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A NEW HIGH-TEMPERATURE THERMOCOUPLE ASSEMBLY FOR HEAT-FLUX DIFFERENTIAL SCANNING CALORIMETRY

FENG HONGTU and P.G. LAYE

School of Chemistry, The University, Leeds LS2 9JT (U.K.)

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ABSTRACT

A new thermocouple assembly has been examined for use in high-temperature differential scanning calorimetry. The assembly has been calibrated using chemical standards and the results expressed as third-order polynomials in temperature. The performance at high temperatures has been tested by making heat capacity measurements. The results clearly point to the need for caution when interpreting such high temperature measurements.

INTRODUCTION

High-temperature differential scanning calorimeters (> 1300 K) have become available from a number of instrument manufacturers. At first sight these instruments promise to make differential thermal analysers obsolete except for specialised very high temperature applications. In reality their mode of operation is one in which the instrument signal is usually derived from a temperature difference. The strictures concerning the calibration of differential thermal analysers and in particular the lack of a universal calibration independent of the nature of the experiment, will be true for this type of differential scanning calorimeter.

We have examined the performance of a new thermocouple assembly designed for simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). The design is the same as that described by Brammer et al. [1] but incorporates platinum–platinum 13% rhodium thermocouples instead of chromel–alumel. The chromel–alumel assembly is used in the low temperature TG–DSC manufactured by PL Thermal Sciences Ltd (model STA 625). In the present work, the new thermocouple assembly has been substituted for the conventional thermocouple hangdown in a high-temperature TG–DTA apparatus (Stanton Redcroft Model 781, now manufactured by PL Thermal Sciences Ltd, Model STA 1500). The quantitative performance of the DTA instrument was investigated recently [2]. Compared with the DTA hangdown, the new assembly has a much greater rigidity. The

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expectation was an improvement in reproducibility, particularly at high temperatures thus allowing the measurement of heat capacity.

EXPERIMENTAL

The thermocouple assembly consists of a heat-flux plate which incorporates the sample and reference plate thermocouples. Each of these is attached to the main plate at three points only and has integral ears to give a positive location for the crucibles. The assembly is attached to a four-bore alumina rod through which pass the thermocouple wires. The rod was suspended from the balance arm and the balance operated to maintain the assembly in the same position in the furnace throughout the calibration experiments. The length of the rod was the same as that used in the DTA apparatus. The thermocouple assembly was bigger than the DTA plate thermocouples which prevented the use of the internal ceramic cup in the furnace. This was replaced by a flat plate fitted below the hangdown to limit the immediate environment of the thermocouples. The atmosphere in the furnace was controlled by gas which passed through the centre of the plate. The furnace temperature was controlled by the Stanton Redcroft programmer (model UTP) using the signal from a platinum–platinum 13% rhodium thermocouple in the windings of the furnace. The differential signal was amplified using a low-noise DC amplifier (Cropico).

The test programme was similar to that described previously [2]. The calibrants were listed in the previous publication together with the enthalpy values used for the transitions. Emphasis was placed on ensuring good thermal contact between the sample and the metal or quartz crucibles and between the crucibles and the thermocouples. With aluminium crucibles the samples were pressed between two crucibles. Care was taken to ensure that the base of the crucibles was flat. The calibration factor, ϵ, was expressed ϵ (W V^{-1}) $= A\Delta H$ (J)/Peak area (V s) where A is the signal amplification. With sapphires the displacement peaks were recorded when the temperature was increased in steps of 40–50 K at a heating rate of 2 K $\min^{-1}$; ϵ was calculated from the area of the peak and the mean heat capacity over the temperature range. This method was preferred to the measurement of signal displacements since these were small at high temperatures ($>$ 1300 K).

RESULTS

The isothermal base line of the new thermocouple assembly showed a change of only 5 μV from 298 to 1450 K. It was reproducible to within the noise level which was $\leqslant 0.3$ μV over the entire temperature range. The temperature trace showed an unacceptably large level of noise above 1450 K

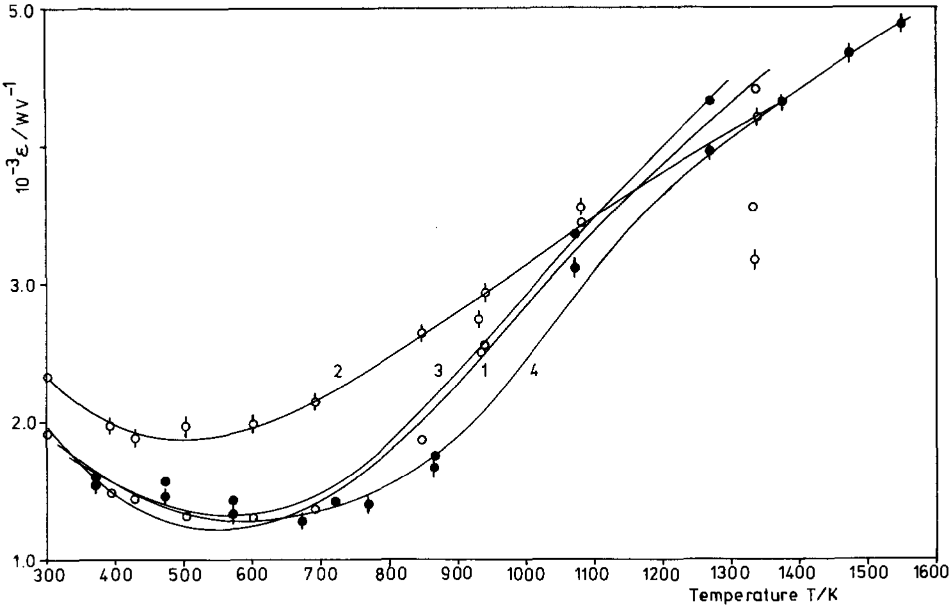

Fig. 1. Calibration results: (1) and (2), chemical calibrants in metal crucibles (○) and quartz crucibles (ϕ); (3) and (4), sapphire standard with original thermocouple assembly (●) and modified version (ɸ).

and initially this determined the maximum operating temperature. The noise was associated with the power supply to the furnace and was absent when the furnace was allowed to cool freely. The dynamic range of the instrument extended over two orders of magnitude measured at 430, 1338 and 1341 K using samples of indium, gold and potassium sulphate, respectively. There was a small, almost linear, decrease (2.5%) in the area of the fusion peak of gold with a change in the heating rate from 1 to 50 K min^{-1}. The effect was smaller than with the DTA apparatus and was absent at lower temperatures. There was no dependence of peak area on the flow rate of the gas when this was less than 75 cm^3 min^{-1}.

The calibration results are shown in Fig. 1. They refer to the use of both metal and quartz crucibles. The sensitivity ($1/\epsilon$) of the new hangdown in argon was less than half that of the DTA apparatus at 303 K (melting temperature of gallium) but became comparable at high temperatures ($>$ 1300 K). As expected, the use of quartz crucibles gave a lower sensitivity but unlike the results from the DTA apparatus the difference disappeared at temperatures > 1175 K. Much more marked was the effect of changing the nature of the atmosphere in the apparatus. Replacing argon by helium reduced the sensitivity by about half.

The calibration result obtained with gold indicated a considerably greater sensitivity than that with potassium sulphate even though the fusion temperatures differ by only 3 K. A discrepancy was also observed in the previous experiments with the DTA apparatus but was restricted to the use of quartz crucibles and with gold showing a lower sensitivity. We have repeated the earlier calibration experiments and confirmed this different pattern of behaviour. The residues obtained from the two experiments were different in form: the new assembly gave several spherical globules of gold whereas a single sphere was obtained with the DTA apparatus. With alumina in the bottom of the crucible the new assembly gave only one sphere and the sensitivity became similar to the value for potassium sulphate.

The calibration results may conveniently be represented by third-order polynomials in temperature

$$\epsilon\ (\mathrm{W\ V^{-1}}) = 5.885 \times 10^{3} - 19.59T\ (\mathrm{K}) + 2.459 \times 10^{-2}T^{2}\ (\mathrm{K}^{2}) - 8.043 \times 10^{-6}T^{3}\ (\mathrm{K}^{3}) \tag{1}$$

$$\epsilon\ (\mathrm{W\ V^{-1}}) = 4.667 \times 10^{3} - 12.15T\ (\mathrm{K}) + 1.605 \times 10^{-2}T^{2}\ (\mathrm{K}^{2}) - 5.389 \times 10^{-6}T^{3}\ (\mathrm{K}^{3}) \tag{2}$$

Equations (1) and (2) refer to the use of metal and quartz crucibles respectively in argon and are valid over the temperature range 303–1341 K. In calculating these equations the results for gold have been omitted. The error in duplicate experimental measurements with metal crucibles was 0.2–0.5% with the exception of potassium chromate (4%), barium carbonate (3%) and gold (2%). With quartz crucibles the experimental error was slightly greater (1–2%), again with the exception of potassium chromate (4%) and barium carbonate (3%). The mean error in representing the data by the polynomials is 4% (metal crucibles) and 2% (quartz crucibles).

The calibration results obtained with a sapphire disc (61 mg) in a metal crucible are also shown in Fig. 1. The results may be expressed by the equation

$$\epsilon\ (\mathrm{W\ V^{-1}}) = 7.243 \times 10^{3} - 24.89T\ (\mathrm{K}) + 3.112 \times 10^{-2}T^{2}\ (\mathrm{K}^{2}) - 1.084 \times 10^{-5}T^{3}\ (\mathrm{K}^{3}) \tag{3}$$

which refers to the temperature range 373–1273 K. The mean error in duplicate measurements was 2% but a much greater error (7%) was incurred in representing the data by the simple polynomial. These errors are considerably greater than those associated with the chemical calibrations and the effect is to mask any systematic difference between the calibration results obtained by the two routes.

We have reduced the overall size of the new assembly by removing part of the heat-flux plate. The idea was to allow the internal cup to be replaced in the furnace. The reduction in the mass of the assembly might be expected to increase the sensitivity of the equipment but by only a small amount. The amount of metal removed was 0.2 g giving a total mass of 2 g for the assembly (excluding the ceramic rod) compared with 0.5 g for the plate thermocouples in the DTA apparatus. More significant was the removal of a support to each of the thermocouples. The calibration results with chemical standards showed a slight gain in sensitivity but with the thermocouple assembly still retaining the rigidity which was a feature of the original design. Replacing the cup in the furnace had the immediate effect of reducing the noise level on the temperature trace. This allowed us to extend temperature measurements to 1550 K with an uncertainty of about 1–2 K. The calibration results with sapphire over the extended temperature range are also shown in Fig. 1. Above 1550 K the noise in the differential temperature signal became too large (0.4–0.8 μV) for precise quantitative results.

The high temperature performance of the equipment has been examined by measuring the heat capacity of platinum. The test is demanding as the enthalpy changes to be measured are small. The need for a large instrument signal places diametrically opposed demands on the experimental procedure. The use of a large sample necessitates a slow heating rate to ensure minimal thermal lag but the slow heating rate in itself reduces the instrument signal. As a compromise we have selected a heating rate of 4 K min^{-1} and sample masses of 141 and 155 mg in two series of measurements. The platinum was 99.95% pure (Johnson Matthey) and was in the form of foil which was contained in a conventional platinum crucible. An identical crucible was used as the reference. The temperature was increased stepwise and the heat capacity calculated from the area of the peak and ascribed to the mean temperature.

The mean values obtained from the two series of measurements (in J K g^{-1}) were 0.159 ± 0.005 (1173 K); 0.165 ± 0.005 (1273 K); 0.170 ± 0.006 (1373 K); 0.181 ± 0.006 (1473 K); 0.190 ± 0.010 (1543 K). A much smaller uncertainty (1–2%) was obtained when repetitive measurements were made on one sample left undisturbed in the apparatus. It is evident that the major source of error is the difficulty in reproducing precisely the geometry of the experiment. This includes both the disposition of the sample in the crucible and the orientation of the crucible on the thermocouple assembly. The reliability of the present measurements may be examined by comparing the results with those obtained by drop calorimetry [3]. At first sight our results are encouraging, with the measurements at 1173–1373 K in agreement with the calorimetric values within the experimental error. On closer inspection, however, it becomes clear that there is a systematic temperature-dependent error which leads to a marked discrepancy at the higher temperatures. Furthermore it is possible to obtain differing results by changing the experimental procedure. As might be expected, the use of quartz crucibles leads to quite different results, almost an order of magnitude smaller. Even using tall-form platinum crucibles instead of the conventional shape or altering the form of the platinum sample gave rise to small changes in the results. The implication is that considerable care is needed in the interpretation of results from thermal analysis.

SUMMARY

The new thermocouple assembly has excellent base line stability, reproducible to within a small noise level. We have not observed a significant deterioration during the present measurements. The rigid structure of the assembly makes it easier to use and less susceptible to damage through the inevitable wear and tear of many experiments. There is some loss of sensitivity compared with the DTA apparatus but an increase in the reproducibility of the results. The less isolated nature of the thermocouples compared with the plate thermocouples in the DTA apparatus leads to peaks with a significantly less extended decay portion. Thus there is a reduction in the thermal impedance measured from the decay of the fusion peaks. The response time derived from the decay of the fusion peak for gold showed a graduation from 1.55 to 1.81 s for samples over the range 1–70 mg which corresponds to a thermal impedance of 35.2 ± 0.4 s K J^{-1}. For indium the value was 178 ± 1 s K J^{-1}. The corresponding values for the DTA apparatus were 59.2 ± 0.6 and 217 ± 1 s K J^{-1} for gold and indium, respectively. It is important that the internal cup is used in the furnace because this gives good atmosphere control and in our apparatus at least, reduced the noise level on the temperature signal.

The calibration equations form the basis of using the apparatus as a heat-flux DSC. With their introduction into suitable computer software a linearised instrument signal becomes possible. The shape of the calibration curves is slightly different from that obtained for the DTA apparatus, showing less temperature dependence. The distinction between the use of different crucibles is less marked but uncertainty still exists concerning the dependence of the calibration on the nature of the sample. For quantitative measurements the present apparatus was restricted to a maximum temperature of 1550 K.

The use of heat capacity measurements to assess the high temperature performance of the apparatus is highly relevant bearing in mind the increasing use of thermal analysis techniques for such measurements. The heat capacity of platinum is small and the test makes particular demands, both on the apparatus and on the expertise of the operator. With attention to experimental detail, we have obtained results with an uncertainty of 2–6%. However the determination of the heat capacities at high temperatures is not a task to be undertaken lightly. The sensitivity of the results to changes in the experimental procedure points to doubts concerning the reliability of the measured values. The apparent convenience of thermal analysis compared with classical calorimetric techniques must be judged against this uncertainty in accuracy. Even apparently 'reasonable' results need to be regarded with some scepticism. In the wider context, doubts must arise concerning the extent to which calibration results at high temperatures can be transferred from one experiment to another.

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