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CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETRY UNITS FOR MINERALOGICAL STUDIES

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ABSTRACT

This paper investigates the use of DSC for mineralogical work and describes DSC calibration using a range of ICTA standards. The instrument parameter K was found to increase by 70% in the temperature range of ambient to 820°C. The increase was essentially linear over most of this range. It was possible to use the determined K values to measure heats of reaction with an accuracy of 4–7% for several common well defined mineralogical specimens.

INTRODUCTION

The technique of differential scanning calorimetry (DSC) is still in its infancy as regards its application to mineral characterisation and analysis. This is partly explained by temperature limitations of earlier DSC units which restricted work to temperature regimes more suitable to polymeric and pharmaceutical studies. With the advent of an extended temperature range however, up to 800–1000°C, DSC can now be seriously considered as a tool for mineralogical analysis. Thermal transformations in mineral species largely occur between 200–1000°C, and most commonly above 400°C. It is necessary, therefore, to establish the usefulness of DSC, particularly at the higher temperature end of the range, for studying mineralogical reactions.

The fundamental equation governing the technique is

$$\Delta H \cdot M = K \cdot A \tag{1}$$

where ΔH is the energy (mJ mg^{-1}) involved for the process under study, M(mg) is the sample mass, K is the ‘instrument parameter’ which has to be determined for each DSC unit, and A is the peak area.

The value of K is determined by using a calibrant material such as indium for which ΔH (fusion) is accurately known. K, however, is temperature dependent and should be determined over a temperature range. The extent

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of this dependence is not altogether clear. Earlier work has claimed [1] that K may be 20% greater at 330°C than at 60°C. Schwenker and Whitwell [2], however, suggest that the variation is only about 4% over the range 156–420°C, and this appears to be supported by O'Neill and Fyans [3]. Nevertheless, Breuer and Eysel [4], who have carried out a thorough study of DSC calibration, report a marked increase in K up to a temperature of about 660°C. It is likely that this variety of results from different workers is partly explained by the different response of commercially available instruments.

The aim of this paper is to describe a convenient method for determining K, measure it over the widest possible temperature range and apply these values to calculating the heats of reaction for several mineral species.

EXPERIMENTAL

Calibrations were performed on a Rigaku Denki Thermoflex 8100 series instrument consisting of TG, DTA and DSC modular units. The DSC unit possessed a range of ± 0.5 to 16 mcal s^{-1} and was operative to a temperature of about 850°C. Runs were recorded using aluminium or platinum pans, with or without corresponding pan lids, as required. Calcined alumina was used as the thermal reference material.

The samples used for calibration comprised a series of low-melting point metals and simple salts including materials designated by ICTA as suitable temperature standards. The enthalpy values associated with the individual melting/inversion processes were obtained from literature sources.

Several mineral species were investigated. The chemical analysis for each is provided in Table 1 as it was felt essential to use minerals of proven purity. Sample masses throughout were in the range 2–40 mg and heating rates 2–10°C min^{-1}. Each weighed sample was heated once only. Chart speed was maintained at either 10 or 20 mm min^{-1}. Peak areas were measured using a Planix 7 Tamaya planimeter.

Calculated heats of reaction for the mineral species were obtained from data stored in the CSIRO–SGTE Thermodata system.

TABLE 1

Chemical analysis of mineral samples investigated

Mineral	Analysis (%)	
Gypsum ($CaSO_4 \cdot 2H_2O$)	Ca (calc.) 23.28	Ca (found) 23.23
Quartz (SiO_2)	Si (calc.) 46.74	Si (found) 46.35
Magnesite ($MgCO_3$) [a]	Mg (calc.) 28.83	Mg (found) 28.49
Pyrolusite (β-MnO_2)	Mn (calc.) 63.19	Mn (found) 62.12

[a] Also contains 0.1% SiO_2, 0.9% $CaCO_3$, trace Fe_2O_3.

RESULTS AND DISCUSSION

Determination of K *values*

It is clear from eqn. (1) that, given ΔH, K can be determined from a known sample mass and peak area. A more precise method involves obtaining the DSC peak for a series of sample masses and plotting the peak area against mass. This procedure yields a straight line for which the slope, N, is the peak area per unit mass, and therefore $K = \Delta H/N$. Examples for several materials are shown in Figs. 1, 2 and 3. Deviations arising from the anomalies of individual sample preparations can be readily detected.

Determinations of K were made at various heating rates and showed essentially no change within the normal heating range of 2–10°C min^{-1}, as seen in Fig. 1. Likewise K appeared independent of the measured peak areas obtained at different chart speeds as shown for $Li_2SO_4 \cdot H_2O$ in Table 2.

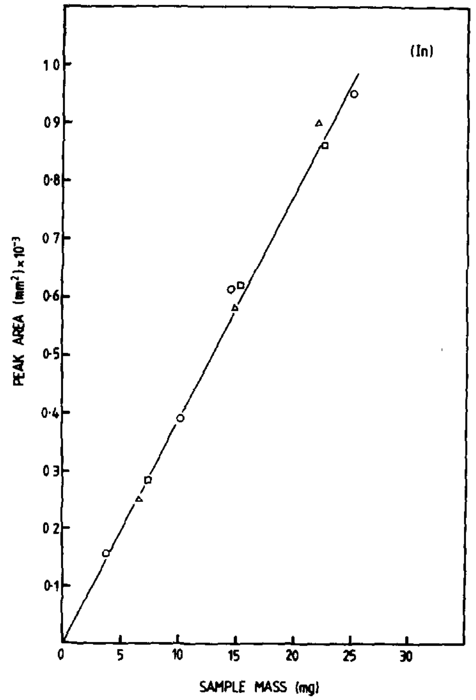

Fig. 1. Plot of peak area (mm^2) versus sample mass (mg) for indium metal. Crimped aluminium cups with lids. Heating rate 10°C min^{-1} (○); heating rate 5°C min^{-1} (△); heating rate 2°C min^{-1} (□).

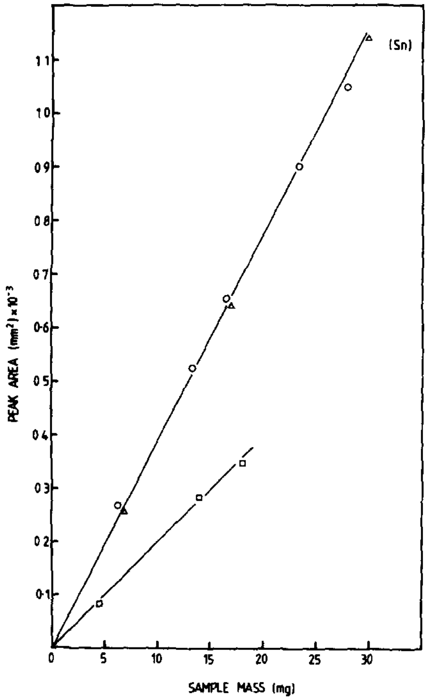

Fig. 2. Plot of peak area (mm^2) versus sample mass (mg) for tin metal. Heating rate 10°C min^{-1}, chart speed 10 mm min^{-1}. Crimped aluminium cups with lids (○); aluminium cups without lids (△); crimped aluminium cups with lids (□), chart speed 20 mm min^{-1}

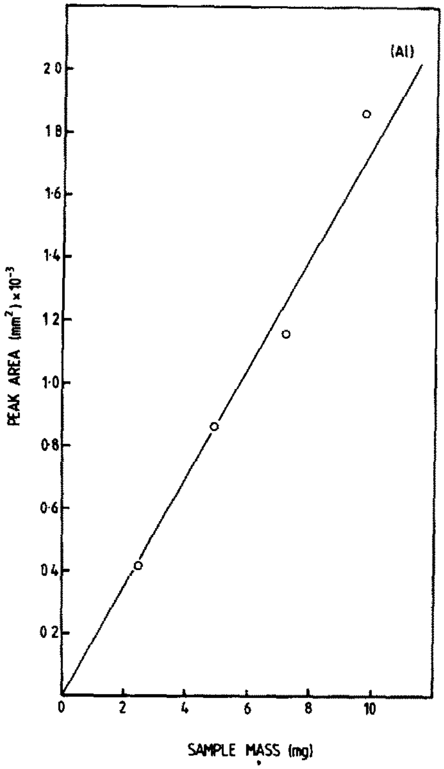

Fig. 3. Plot of peak area (mm^2) versus sample mass (mg) for aluminium metal. Platinum cups with lids, heating rate 10°C min^{-1}.

The precision of measurement is within about 3% and generally represents the best attainable value for determining K reproducibly.

Standard materials were heated in aluminium and platinum cups, with and without corresponding lids. The value of K was essentially unaffected as indicated in Fig. 2. The presence of a lid, however, did improve baseline

TABLE 2

K values for $Li_2SO_4 \cdot H_2O$ determined at various chart speeds (mm min^{-1})

Sample mass (mg)	Chart speed (mm min^{-1})	Peak area (mJ [a])	K
15.40	25	598	1.18
15.38	5	555	1.27
15.62	10	570	1.25
15.71	20	570	1.26
15.31	40	552	1.27
15.64	80	547	1.31
Mean		565 ± 19	1.26 ± 0.04

[a] Area (mm^2) normalised to energy values.

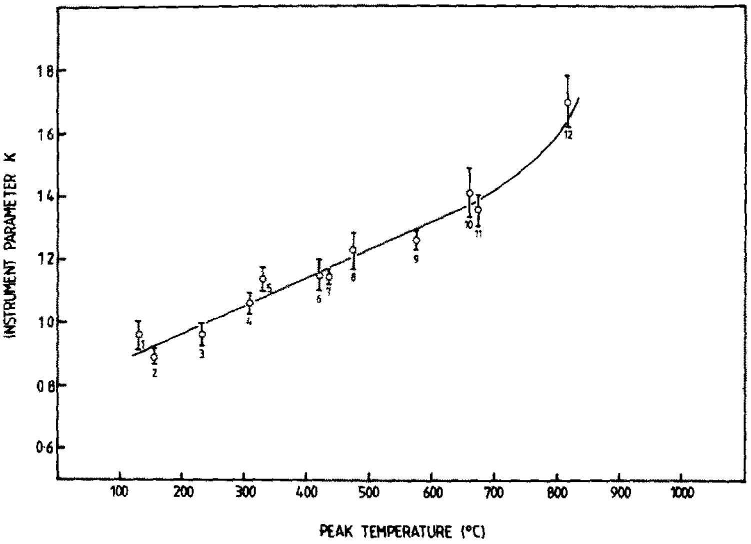

Fig. 4. Plot of instrument parameter *K* as a function of peak temperature (°C) for the following materials. (1) KNO_3; (2) In; (3) Sn; (4) $KClO_4$; (5) Pb; (6) Zn; (7) Ag_2SO_4; (8) CsCl; (9) $Li_2SO_4 \cdot H_2O$; (10) Al; (11) K_2CrO_4; (12) $BaCO_3$.

characteristics since overall thermal conductivity of the system was enhanced and gas convection current effects in contact with the sample were prohibited.

Of the series of materials used to establish *K* across a temperature range (Fig. 4), a number were found to be unsuitable and rejected. Quartz was confirmed as being unsuitable due to baseline problems as already noted by other workers [4,5]. Likewise, K_2SO_4 was rejected. The salt K_2CrO_4 also produced some baseline problems but was generally reliable. Aluminium, which is not a recognised ICTA standard, appears to be a useful material in this temperature regime. The silver salt Ag_2SO_4 yielded reproducible results provided it was shielded from the effects of photodecomposition.

The overall measured precision of *K* fell within the range of 2–7%. Best reproducibility was obtained with $KClO_4$, Pb, Ag_2SO_4 and $Li_2SO_4 \cdot H_2O$ (2–4%), and the worst with CsCl, Al and $BaCO_3$ (6–7%). The remainder of the materials occurred in the range of 4–5%.

From Fig. 4 it is apparent that *K* reveals a marked dependence upon temperature. An increase of almost 80% occurs to the limit of the DSC temperature range. Essentially, the dependence is linear although a deviation from linearity appears to occur at the high temperature end. Unfortunately only one ICTA standard was available in this temperature region. Nevertheless, Fig. 4 confirms the marked dependence, and apparent non-linearity at high temperature, of *K*, as reported by Breuer and Eysel [4].

It was clear that, in studying many mineralogical reactions, the *K* value determined at one temperature cannot be assumed to hold fast for some higher temperature. For reactions (e.g., the decomposition of carbonates, coal oxidation) which occur at elevated temperatures, or possibly over an extended range, K must be determined at the temperature of interest or taken from a plot such as Fig. 4 before the heat of reaction can be calculated with any reliability.

Heats of reaction for mineral species

The validity of using measured K values to calculate heats of reaction was tested on several different mineral species (Table 3). The minerals chosen exhibit common thermal phenomena. Namely dehydration (gypsum), α–β crystallographic inversion (quartz) and thermal decompositions involving the loss of oxygen (pyrolusite) and carbon dioxide (magnesite). The heats of reaction obtained using K values determined at respective peak temperatures were compared with the calculated data.

The results in Table 3 indicate reasonable agreement between observed and calculated values for all species except quartz. The α–β transition for quartz involves a small energy change yielding a peak that cannot be adequately corrected since the beginning and the end of the transition are not well defined. Otherwise the observed energy values agree with the calculated data within 4–7%, being best for gypsum and worst for pyrolusite. Within the limitations of the accuracy of the determined K values, the measured heats of reaction for these minerals are probably as good as can be expected. The reproducibility, however, is such that more accurate comparative assessments of different contents of the same mineral by DSC are likely.

After following the calibration procedure, it appears that high temperature DSC may be applied with confidence using specific instrument K values which increase linearly up to about 700°C. Above this temperature the K values increase disproportionately with temperature. This latter represents an area where more detailed calibration and attention is required to obtain valid results. This is particularly so as these added and comparative effects of individual instruments, at this stage, have not been documented.

TABLE 3

Measured heats of reaction for several mineral species

Mineral	Peak temp. (°C)	No. runs	ΔH_{obs} (kJ mol^{-1})	ΔH_{calc} (kJ mol^{-1})
Gypsum	140–160	8	106 ± 3	102
Quartz	573	6	0.46 ± 0.04	0.396
Magnesite	600	5	115 ± 6	110
Pyrolusite	600	5	36.0 ± 1.4	38.6

The way now appears clear, therefore, for the dependable application of high temperature DSC to minerals and rapid applications in the coal, oil shale, ceramic and mineral processing industries can be expected.

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