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Note

Determination of specific heat by differential scanning calorimetry at low temperature

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The specific heat of calcium oxalate dihydrate can be determined at −60°C using a DuPont DSC cell (900 thermal analyser). Results compare favourably with an estimate obtained using 'Kopp's Law'.

If the thermal capacities of a sample plus holder are compared to that of an empty holder using a DSC cell at high heating rate, the resulting trace will show a displacement which is dependent on the specific heat of the sample[2]. In the experiment a temperature range of −80°C to −20°C was selected as the DSC trace of calcium oxalate dihydrate ($CaC_2O_4 \cdot 2H_2O$) showed no energy changes in this region. The calculation of specific heat (and ΔH) both require the value of a 'calibration coefficient' for the specific instrument used, therefore this is also described.

The calibration coefficient E is given by the equation:

$$E = \frac{\Delta H M a}{A \Delta T_s T_s} \qquad (1)$$

where M = sample mass (mg)
a = heating rate (°C min^{-1})
A = peak area (sq. in.)
ΔT_s = Y-axis sensitivity °C in.$^{-1}$
T_S = X-axis sensitivity °C in.$^{-1}$

The specific heat $(C_p)_T$ is given by:

$$(C_p)_T = \frac{(\Delta T_x + \Delta T_{blank}) E_T}{Ma}$$

where ΔT_x = absolute differential temperature for sample (°C)
ΔT_{blank} = absolute differential temperature for blank (°C)
E_T = calibration coefficient (at temperature T)
M = sample mass (mg)
a = heating rate (°C min^{-1})

Calibration coefficient, E_T

DSC analysis of the metals mercury, indium, tin, lead were carried out and the results plotted on a graph of calibration coefficient against specific heat (Fig. 1). The peak areas were determined by weighing and then substitued in eqn (1). Calibration coefficient at -60°C was determined from the graph, i.e., $E_{-60} = 157$ mcal °C^{-1} min^{-1}.

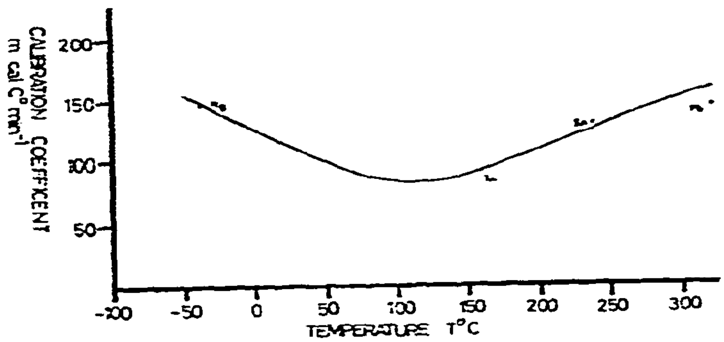

Fig. 1. Determination of calibration coefficient.

Specific heat, $(C_p)_T$

The apparatus was allowed to equilibrate at -80°C, with the heater control on the 900 consul set at 'Hold'[2]. When the pen became steady, the controls were reset to 'Heat' at a rate of 20°C min^{-1} and the temperature allowed to rise to -20°C before again equilibrating in the 'Hold' position. The experiment was carried out under 'blank' condition, i.e., both sample pans empty, and repeated with the sample in the pan on the rear cell platform. The initial and final temperature of both the 'blank' and sample runs should be identical. The results are shown in Fig. 2. ΔT values can be measured.

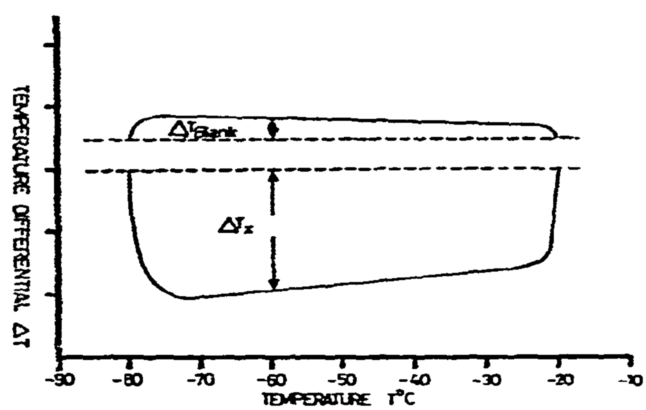

Fig. 2. Determination of specific heat of calcium oxalate dihydrate at 213 K (-60°C).

SPECIMEN RESULTS AND CALCULATION OF SPECIFIC HEAT $(C_p)_T$ FOR $Ca(COO)_2 \cdot 2H_2O$

(i) We have $(C_p)_{-60} = \frac{(\Delta T_x + \Delta T_{blank}) \cdot E_{-60}}{Ma}$

where $\Delta T_x = 0.175°C$
$\Delta T_{blank} = 0.045°C$
$E_{-60} = 157$ mcal °C^{-1} min^{-1}
$M = 9.1$ mg
$a = 20°C$ min^{-1}

$$(C_p)_{-60} = \frac{(0.175 + 0.045) \times 157}{9.1 \times 20}$$

specific heat at = 0.190 mcal mg^{-1} °C^{-1}

(ii) Kopp's law states, that the specific heat of a compound is approximately equal to that of the elements, and that an approximate value can be calculated by assigning the following atomic heat capacities to the elements[1]:

C = 1.8, H = 2.3, O = 4.0, Ca = 6.2

For 1 mole of calcium oxalate dihydrate, $CaC_2O_4 \cdot 2H_2O$ we obtain:

$C_p = 6.2 + (2 \times 1.8) + (4 \times 4.0) + (4 \times 2.3) + (2 \times 4.0)$

g cal g^{-1} °C^{-1} = 43.0 g cal g^{-1} °C^{-1}

Now molecular weight = 164.12

$$\text{Specific heat } C_p = \frac{43.0}{164.12} \text{ cal g}^{-1}\ °\text{C}^{-1}$$

$$= 0.262 \text{ mcal mg}^{-1}\ °\text{C}^{-1}$$

It can be seen that, once calibrated, the DuPont DSC provides an easy rapid method for determining the specific heat of a material over a wide temperature range, and gave a result at −60°C that compared with the approximate value obtained by Kopp's rule.

REFERENCES

1 For example; G. S. Parks and K. K. Kelly, *J. Phys. Chem.*, 30 (1926) 1175.
2 Du Pont Instruments, *Instrumentation Manual*, 900 Thermal Analyser and Modules, Section 9, 1968.