

SPECIFIC HEATS OF CLAY MINERALS: SODIUM AND CALCIUM KAOLINITES, SODIUM AND CALCIUM MONTMORILLONITES, ILLITE, AND ATTAPULGITE

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ABSTRACT

We have used a differential scanning calorimeter for the measurement of specific heats of clay minerals (sodium and calcium kaolinites, sodium and calcium montmorillonites, illite, and attapulgite) from 300 to 700 K. Results are tabulated at intervals of 20 K and are also summarized by various equations of the type $C_p = f(T)$ with empirical coefficients.

INTRODUCTION

We have recently become interested in the heat capacities or specific heats of clays in connection with the thermal properties of the minerals in various oil sand deposits [1]. Unfortunately, there are very few heat capacities or specific heats available for clay minerals. For example, three generally useful books about clays and other mineral colloids [2–4] contain no information about such specific heats or heat capacities. One section in ref. [5] is devoted to thermal analysis, DTA, TG, DTG, but contains no information about the thermal properties of particular interest to us. Some industrial literature [6,7] provides useful information about applications of differential thermal analysis and thermogravimetry to clay minerals, but presents no information about heat capacities or specific heats. The excellent summary of thermodynamic properties of many minerals by Robie et al. [8] contains very little information about clays.

Because of the general shortage of information about heat capacities or specific heats of clays as indicated above, we have undertaken the present investigation leading to specific heats of six clays from 300 to 700 K.

Many researchers interested in reasonably accurate thermodynamic data have regarded differential scanning calorimetry as an unsatisfactory method,

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largely on the basis of inaccurate data that were published a decade and more ago. More recently, as a result of improvements in the instruments and greater care in their operation, it has been demonstrated that differential scanning calorimetry can yield thermodynamically accurate results as summarized in several papers [9–16]. We have therefore adopted this method for most of our investigations of specific heats of oil sands and related substances [1,17].

EXPERIMENTAL

Specific heat measurements have been made with a Perkin-Elmer DSC-2 differential scanning calorimeter with output recorded on a Perkin-Elmer single channel multi-range thermal analysis recorder. The calorimeter was operated as follows for most experiments: heating rate $10^{\circ}\text{C min}^{-1}$, range selection 2 mcal sec^{-1} , and recorder sensitivity 10 mV for full scale deflection. The method we have used, similar to the scanning method described by Mraw and Naas [11], involved comparison measurements of empty pan vs. Calorimetry Conference synthetic sapphire and empty pan vs. sample of interest, with heat capacity data for sapphire taken from Ginnings and Furukawa [18]. Dry nitrogen of 99.9% purity was used as purge gas. Most sample sizes were about 10 mg.

Well-characterized clay minerals were obtained from Source Clay Minerals Repository, Department of Geology, University of Missouri, Columbia, Missouri, U.S.A. Kaolinite CMS-K6a-1 is a well-crystallized mineral from Washington County, Georgia. Preparation of Na-kaolinite and Ca-kaolinite from this material followed a procedure previously used in this laboratory [19], based on a procedure described earlier by Ferris and Jepson [20]. Na-montmorillonite CMS-SWy-1 came from Crook County, Wyoming, and Ca-montmorillonite CMS-Tx-1 came from Texas. Illite CMS-IMt-1 came from Silver Hill, Montana, and attapulgite CMS-PF-1 came from a deposit in Florida. Considerable information about these clays has been reported [5].

All clay samples were dried in an oven at 120°C for at least one week, and then stored in desiccators until measurements were begun.

Because our well-dried clay samples had a considerable tendency to absorb water from the atmosphere in the interval between being removed from a desiccator and being heated in the DSC, we used several sequences involving weighing, heating in the calorimeter, calorimetric measurements, re-weighing, etc. Most such sequences of measurements were carried out over 50° intervals. In addition to yielding the specific heats that were the principal aim of this investigation, these measurements also provided weight loss data of the kind often obtained in traditional TG.

Calorimetric uncertainties in the specific heats that we have determined by the procedure summarized above amount to about 1%.

RESULTS

Total weight losses from clays that had been dried at 120°C, exposed briefly to room temperature air while being transferred to desiccators, and further exposed to room temperature air while being weighed and transferred to the calorimeter have been determined at various temperature intervals (mostly 50°) over the range 300–700 K. Total weight losses amounted to no more than 1% for Na-kaolinite, Ca-kaolinite, Na-montmorillonite and illite. Total weight loss over this same temperature range was 3% for Ca-montmorillonite and more than 8% for attapulgite. All of these results are summarized in Fig. 1.

Most of our calorimetric measurements led to specific heats, calculated on the basis of dry weight of clay, at 20° intervals over the temperature range 300–700 K. At least three runs were made on different samples of each clay. In addition, some duplicate runs were made on the same sample of each

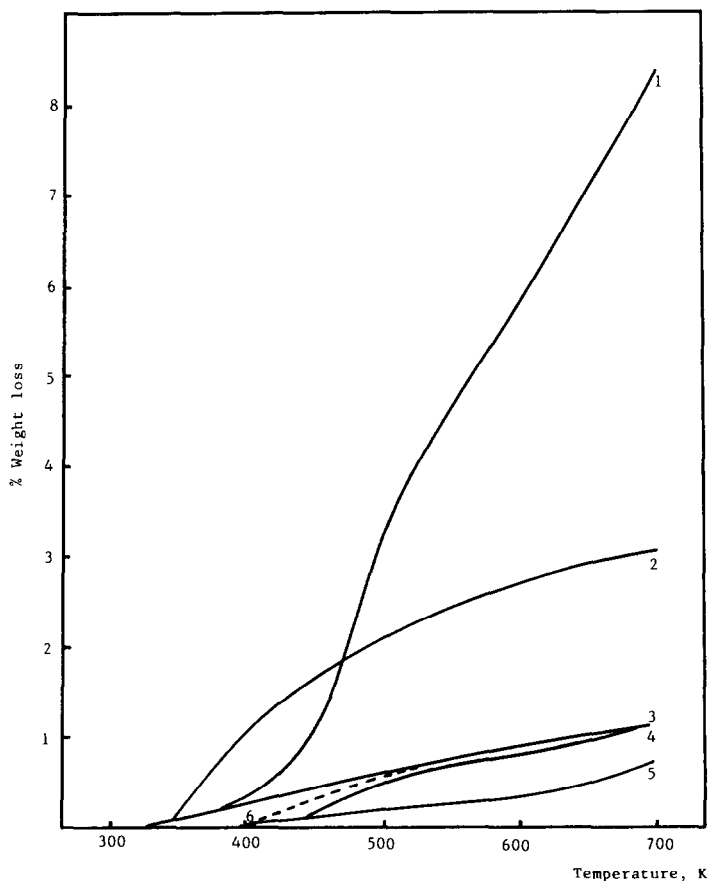


Fig. 1. Weight loss for the clay minerals vs. temperature. 1, Attapulgite; 2, Ca-montmorillonite; 3, Ca-kaolinite; 4, illite; 5, Na-kaolinite; 6, Na-montmorillonite (broken line).

TABLE I

Specific heats of clays^a

<i>T</i> (K)	<i>C_p</i> (J K ⁻¹ g ⁻¹)					
	I	II	III	IV	V	VI
300	0.962	0.931	0.811	0.779	0.808	0.742
320	1.004	0.977	0.853	0.824	0.841	0.780
340	1.042	1.020	0.895	0.869	0.880	0.825
360	1.082	1.058	0.929	0.908	0.907	0.864
380	1.125	1.095	0.962	0.945	0.932	0.900
400	1.151	1.131	0.996	0.982	0.955	0.935
420	1.182	1.159	1.017	1.012	0.978	0.960
440	1.205	1.187	1.038	1.040	0.997	0.985
460	1.230	1.209	1.054	1.063	1.014	1.008
480	1.251	1.229	1.071	1.085	1.030	1.022
500	1.270	1.245	1.084	1.105	1.046	1.038
520	1.284	1.262	1.096	1.122	1.060	1.051
540	1.293	1.275	1.105	1.135	1.072	1.063
560	1.301	1.289	1.113	1.144	1.083	1.074
580	1.310	1.299	1.121	1.154	1.092	1.083
600	1.318	1.310	1.130	1.166	1.102	1.089
620	1.326	1.322	1.142	1.177	1.114	1.095
640	1.333	1.331	1.151	1.186	1.124	1.101
660	1.337	1.339	1.157	1.193	1.131	1.106
680	1.339	1.343	1.163	1.199	1.141	1.112
700	1.343	1.347	1.167	1.203	1.150	1.117

^a Roman numerals I–VI represent Na-kaolinite, Ca-kaolinite, Na-montmorillonite, Ca-montmorillonite, illite, and attapulgite, respectively.

clay. All of these measurements led to about one hundred specific heats for each kind of clay. Suitably averaged results of all these measurements are summarized in Table 1.

It has been customary and useful to summarize heat capacities or specific heats of solids by means of various algebraic equations, $C_p = f(T)$, with empirical coefficients.

We have begun with two three-parameter equations

$$C_p = a + bT + cT^{-2} \quad (1)$$

$$C_p = a + bT + cT^2 \quad (2)$$

Equations of the form of eqn. (1) do not give good fits to our measured specific heats of clays and will not be discussed further in this paper.

Equations of the form of eqn. (2) provide reasonably good fits to all of our specific heats in Table 1. Maximum deviations of calculated specific

TABLE 2
Coefficients for eqn. (2)

Clay minerals	a ($\text{J K}^{-1} \text{g}^{-1}$)	$b \times 10^3$ ($\text{J K}^{-2} \text{g}^{-1}$)	$c \times 10^6$ ($\text{J K}^{-3} \text{g}^{-1}$)
Na-kaolinite	0.08854	3.8035	-2.898
Ca-kaolinite	0.08546	3.6576	-2.670
Na-montmorillonite	0.09107	3.1616	-2.349
Ca-montmorillonite	-0.10606	3.8274	-2.819
Illite	0.23219	2.4544	-1.653
Attapulgite	-0.09973	3.6783	-2.803

heats from measured specific heats amount to 2%, which is only slightly larger than the 1% experimental uncertainty. Values of the coefficients a , b and c for all six clays are given in Table 2; specific heats, C_p , are expressed in $\text{J K}^{-1} \text{g}^{-1}$ and temperatures, T , are expressed in kelvins.

Equations of type (2) with the coefficients given in Table 2 are less than ideally satisfactory in terms of accuracy of fit to the experimental specific heats (Table 1) and also in another way. We illustrate this latter deficiency by differentiating eqn. (2) with respect to temperature and setting the derivative equal to zero to obtain

$$T_m = -\frac{b}{2c} \quad (3)$$

as the temperature at which the equation predicts a maximum in specific heat. The best-fit coefficients in Table 2 lead to $T_m = 742 \text{ K}$ for illite and to T_m values between 656 and 685 K for the other clays. These predicted maxima at temperatures below 700 K are unsatisfactory in that the experimental results in Table 1 show no maxima within the range 300–700 K.

The next step in fitting equations to our results has involved equations of the form

$$C_p = a + bT + cT^2 + dT^{-1} + eT^{-2} \quad (4)$$

Multiplication of eqn. (4) by T^2 and rearrangement leads to

$$T^2 C_p = e + dT + aT^2 + bT^3 + cT^4 \quad (5)$$

Equation (5) is handled easily by standard polynomial fitting programs. Coefficients that result from our fitting of equations of type (5) and thence (4) to the experimental results in Table 1 are given in Table 3. All differences between specific heats calculated with equations of type (4) and the coefficients in Table 3 are less than 1% and most such differences are less than 0.2%. We therefore take equations of type (4) with the coefficients in Table 3 as representing *all* of our experimental specific heats without *any* loss of accuracy.

TABLE 3
Coefficients for eqn. (4)

Clay	a (J K ⁻¹ g ⁻¹)	$b \times 10^3$ (J K ⁻² g ⁻¹)	$c \times 10^6$ (J K ⁻³ g ⁻¹)	d (J g ⁻¹)	$e \times 10^{-4}$ (J K g ⁻¹)
Na-kaolinite	6.816	-6.609	2.916	-1856	18.48
Ca-kaolinite	2.804	-1.321	0.450	-581.1	3.78
Na-montmorillonite	2.535	-1.894	1.042	-391.1	0.452
Ca-montmorillonite	5.320	-4.869	2.170	-1431	13.44
Illite	3.055	-2.437	1.312	-663.3	5.20
Attapulgit	6.613	-7.023	3.312	-1783	16.91

Because of the maxima in specific heats predicted by equations of type (2) for five of the six clays we have investigated, equations of this type should not be used for estimating specific heats at temperatures above 700 K. On the other hand, equations of type (4) do not predict unrealistic maxima in the specific heats in the experimental temperature range 300–700 K nor over a considerable range of temperature above 700 K. These equations are therefore of some use for making extrapolations to temperatures slightly higher than 700 K and may be useful to considerably higher temperatures.

We now turn to a few comparisons of our results with those of earlier investigators.

King and Weller [21] have measured heat capacities of kaolinite from 53 to 296 K. At their highest temperature (296 K) their specific heat is 0.9460 J K⁻¹ g⁻¹, which is in good agreement with our results (Table 1) at our lowest temperature (300 K). More recently, Hemingway et al. [22] have reported the results of their measurements of heat capacities of kaolinite from 340 to 600 K. Their specific heats generally differ by about 2% from our values in Table 1.

Oster and Low [23] determined average specific heats over the temperature range 273–303 K for both Na-montmorillonite and Ca-montmorillonite. Their average specific heat of Na-montmorillonite is 1.2% smaller than our value at 300 K, while their average specific heat of Ca-montmorillonite is 0.6% larger than our value at 300 K.

Robie et al. [24] have measured specific heats of illite (and other minerals) from low temperatures up to about 375 K. Their tabulated specific heats for illite are consistently about 3% larger than our values over the same temperature range. This difference, which is larger than the differences cited in the two preceding paragraphs, is near the upper limit of what we can account for on the basis of likely calorimetric uncertainties and differences in samples.

We do not know of any other comparisons to be made involving our specific heats and the results of other workers' measurements on similar substances.

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