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ASSESSMENT OF THE QUANTITATIVE PERFORMANCE OF THE STANTON REDCROFT SIMULTANEOUS THERMAL ANALYSER (MODEL 781)

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ABSTRACT

The Stanton Redcroft Simultaneous Thermal Analyser (Model 781) has been calibrated for quantitative measurements using conventional chemical standards. The results have been expressed as third-order polynomials in temperature where different expressions hold for the use of metal and quartz crucibles. With sapphire the results indicate a calibration dependent on the surface area of contact between the sample and crucible.

INTRODUCTION

The Stanton Redcroft Simultaneous Thermal Analyser allows simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) on the same sample. The advantages of the simultaneous approach are widely recognised. However, in common with other thermal analysers, the DTA facility is usually regarded as qualitative, not allowing the precise measurement of enthalpy (or energy) changes. The design of the head assembly is of the Boersma-type with the thermocouples outside the sample. The distinction between Boersma DTA and heat flux differential scanning calorimetry (DSC) is rather fine. For practical purposes it lies in the instrument signal: for DTA it is proportional to the differential temperature between the sample and reference $T_s - T_r$, whereas for DSC the instrument signal is proportional to the differential thermal power $d\Delta q/dt$. For DSC the design of the equipment must ensure a reproducible thermocouple signal which may then be corrected electronically to give a constant calorimetric sensitivity over the operating temperature range.

In the present work, the operation of the DTA facility of the Stanton Redcroft model STA 781 has been examined. The theory of DTA requires a description of the temporal and spatial distribution of heat in the sample and its environment. Inevitably, assumptions are made in constructing the mathematical model: often the effect of these assumptions is minimized in

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the design of the equipment. Our approach has been an empirical one in which we have measured the area of peaks recorded for processes of known enthalpy. We have chosen to examine our data using the model discussed by Gray [1] which has the advantage of conceptual and mathematical simplicity.

EXPERIMENTAL

The design of the Stanton Redcroft Simultaneous Thermal Analyser has been described by Charsley et al. [2]. The head assembly consists of plate-type thermocouples made of platinum–13% rhodium/platinum. It is suspended in a water-cooled furnace from an electrical microbalance. The maximum operating temperature of model 781 is 1773 K. The furnace temperature was controlled by the Stanton Redcroft Programmer (model UTP) using the signal from a platinum–13% rhodium/platinum thermocouple in the windings of the furnace. The DTA signal was amplified using a low noise DC amplifier (Cropico). The results were recorded either on a chart recorder or using a microcomputer.

The apparatus was calibrated using the substances listed in Table 1. Also given in the table are the values assumed for the enthalpy changes of the transitions. The substances were fine powders except gallium which was in the form of a foil. They were studied using both quartz and metal crucibles: aluminium for temperatures less than 900 K and inconel for higher temperatures. The aluminium crucibles were cleaned in dichloromethane. All the crucibles were heated over the relevant temperature range before use. The reference substance was alumina. Good thermal contact between the sample

TABLE 1

Calibration materials and enthalpy changes

Material	Enthalpy change (J g^{-1})
Gallium (Koch Light, 99.9999% pure)	80.1 (fus. 303 K)
Indium (Koch Light, 99.999% pure)	28.4 (fus. 430 K)
Tin (Koch Light, 99.999% pure)	60.0 (fus. 505 K)
Lead (Koch Light, 99.999% pure)	23.0 (fus. 601 K)
Zinc (Koch Light, 99.999% pure)	112 (fus. 693 K)
Aluminium (Koch Light, 99.95% pure)	400 (fus. 934 K)
Gold (Johnson Matthey, 99.99% pure)	63 (fus. 1338 K)
Benzoic acid (BDH 99.999% pure)	148 (fus. 395 K)
Lithium sulphate (BDH, > 99.0% pure)	259 (trans. 849 K)
Potassium chromate (ICTA standard)	35 (trans. 942 K)
Barium carbonate (BDH, 99.5% pure)	95 (trans. 1083 K)
Potassium sulphate (BDH, 99.5% pure)	210 (fus. 1341 K)

and crucible was obtained by using a uniform distribution of material in the crucible and pressing the sample over the base of the crucible. With aluminium crucibles the sample was pressed between two crucibles. Care was taken to ensure that the bases of the crucibles were flat and the crucibles were a snug fit between the locating ears on the plate thermocouples. Each sample was used for three experiments only. The peak from the first experiment was ignored if it was of a poor shape. Samples were weighed to 1 μg and counterpoised using the electrical microbalance to ensure that the thermocouple assembly was in the same vertical position in the furnace from one experiment to the next. The measurements were carried out with the sample in flowing nitrogen (40 cm^3 min^{-1}) at atmospheric pressure. The heating rate was 10 K min^{-1}.

RESULTS AND DISCUSSION

The results of the calibration experiments are shown in Fig. 1. The calibration factor ϵ has been expressed ϵ $(WV^{-1}) = A\Delta H$ (J)/Peak area (Vs) where A is the signal amplification. We have analysed the peaks from both fusion and solid state transitions and compared the use of quartz and metal crucibles. We have been able to compare the performance of two

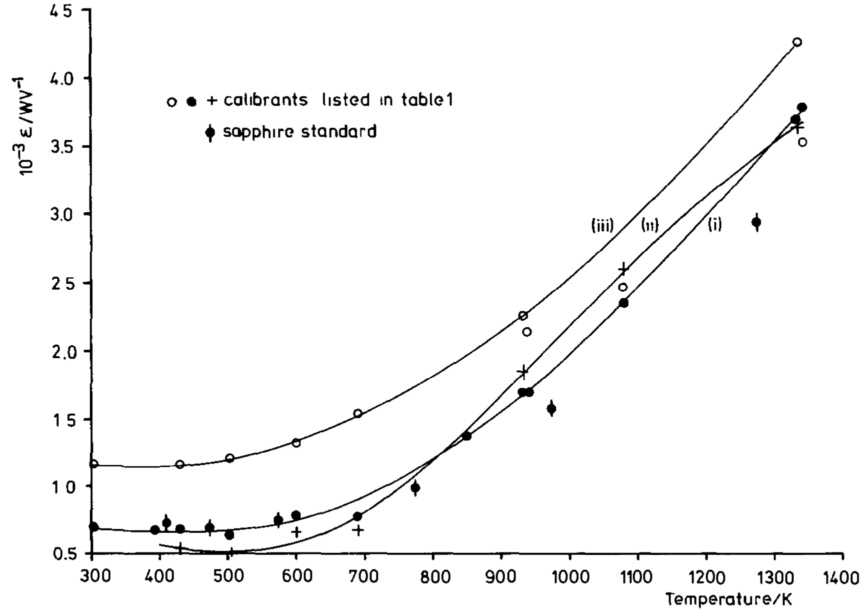

Fig. 1. Calibration curves for the Stanton Redcroft Thermal Analyser (model STA 781): (i) new thermocouple assembly, metal crucibles (● ⧫); (ii) old thermocouple assembly, metal crucibles (+); (iii) new thermocouple assembly, quartz crucibles (○).

instruments: ours which was fitted with a new thermocouple assembly and a second where the assembly had been in use for over a year. The values of ϵ are the means of the results from two samples, each of mass 10 mg. The mean experimental errors were 2% for the samples in metal crucibles and 3% for quartz crucibles. The shape of the peaks was generally good with the exception of those obtained with gold. These often showed ill-defined shoulders and in some instances became almost double peaks. Notwithstanding their poor shape, the area of the peaks was reproducible.

The calibration values lie on remarkably smooth curves. The equations of the curves expressed as third-order polynomials in temperature (K) are

$$\epsilon = 1.756 \times 10^3 - 5.394T + 6.912 \times 10^{-3}T^2 - 1.321 \times 10^{-6}T^3 \tag{1}$$

$$\epsilon = 4.096 \times 10^3 - 16.05T + 2.119 \times 10^{-2}T^2 - 7.052 \times 10^{-6}T^3 \tag{2}$$

$$\epsilon = 1.838 \times 10^3 - 3.619T + 5.125 \times 10^{-3}T^2 - 7.951 \times 10^{-7}T^3 \tag{3}$$

Equations (1) and (2) refer to the calibration of the instruments with the samples in metal crucibles. The mean error in best-fitting the experimental data to these equations is about 5%. Judged on the basis of reproducibility there was no deterioration in the performance of the older instrument although the calibration curve is of a different shape. Equation (3) refers to the use of quartz crucibles but with the calibration results obtained using potassium chromate, barium carbonate and potassium sulphate omitted from the best-fitting routine. The average error in representing the remaining data by the equation is 1%. Comparison between eqns. (1) and (3) shows that the calibration factor with quartz crucibles is considerably greater than with metal crucibles: at low temperatures (< 700 K) the use of quartz crucibles almost halves the sensitivity of the equipment. It is crucially important to recognise this dependence on the nature of the crucible. It will apply not only to the present equipment but also to differential scanning calorimeters of the same generic design.

Equations (1)–(3) represent the practical route to using the apparatus as a calorimeter: the product of the instrument signal S (V) and the calibration factor gives the thermal power (in W). We have investigated the dynamic range of the instrument at 1338 and 430 K using samples of gold and indium, respectively, and obtained an excellent linear relationship (correlation coefficient = 0.999) between the peak area and mass over the 2–110 mg range. Less desirable was a small but monotonic dependence of peak area on heating rate with the gold sample (1338 K). The effect was to give a linear increase of 5% in the calibration factor over a change in the heating rate from 2 to 50 K min^{-1}. At lower temperatures the dependence of the calibration on heating rate disappeared. At temperatures > 900 K, there is a further source of uncertainty when using quartz crucibles: there is a clear difference between the result obtained with gold and those for potassium chromate, barium carbonate and potassium sulphate which is not observed with inconel crucibles *. The indications are that this difference becomes more significant at higher temperatures and must cast doubt on the use of thermal analysers with quartz crucibles for high temperature quantitative measurements.

The theory set out by Gray [1] provides a theoretical basis for the present calibration experiments. The theory follows the earlier work of Vold [3] and assumes that the DTA experimental configuration may be represented by a sample and a reference together with the surroundings at the uniform temperatures T_s, T_r and T_p, respectively. It is also assumed that there is a single thermal impedance R between both the sample and reference and the surroundings. With these assumptions the operating equation for DTA is

$$R\,\mathrm{d}q/\mathrm{d}t = (T_s - T_r) + R(C_s - C_r)\,\mathrm{d}T_r/\mathrm{d}t + RC_s\,\mathrm{d}(T_s - T_r)/\mathrm{d}t \tag{4}$$

where $\mathrm{d}q/\mathrm{d}t$ is the thermal power associated with an event in the sample. The heating rate $\mathrm{d}T_p/\mathrm{d}t = \mathrm{d}T_r/\mathrm{d}t$ and is assumed to be constant. C_s and C_r are the heat capacities of the sample and reference respectively, which are also assumed to be constants. Application of eqn. (4) to a fusion process where the temperature of the entire sample is assumed to remain constant leads to a description of the DTA endotherm. The area of the peak enclosed by the instrument signal and the base line is proportional to $R\Delta H$. Thus the calibration factor is related to the thermal impedance $\epsilon = 1/R$ where R may be expressed in the units (s K J^{-1}) by incorporating the temperature coefficient of the thermocouple signal. The apparently incompatible requirements of a small value of R for fast response and a large value for sensitivity are met by signal amplification. Our measurements indicate that the value of R is independent of the mass of the metal samples over almost two orders of magnitude.

An alternative route to the thermal impedance is a more detailed analysis of the shape of the fusion endotherm. Gray [1] represented the decay portion of the peak by the equation

$$\Delta T = \Delta T_{\mathrm{max}} \exp(-t/RC_s) \tag{5}$$

ΔT is the temperature signal measured from the base line of the peak and ΔT_{max} is the value corresponding to the peak maximum. Figure 2 shows $\ln \Delta T/\Delta T_{\mathrm{max}}$ plotted against time for a number of different samples. We find that a large portion of the decay can be represented by a single exponential. The gradient $-[\mathrm{d}\ln(\Delta T/\Delta T_{\mathrm{max}})/\mathrm{d}t]^{-1} = RC_s$ defines the response time: to obtain R requires a knowledge of the heat capacity of the sample. In this context 'sample' means the conventional sample, the crucible and part of the thermocouple assembly. Values are available for the heat

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* The authors thank Mr E.L. Charsley for drawing attention to the likely presence of this discrepancy.

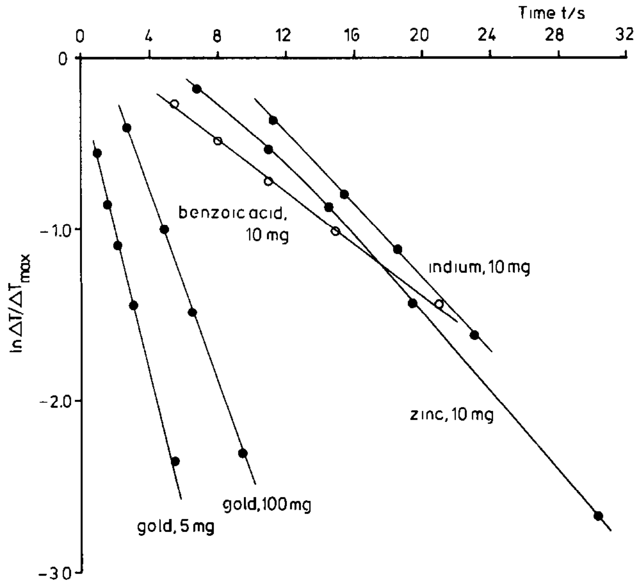

Fig. 2. Exponential decay of the fusion peak of metals (●) and benzoic acid (○) in metal crucibles recorded with the new thermocouple assembly.

capacity of the molten metals and crucible materials: for the thermocouple assembly we have estimated the heat capacity. Figure 3 shows the values of *R* derived from the decay of the fusion peak and the calibration factor ϵ.

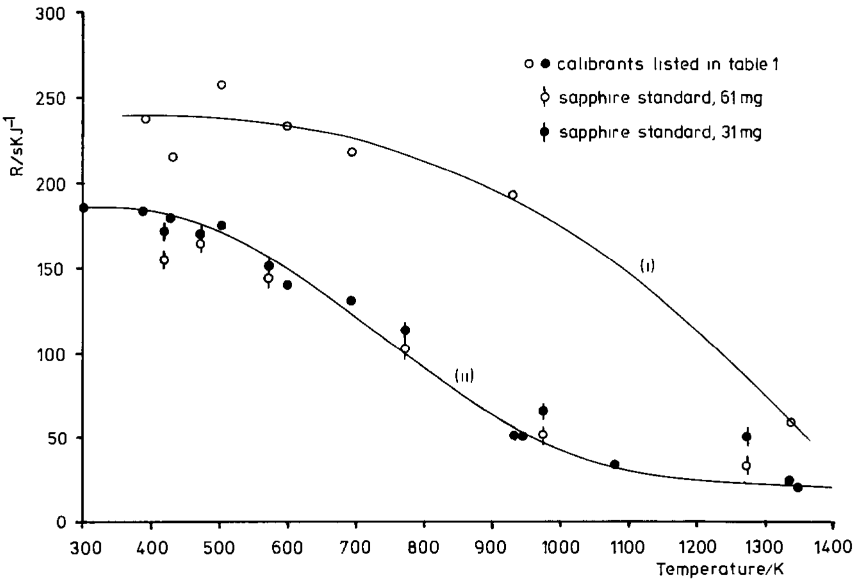

Fig. 3. The thermal impedance calculated from (i) the decay of the fusion peak (○) and (ii) the calibration constant (● ♦ ◊) for the samples in metal crucibles recorded with the new thermocouple assembly.

Our measurements with samples of gold showed a gradation in the response time from 2.58 to 3.29 s over the range of sample mass 5–100 mg which gave rise to the value $R = 59.2 \pm 0.6$ s K J^{-1} shown in Fig. 3. The error was random with no evident trend between the results and sample mass. Similarly, measurements with indium and benzoic acid gave values of R independent of mass. The results in Fig. 3 show an obvious discrepancy between the two routes to the thermal impedance and highlights the shortcomings of a simple description of instrument behaviour and the fusion process. The model of the DTA instrument may be modified by replacing the single sample system by a two- or three-element model where the sample, crucible and thermocouple form a linear system in which there is more than one thermal impedance [4,5]. Despite its inadequacies the simple model has been widely used as a basis for the construction of base lines.

We have also investigated the use of heat capacity measurements for calibrating the equipment. This technique is well established but usually restricted to DSC instruments: it makes particular demands on performance since the enthalpy changes are small and any temperature dependence of the base line must be reproducible. We have recorded the thermal analysis curves for a sapphire disc (61 mg) over 20–50 K intervals at a heating rate of 2 or 5 K $\min^{-1}$. The calibration factor was calculated from the difference between the area enclosed by the curves for the metal crucible with the sapphire sample and the empty crucible. The mean heat capacity over the relevant temperature ranges was calculated from the data in ref. 6. It is important that the position of the thermocouple assembly should be reproduced as closely as possible from one experiment to the next. With the present equipment there is the possibility of both movement of the suspension and flexing of the thermocouple assembly. This is likely to be exacerbated by the use of large samples. Thus the results obtained were far better than we had expected with an experimental error between duplicate measurements of about 2% at temperatures < 1000 K but increasing to 5% at higher temperatures. The results are shown in Fig. 1. They agree with those from the chemical standards over the temperature range 400–800 K but there is a marked difference at higher temperatures.

Area measurements with smaller sapphires (31 and 20 mg) were subject to relatively large experimental errors. Even so, it was clear that a systematic difference existed between the calibration obtained with the larger sapphire and the values for the two smaller sapphires where there was agreement within the experimental error. There was a considerable disparity between the surface area of contact of the larger sapphire with the crucible (18 mm^2) and that for the two smaller sapphires (8 mm^2). It is tempting to attribute the difference in the calibration results to this disparity. The values for the thermal impedance are included in Fig. 3. They are in accordance with the earlier observation [7] that R is inversely proportional to the contact area. We have not observed this with the molten samples. We assume that despite the different shapes observed for the molten surfaces, good thermal contact is maintained between the sample and crucible.

SUMMARY

The present experiments show that it is possible to calibrate the Stanton Redcroft DTA 781 over the temperature range 290–1350 K, using conventional chemical standards, with a precision of about 5%. However the relevance of the calibration is by no means assured and cannot be considered as a 'universal' calibration independent of the nature of the crucible and sample. Over the entire temperature range of the experiments the calibration factor is dependent on whether the crucibles are made of metal or quartz. At high temperatures the use of quartz crucibles leads to results which depend on the nature of the sample. The transparent nature of quartz crucibles compared with inconel suggest that the feature of importance is the emissivity of the sample. Inevitably, high temperature quantitative measurements will pose problems of calibration. Heat capacity measurements may offer a solution but for the present apparatus the results obtained at high temperatures are unreliable.

The present results cast doubt on the wisdom of attempting to obtain precise calorimetric results from differential thermal analysers. This is not a reflection on the particular apparatus tested in this work. Rather it is a consequence of the complexity of the relationship between the instrument signal and the thermal power associated with the sample. Wendlandt [8] has listed 16 factors which influence the shape of thermal analysis curves. Some are embodied in the design of an instrument, others can be varied by the experimentalist and may impinge directly on the energy calibration. Of greater importance, our conclusions regarding calibration are likely to apply to DSC instruments of similar design. With such instruments there is the temptation to be content with a more cursary investigation of the calibration or even to accept without question its correctness. In contrast DTA is recognised as being more qualitative and therefore as requiring greater care in obtaining even approximate calorimetric values.

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