152	270.26	1.1488	37.35	0.0986*
186.78	0.7363	272.12	1.1741	41.54	0.1150
192.21	0.7576	273.97	1.2119	46.24	0.1337
197.62	0.7777	275.81	1.2603	51.48	0.1544
203.02	0.7978	277.64	1.3319	57.31	0.1784
208.40	0.8190	279.16	1.4082		
213.77	0.8393	280.22	1.4747	Series 5	
219.12	0.8594	281.14	1.5487	28.67	0.0634
224.45	0.8813	282.04	1.6387	30.68	0.0690
229.18	0.9016	282.94	1.7548	33.09	0.0792
235.12	0.9228	283.82	1.8750	35.92	0.0909
240.47	0.9449	284.70	2.0368	39.72	0.1085
245.81	0.9678	285.56	2.3038	43.97	0.1248
251.15	0.9922	286.40	2.7147	48.48	0.1439
256.48	1.0211	287.25	2.9901		
261.80	1.0570				
267.11	1.0170				

* Adiabatic shield not in control.

2 K in order to refine the shape of the curve in the region of anomalous heat capacities. The two sets of data are in excellent agreement, ±0.2%, and show no sign of hysteresis.

The shape of the specific heat curve for the kaolinite:DMSO intercalate in Figure 3 is very similar to that obtained for pure DMSO by Clever and Westrum (1970). Two differences stand out: (1) the "melting point" of DMSO in the intercalate 288.0 ± 0.2 K is significantly lower than that of the pure DMSO, 291.6 K, and (2) the heat capacity of pure DMSO liquid is roughly 25% greater than that of the solid (extrapolated into the liquid region), yet the heat capacity of the DMSO in the intercalate (in the liquid region) is very nearly the same as that of the solid DMSO in the in-

tercalate. We interpret this behavior to imply that above the melting point the intercalated DMSO retains some of the order of the solid. That is, the intercalated "liquid" has fewer degrees of freedom than the pure DMSO liquid, and thus a smaller heat capacity. This is what one expects from the structural models proposed by Johnston et al. (1984) and Thompson and Cuff (1985). The DMSO molecules are constrained within the kaolinite layers by hydrogen bonding between the sulfonyl group oxygen and the OH of the inner surface hydroxyls (gibbsite layer) of the kaolinite.

Over the temperature range 80 to 240 K the specific heat of the intercalate behaves as an additive function of the weight fraction of the two components (kaolinite and solid DMSO) to within 5%. Thus if c_K is the specific
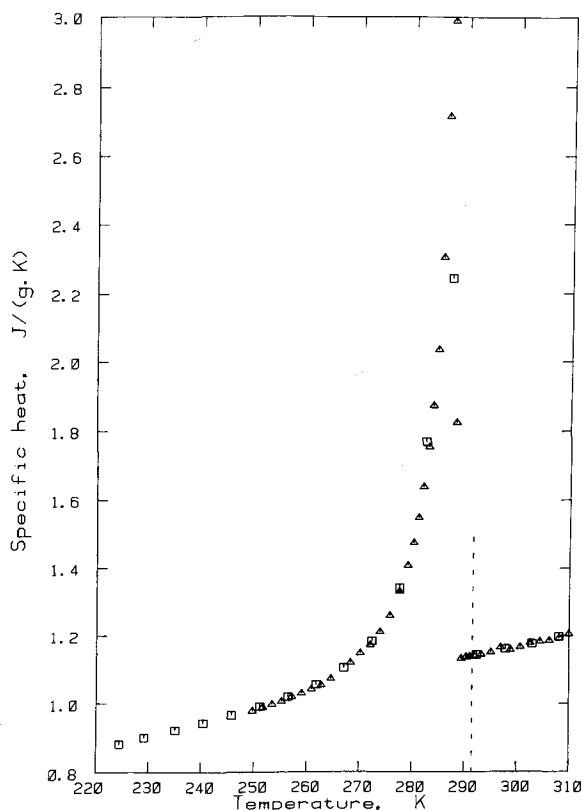
Figure 3. Specific heats of the kaolinite:DMSO intercalate in the region of the melting point of pure DMSO. Open squares are data of series 1 and 2 in Table 3 and were made with temperature increases of approximately 5 K. Open triangles are data from series 3 and were made using temperature increases of 1 to 2 K. Vertical dashed line is the melting point of pure DMSO, 291.6 K.

heat of kaolinite, c_D the specific heat of DMSO, and c_I the specific heat of intercalate, all in $J \cdot g^{-1} \cdot K^{-1}$, and x the weight fraction of kaolinite, 0.78, and $1 - x$ the weight fraction of DMSO, then

$$c_I \cong [x(c_K) + (1 - x)(c_D)].$$

If one assumes that this additive relation holds above the 288 K "melting point" of DMSO in the intercalate, one can calculate a heat capacity of "liquid" DMSO in the intercalate. The result is that pure, liquid DMSO has a heat capacity at 300 K, which is greater than DMSO in the intercalate by about $0.067 \ J \cdot g^{-1} \cdot K^{-1}$ or $5.2 \ J \cdot mol^{-1} \cdot K^{-1}$. This is of the order of 0.6 R (R = $8.3145 \ J \cdot mol^{-1} \cdot K^{-1}$). The "melting transition" in the DMSO-intercalated kaolinite was not observed by Lipsicas et al. (1986), in part because their measurements terminated at 280 K, and 8 K below the transition temperature.

We have considered the possibility that the anomalous heat capacities between 260 and 288 K arise from

the presence in our sample of interstitial, nonintercalated DMSO. The excess enthalpy between 260 and 288 K was obtained by numerical integration of the observed C_p°-estimated normal C_p. This we did by extrapolating the measured heat capacities above 290 K linearly backward to 260 K:

$$\text{excess enthalpy} = \int_{260}^{288} [C_p^\circ(\text{obs.}) - C_p^\circ(\text{normal})] \ dT.$$

The value obtained was $11.3 \ J \cdot g^{-1}$. The enthalpy of fusion of pure DMSO is $183.9 \ J \cdot g^{-1}$ (Clever and Westrum, 1970). In a 1 g sample of $Al_2Si_2O_5(OH)_4 \cdot 0.94$ DMSO, there is 0.22 g of DMSO. Therefore, if all the DMSO were present as a second, nonintercalated phase, the enthalpy effect in heating from 260 to 288 K would be $(0.22 \ g)(183.9 \ J \cdot g^{-1}) = 40.4 \ J$. Thus the observed 11.3 J excess enthalpy could arise by having 28% of the DMSO in our sample be intergranular and nonintercalated. This is at variance with the X-ray data that indicate that the sample is at least 95% intercalated. Therefore, one must conclude that the "melting" transition in the intercalate is real and does not arise from the presence of free DMSO.

REFERENCES

Clever, H. L. and Westrum, E. F., Jr. (1970) Dimethyl sulfoxide and dimethyl sulfone. Heat capacities, enthalpies of fusion, and thermodynamic properties: *J. Phys. Chem.* **74**, 1309–1317.

Dugdale, J. S., Morrison, J. A., and Patterson, D. (1954) The effect of particle size on the heat capacity of titanium dioxide: *Proc. Roy. Soc. London Ser. A*, **A224**, 228–235.

Ginnings, D. C. and Furukawa, G. T. (1953) Heat capacity standards for the range 14–1200° K: *J. Amer. Chem. Soc.* **75**, 522–527.

Hemingway, B. S., Robie, R. A., Fisher, J. R., and Wilson, W. H. (1977) The heat capacities of gibbsite Al(OH)₃, between 13 and 480 K and magnesite, MgCO₃, between 13 and 380 K and their standard entropies at 298.15 K, and the heat capacities of calorimetry conference benzoic acid between 12 and 316 K: *J. Research, U.S. Geol. Surv.* **6**, 797–806.

Hemingway, B. S., Robie, R. A., and Kittrick, J. A. (1978) Revised values for the Gibbs free energy of formation of [Al(OH)₄⁻ₐq], diaspore, boehmite and bayerite at 298.15 K and 1 bar, the thermodynamic properties of kaolinite to 800 K and 1 bar, and the heats of solution of several gibbsite samples: *Geochim. Cosmochim. Acta* **42**, 1533–1543.

Hemingway, B. S., Robie, R. A., and Apps, J. A. (1991) Revised values for the thermodynamic properties of boehmite, AlO(OH), and comments on the relative stabilities of the aluminum hydroxide and the oxyhydroxide phases: *Amer. Mineral.* **76**, 445–457.

Hemingway, B. S. and Sposito, G. (1989) Inorganic aluminum bearing solid phases: in *The Environmental Chemistry of Aluminum*, G. Sposito, ed., CRC Press, Boca Raton, Florida, 55–86.

Johnston, C. T., Sposito, G., Bocian, D. F., and Birge, R. R. (1984) Vibrational spectroscopic study of the interlamellar kaolinite-dimethyl sulfoxide complex: *J. Phys. Chem.* **88**, 5959–5964.

King, E. G. and Weller, W. W. (1961) Low-temperature

heat capacities and entropies at 298.15°K of diaspore, kaolinite, dickite and halloysite: *U.S. Bur. Mines Rept. Invest.* **5810,** 6 p.

Lipsicas, M., Raythatha, R., Giese, R. F., and Constanzo, P. M. (1986) Molecular motions, surface interactions, and stacking disorder in kaolinite intercalates: *Clays & Clay Minerals* **34,** 635–644.

Nagelschmidt, G., Donnelly, H. F., and Morcom, A. J. (1949) On the occurrence of anatase in sedimentary kaolin: *Mineral. Mag.* **28,** 492–495.

Robie, R. A. (1987) Calorimetry: in *Hydrothermal Experimental Techniques,* G. C. Ulmer and H. L. Barnes, eds., Wiley-Interscience, New York, 389–422.

Robie, R. A. and Hemingway, B. S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements: *U.S. Geol. Surv. Prof. Pap.* **755,** 32 p.

Robie, R. A. Hemingway, B. S., and Wilson, W. H. (1976) The heat capacities of calorimetry conference copper, muscovite $KAl_2[AlSi_3]O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, and illite $KAl_4[Si_7Al)O_{20}(OH)_4$ between 15 and 375 K and their standard entropies at 298.15°K: *J. Research, U.S. Geol. Surv.* **4,** 631–644.

Shomate, C. H. (1947) Heat capacities at low temperatures of titanium dioxide (rutile and anatase): *J. Am. Chem. Soc.* **69,** 218–219.

Thomas, J. M. (1982) Sheet silicate intercalates, new agents for unusual chemical conversions: in *Intercalation Chemistry,* M. S. Whittingham and A. J. Jacobson, eds., Academic Press, New York, 55–99.

Thompson, J. G. and Cuff, C. (1985) Crystal structure of kaolinite: dimethyl sulfoxide intercalate: *Clays & Clay Minerals* **33,** 490–500.

van Olphen, H. and Fripiat, J. J. eds. (1979) *Data Handbook for Clays and Other Non-Metallic Materials:* Pergamon Press, Oxford, 346 pp.