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Single-run heat capacity measurement by DSC: principle, experimental and data analysis [1]

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Abstract

A single-run heat capacity measurement has been proposed based on standard heat-conduction-type differential scanning calorimetry (DSC) equipment. The experimental tests were in the range 130–560 K. The equipment used was the dual sample DSC and autosampler from TA Instruments. The RMS error of all measurements when compared to well-established adiabatic calorimetry is <1% above 300 K, <3% below 200 K, and <2% between 200 and 300 K. Software for data analysis has been developed with options for all necessary corrections, namely temperature lag, heating rate, asymmetric correction, non-linear temperature calibration, etc. Since the initial setup of the instrument, more than 30 different samples have been analyzed. It is shown in this paper that this technique can improve the precision and reduce the experimental time compared to the normal, triple-run DSC. For the low-temperature experiment, some important modifications of the instrument have been made which improve the baseline performance. Some hands-on experience is discussed.

INTRODUCTION

Heat capacity C_p is one of the basic properties of any material. The improvement of C_p measurement by DSC is, thus, one of the goals of our Advanced THermal AnalysiS (ATHAS) laboratory. In the past, comparison between various DSCs were made in high [1] and low temperature ranges [2], direct computerization was pioneered [3], and a new single-run C_p measurement was proposed [4] and finally tested [5, 6].

In a series of papers [5–8], the feasibility of single-run C_p measurements at subambient [6] and above room temperature [5], was demonstrated and a data analysis program was developed [7]. Recently, better baselines and repeatability have been achieved at subambient temperature, which now allows measurement down to 130 K [8]. In this paper, we will briefly

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summarise the principle of the single-run C_p measurement, discuss experimentation and data analysis, and propose an improved technique.

INSTRUMENTATION

A commercial TA Instrument 2100 thermal analyzer system with a 912 dual sample DSC (DSDSC) and DSC autosampler (AS) was used for all experiments. The instrument is controlled by an IBM PS/2 Model 60 computer. The computer can be used either under MS-DOS 3.3 for general computation, or with the TA system for thermal analysis. Figure 1 shows a schematic drawing of the DSDSC cell and the standard single-sample DSC cell. Both need an empty pan on R, the reference position. For DSDSC, two samples, one placed on A and one on B, can be analyzed at the same time in the same thermal environment. This is not only an advantage because of time savings, but it also reduces systematic experimental errors when one of the samples is a calibration standard for heat flow (such as Al_2O_3). The DSC autosampler minimizes the error in sample placement (error within ±0.2 mm) and permits the use of the DSC during the night and on weekends when environmental changes in temperature are minimal.

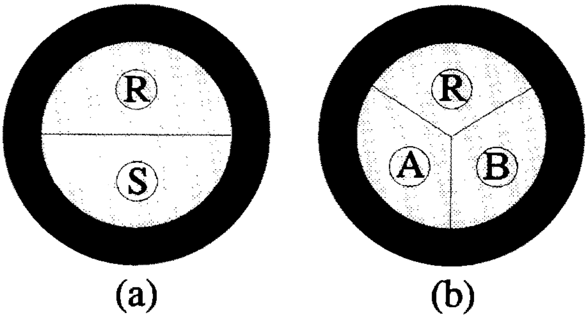

Fig. 1. Schematic of the discussed DSC cells: (a) normal DSC; (b) dual-sample DSC. H, heater block; R, reference; A, B and S, samples.

PRINCIPLE

As discussed earlier [4], the C_p based on the standard heat-conduction DSC should be expressed as follows

$$C_p = K\Delta T/q + [(C_p' + K\Delta T/q)(\mathrm{d}\Delta T/\mathrm{d}T_s)] \qquad (1)$$

where ΔT is the temperature difference between reference and sample, T_s is the sample temperature, K is a temperature-dependent constant, calibrated at each temperature with a standard such as sapphire (Al_2O_3) [9], q is the (linear, steady-state) heating rate and C_p' is the heat capacity of the empty aluminum pan [10]. The term in brackets is small, but not directly recorded in standard DSC. It corrects for the difference in heating rate between reference and sample (about 0.3% error in a typical C_p measurement, see for example ref. 5). Because ΔT is proportional to the heat flow recorded by the DSC [6], $\mathrm{d}\Delta T/\mathrm{d}T_s$ is proportional to the slope of the heat flow versus temperature curve. Only for a horizontal baseline (slope = 0) is C_p exactly equal to $K\Delta T/q$. Obviously this is not true in most cases, and eqn. (1) must be used for correction.

For a single-run C_p measurement with the DSDSC (Fig. 1(b)), C_p can be expressed

$$\frac{C_{pB}}{C_{pA}} = \frac{K_B\Delta T_B/q + [(C_p' + K_B\Delta T_B/q)(\mathrm{d}\Delta T_B/\mathrm{d}T_B)]}{K_A\Delta T_A/q + [(C_p' + K_A\Delta T_A/q)(\mathrm{d}\Delta T_A/\mathrm{d}T_A)]} \tag{2}$$

where all symbols are as in eqn. (1). The subscripts A and B refer to the two sample positions in the DSDSC cell shown in Fig. 1.

By placing a sapphire standard on position A and an unknown sample on position B, one can calculate the heat capacity of an unknown sample from the heat flows recorded in a single DSC run. The advantages of the single-run expriment are not only the saving of two calibration runs that should be carried out with *every* measurement using standard DSC, but also a simple computation of the results and an internal compensation of thermal fluctuations during the run. In the three runs needed for standard DSC (sample calibration and baseline), such fluctuations cause systematic errors that are difficult to assess. The new problem, however, not present in standard DSC, is the need to calibrate for the asymmetry of the cell.

EXPERIMENTAL

For the experiment at subambient temperature, liquid nitrogen (LN) must be used as coolant to attain starting temperatures as low as 130 K. Ideally, the autosampler can also be used with the liquid nitrogen cooling accessory II (LNCA-II) in the fully automatic mode. It has been found, however, that at temperatures below 180 K, the baseline is unstable and noisy [6]. In addition, there is considerable baseline curvature during the recording of isotherms and on heating. The economy of such an operation is also poor because an LNCA-II tank of 50 l lasted typically for only about two runs.

The main reason for the baseline problems is the changing temperature of the DSC cell base and of connector between the DSC cell and the cell base, due to the cold nitrogen flow. This (unequal) change in temperature disturbs the temperature sensing. After more than 30 min of cooling and isotherm operation, the cell base becomes so cold that ice forms on the surface of the cell base, further complicating the problem. When the LN feeding stops during heating, the cell base warms up, and the cell base and connector temperatures change again, causing baseline curvature.

In order to improve the baseline performance, several attempts have been made to maintain the temperature of the cell base and connector constant: namely, by changing the LN gas flow route; by purging dry

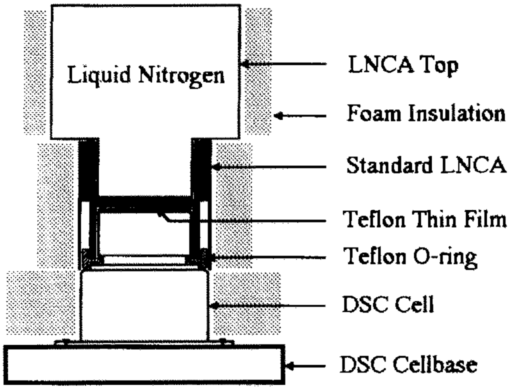

Fig. 2. Schematic of the modifications of the normal LNCA.

nitrogen gas through the connector, as suggested by the manufacturer; by keeping the cell base warm by external heating; and by using the standard liquid nitrogen accessory (LNCA) provided with the DSC for quenching in the manual mode. Because of the small capacity of the standard LNCA, it is, however, unable to maintain a stable baseline during the length of the experiment.

To remove these problems, some modifications have been made to the experimental set-up, as shown schematically in Fig. 2. The reasoning behind the modifications are as follows: the increased volume of the LNCA (>1 l of LN) extends its use without refill to more than one hour (refilling always disturbs the baseline); the Teflon O-ring blocks the cold air from the connector and the cell base; the Teflon film reduces the baseline noise caused by the boiling of LN; and the foam insulation avoids the cooling of the cell base. With these special modifications, the baseline and experiment performance was considerably improved. Figure 3 shows the

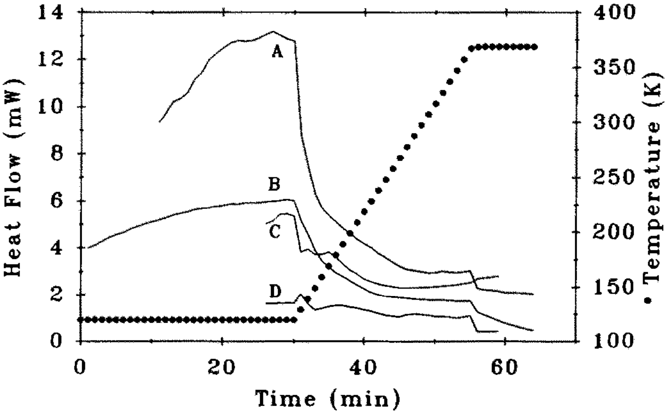

Fig. 3. Baseline comparison under different conditions (for details see text).

baseline comparisons for several different conditions under a temperature program indicated by the heavy dotted line (right ordinate). With the LNCA-II, the isotherm and baseline were unacceptable below 180 K (left ordinate, curve A); while purging dry nitrogen gas through the connector could improve the baseline somewhat (curve C), the nitrogen flow must be very high in order to maintain a gas pressure of about 5 psi. In addition, the nitrogen must be extra dry to avoid moisture condensation in the connector. With the modified LNCA of Fig. 2, we can get an almost straight baseline without significant curvature (curve D). Using these modifications, except the changed LNCA, the baseline still show some curvature (curve B), but the performance is better than the LNCA-II.

DATA ANALYSIS

Although commercial software for C_p measurement by DSC is available from TA Instruments, it still cannot be applied to the DSDSC for the single-run C_p measurement. We have thus developed our own software which includes most features of the commercial software and some additional options, such as corrections for cell asymmetry, non-linear temperature calibration, heating rate differences between sample and reference, etc. A publication is available and can be requested from the authors [7].

Briefly, in order to establish the proper heat flows at a given temperature, several data corrections must be made before calculating C_p using eqn. 2: non-linear temperature calibration; temperature lag proportional to the amplitude of heat flow; temperature lag as a function of heating rate; heat flow changes caused by varying heating rates; heat flow changes caused by differences in the pan masses; and asymmetry between cells A and B, i.e. $K_\mathrm{A}/K_\mathrm{B}$ is not equal to 1.

LOW-TEMPERATURE PERFORMANCE AND EXAMPLES

Figure 4 shows the change with temperature of the C_p calibration constant ($K_\mathrm{A}/K_\mathrm{B}$) of the DSDSC, determination with the modified LNCA. Compared to the earlier work [6], not only can we reach much lower temperatures, but also the performance is better. The present average and RMS of the calibration constant is 0.968 ± 0.011 from 130 to 360 K, and 0.967 ± 0.010 in the limited temperature range of 180–360 K, as compared with the earlier results of 0.980 ± 0.016 from 180–373 K for measurements using the LNCA-II.

The accuracy of the heat capacity measurements was established by analysis of standard samples of sapphire, selenium, aluminum, quartz,

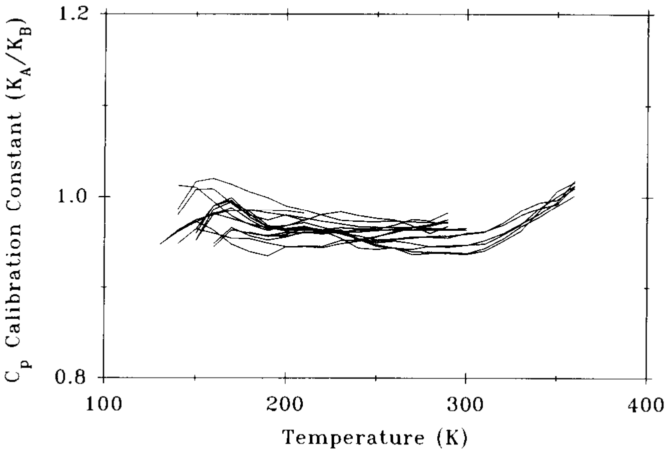

Fig. 4. Heat capacity calibration constants as a function of temperature for sixteen runs.

polystyrene, and sodium chloride between 130 and 550 K. The RMS errors of all measurements on comparison with data from well-established adiabatic calorimetry is estimated to be <1% above 300 K, <3% below 200 K, and <2% between 200 and 300 K.

More than 200 C_p runs on more than 30 research samples have been made with the modified equipment over the last year, including a series of *n*-paraffins [11], several polysilylenes [12], *N,N'*-bis-(4-*n*-octyloxybenzal)-1,4-phenylenediamine [13], a number of perfluorinated *n*-paraffins [14], some polysulfones [15], mesophase-forming aromatic polyethers [16], poly(ethylene terephthalate) fibers of different thermal and mechanical history [17], two fullerenes (C_{60} and C_{70}) [18], a bisphenol [19] and polypivalolactone [20]. All data have been added, together with information from the literature, to our critically evaluated ATHAS data bank. At present the data bank contains information, including calculated heat capacities based on the analysis of vibrational spectra, for nearly 200 linear macromolecules and related small molecules [21]. The agreement between experimental and calculated data is usually better than ±3%, the same accuracy that is possible with the single-run instrumentation described here.

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