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SPECIFIC HEAT CAPACITIES OF MINERALS FROM OIL SANDS AND HEAVY OIL DEPOSITS

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ABSTRACT

We have used a differential scanning calorimeter for measurement of specific heat capacities of mineral matter from the following oil sands and heavy oil deposits: Athabasca, Alberta; Cold Lake, Alberta; Peace River, Alberta; Grosmont, Alberta; Zaire; Asphalt Ridge, Utah; Malagasy; Nigeria. Results have been summarized by means of equations of type $C_p = a + bT + cT^2$ and $C_p = a + bT + cT^{-2}$.

INTRODUCTION

Among the parameters needed for proper design and evaluation of all thermal processes are the specific heat capacities of the various substances to be heated or cooled. It is for this reason that we have been measuring [1,2] specific heat capacities of oil sands, bitumen, heavy oils, and various reservoir minerals. In this paper we report the results of the measurements on a number of different minerals.

EXPERIMENTAL

Specific heat capacity 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 method we have used, similar to the "scanning method" of Mraw and Naas [3], involved

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comparison measurements of empty pan vs. Calorimetry Conference synthetic sapphire and empty pan vs. sample of interest, with specific heat capacity data for sapphire being taken from Ginnings and Furukawa [4] and from Ditmars et al. [5]. Dry nitrogen of 99.9% purity was used as purge gas. Most sample sizes were about 10 mg, but we also made some measurements with larger samples as part of our effort to minimize the consequences of sample non-homogeneity. Sample handling and operating procedures have been described [1,2] in detail.

RESULTS

Our specific heat capacity measurements on several different samples of several different minerals at many different temperatures have led to nearly four thousand "data points" that might be reported for the minerals under consideration here. Because it is generally more useful to have summarizing equations than to have page after page of numbers, we limit our presentation here to such summarizing equations, accompanied by appropriate identifications of substances, temperature ranges and estimates of uncertainties.

In our earlier report [1] on the specific heat capacities of minerals from the Athabasca oil sands deposit, we expressed our results in terms of equations of the form

$$C_p = a^* + b^*t + c^*t^2 \tag{1}$$

in which C_p represents the specific heat capacity, t represents the temperature on the Celsius scale, and the constants (a, b and c) are marked here with an asterisk to indicate that they are to be used with Celsius temperatures. Equations of type (1) have also been used by other authors. Because most other laboratories (U.S. Geological Survey, U.S. Bureau of Mines, etc.) are reporting their heat capacity results in terms of Kelvin temperatures (represented by T), we now want to convert our old equations [1] of the form of (1) to new equations of the form

$$C_p = a + bT + cT^2 \tag{2}$$

To convert equations of type (1) into equations of type (2) we substitute ($T - 273.15$) for t in eqn. (1) and do some algebra to obtain

$$C_p = \left[a^* - 273.15b^* + (273.15)^2c^*\right] + \left[b^* - 2(273.15)c^*\right]T + c^*T^2 \tag{3}$$

Comparison of eqns. (2) and (3) leads to

$$a = a^* - 273.15b^* + (273.15)^2c^* \tag{4}$$

$$b = b^* - 2(273.15)c^* \tag{5}$$

$$c = c^* \tag{6}$$

Equations of types (1) and (2) are generally of limited value for extrapolation to higher temperatures. We illustrate this limitation by differentiating (1) and (2) with respect to temperature and setting the derivatives equal to zero to obtain

$$t_m = \frac{-b^*}{2c^*} \qquad (7)$$

and

$$T_m = \frac{-b}{2c} \qquad (8)$$

in which the subscript m indicates the temperature at which the equations predict a maximum in the heat capacities. Since such maxima are not generally observed, it follows that equations of types (1) and (2) should not be used above t_m or T_m. Further, these equations are expected to be less than ideally accurate at temperatures approaching t_m or T_m.

It is sometimes appropriate to summarize heat capacities by way of equations of forms different from either (1) or (2). The only other three-constant equation that has been widely used is

$$C_p = a + bT + cT^{-2} \qquad (9)$$

in which the constants a, b and c are not the same as in eqn. (2). With typical values of the constants a, b and c in equations of type (9) there is generally no problem with respect to unrealistic calculated maxima in C_p in the temperature range of interest here.

Results of many measurements of specific heat capacities of minerals from various oil sands and heavy oil deposits are summarized in Table 1, making use of constants that are appropriate to eqn. (2). Results of all these measurements are also summarized in Table 2, making use of constants that are appropriate to eqn. (9). All specific heat capacities are expressed in terms $J\ K^{-1}\ g^{-1}$.

We estimate that the purely calorimetric uncertainties in our results are between ±1 and ±2%. This estimate is based on results of duplicate runs with sapphire and on results obtained for other pure substances (such as $CaCO_3$) for which heat capacities are apparently well-known from earlier calorimetric investigations. Additional uncertainties due to variability and non-homogeneity of samples are about ±2%, making the total uncertainties in our results a little less than ±4%. We emphasize that the fitting of equations (2) and (9) introduce no additional uncertainties.

Equations of types (2) and (9) fit the experimental specific heat capacities about equally well over the temperature ranges we have investigated. It therefore follows that choices between equations of types (2) and (9) for use within the experimental temperature ranges can properly be based on convenience or habit. However, if it is desired to use our equations for extrapolations to temperatures above the range of our measurements, equa-

TABLE 1

Specific heat capacities of minerals summarized by way of constants appropriate to eqn. (2)

Substance/source	T range	a ($\mathrm{J\,K^{-1}\,g^{-1}}$)	$b \times 10^3$ ($\mathrm{J\,K^{-2}\,g^{-1}}$)	$c \times 10^6$ ($\mathrm{J\,K^{-3}\,g^{-1}}$)
Athabasca coarse solids, mostly SiO_2 [a]	323–573	0.172	2.625	−2.026
Athabasca coarse solids, mostly SiO_2 [b]	300–700	0.168	2.442	−1.611
Athabasca fine solids, mostly clay [a]	323–573	0.324	1.927	−0.964
Athabasca fine solids, mostly clay [c]	320–680	0.342	1.873	−0.926
Cold Lake, Alberta [d]	300–700	0.128	2.692	−1.890
Peace River, Alberta [e]	320–600	0.032	3.138	−2.392
Grosmont, Alberta [f]	320–600	0.303	2.296	−1.438
Zaire [g]	300–700	0.047	2.894	−1.988
Asphalt Ridge, Utah [g]	300–700	0.170	2.425	−1.506
Malagasy [g]	300–700	0.158	2.630	−1.840
Nigeria [g]	300–700	0.041	3.022	−2.126

[a] Results that were reported in ref. 1 in the form of eqn. (1) have been recalculated as described in the text to conform to eqn. (2).

[b] The constants given here are based on our old results (ref. 1, 323–573 K) and our more recent results (300–700 K). The results from our old and our new measurements agree very well up to nearly 500 K. Above this temperature the new specific heat capacities are larger than the old ones and have been weighted more heavily in obtaining the tabulated constants, which are now recommended.

[c] The constants given here are based on our old results (ref. 1, 323–573 K) and our more recent results (320–680 K), all of which are in good agreement. We recommend these latter constants, primarily because they are applicable over a wider range of temperature than those given previously.

[d] Sample obtained from Esso Resources Canada Ltd., Calgary, Alberta.

[e] Sample obtained from Shell Canada Resources Ltd., Calgary, Alberta.

[f] Sample obtained from Union Oil Company of Canada Ltd., Calgary, Alberta.

[g] Samples obtained from the Alberta Research Council.

TABLE 2

Specific heat capacities of minerals summarized by way of constants appropriate to eqn. (9)

Substance/source	T range	a ($\mathrm{J\,K^{-1}\,g^{-1}}$)	$b \times 10^3$ ($\mathrm{J\,K^{-2}\,g^{-1}}$)	$c \times 10^{-4}$ ($\mathrm{J\,K\,g^{-1}}$)
Athabasca coarse solids, mostly SiO_2	300–700	0.914	0.331	−2.415
Athabasca fine solids, mostly clay	320–680	0.787	0.644	−1.559
Cold Lake, Alberta	300–700	0.986	0.244	−2.774
Peace River, Alberta	320–600	0.997	0.243	−2.961
Grosmont, Alberta	320–600	0.877	0.563	−1.745
Zaire	300–700	0.955	0.313	−2.946
Asphalt Ridge, Utah	300–700	0.825	0.512	−2.017
Malagasy	300–700	1.024	0.205	−2.906
Nigeria	300–700	1.024	0.243	−3.230

tions of type (9) are generally better than equations of type (2), especially for those substances with relatively low values of T_m as calculated with eqn. (8).

DISCUSSION

Our specific heat capacities of mineral matter from oil sands and heavy oil deposits can be compared with heat capacities for certain well-defined materials as follows.

It is known that the mineral matter from the Grosmont deposit is mostly (calcium and magnesium, dolomitic) carbonate. Our specific heat capacities for this mineral matter (Tables 1 and 2) differ by less than 1% (less than a combination of experimental uncertainty and variability in samples) from results summarized by Robie et al. [6] for dolomite of composition $CaMg(CO_3)_2$. We also note that the specific heat capacities for our Grosmont mineral and for pure dolomite are intermediate between those [6] for pure $MgCO_3$ and pure $CaCO_3$.

The fine solids (less than 325 mesh) from the Athabasca oil sands deposit consist mostly of clays (kaolinite, illite and montmorillonite) and some finely divided silica. Our previous measurements [2] have shown that the specific heat capacities of these clays are in the order kaolinite > montmorillonite > illite, and we calculate from the molar heat capacities summarized by Robie et al. [6] that the specific heat capacities of silica are a few percent smaller than for illite at corresponding temperatures. Our specific heat capacities of Athabasca fine solids are intermediate between those of kaolinite and silica, as expected for material that is a mixture of clays and fine silica.

The other minerals (Athabasca coarse solids, Cold Lake, Peace River, Zaire, Asphalt Ridge, Malagasy and Nigeria) are mostly silica. Our specific heat capacities for the mineral matter from Asphalt Ridge and Nigeria are in close agreement (~ 1%) over our entire temperature range with specific heat capacities calculated from the molar heat capacities for SiO_2(quartz) tabulated by Robie et al. [6]. Our specific heat capacities for our other (mostly silica) minerals (Athabasca, Cold Lake, Peace River, Zaire and Malagasy) are also in close agreement (~ 1%) with those for quartz [6] over most of our temperature range, but our specific heat capacities for these latter minerals are all slightly smaller (~ 4%) than the corresponding specific heat capacities of quartz [6] in the higher temperature range (600–700 K).

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