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DETERMINATION OF CELL ASYMMETRY IN TEMPERATURE-MODULATED DSC

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Abstract

The quality of measurement of heat capacity by differential scanning calorimetry (DSC) is based on the symmetry of the twin calorimeters. This symmetry is of particular importance for the temperature-modulated DSC (TMDSC) since positive and negative deviations from symmetry cannot be distinguished in the most popular analysis methods. Three different DSC instruments capable of modulation have been calibrated for asymmetry using standard non-modulated measurements and a simple method is described that avoids potentially large errors when using the reversing heat capacity as the measured quantity. It consists of overcompensating the temperature-dependent asymmetry by increasing the mass of the sample pan.

Keywords: asymmetry correction, calibration, heat flux calorimeter, heat capacity, power compensated calorimeter, temperature modulated differential scanning calorimetry, TMDSC

Introduction

Twin calorimetry has been invented to reduce the basic problem of any heat measurement, the heat loss or gain due to extraneous flux [1]. The differential measurement between a reference and the sample calorimeter should approach zero losses and thus needs only minor corrections for residual asymmetry. In this paper the problem arising from the remaining asymmetry of the two calorimeters will be analyzed for standard DSC and temperature-modulated DSC (TMDSC [2, 3]) if the reversing heat capacity is used as measured quantity. A simple recipe will be given for better thermal analysis.

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Mathematics of the measurement by DSC and TMDSC

In standard DSC the heat capacity can be determined under two conditions [1]: 1.) If steady state is reached throughout the instrument, i.e. the heating rate $q = dT/dt$ is the same at any point in the calorimeter and its immediate surroundings; and 2.) if the temperature gradient within the sample is negligible. Using Newton's law of cooling, one can write under these conditions for either calorimeter, each usually consisting of an aluminum pan and its content, the following heat-flow equation:

$$\frac{dQ}{dt} = K[T_b(t) - T(t)] \tag{1}$$

where T_b is the block or heater temperature, and K is the geometry and materials dependent constant of the path from heater to sample or reference calorimeter. The respective heat flows raise the temperature of the sample or reference calorimeters proportionally to their corresponding heat capacities C_s and C_r, and one can derive the basic equation [1]:

$$T_r - T_s = \frac{(C_s - C_r)}{K}\frac{dT_s}{dt} - \frac{C_r}{K}\frac{d(T_r - T_s)}{dt} \tag{2}$$

At steady state, which yields a horizontal baseline and $dT_s/dt = dT_r/dt = dT_b/dt = q$, the second term on the right-hand side of Eq. (2) is zero. Assuming that the reference pan is empty and identical in aluminum content to the sample pan, ΔT, the temperature difference $T_r - T_s$, is simply mc_pq/K, where m is the sample mass, and c_p is the specific heat capacity of the sample. If the sample heat capacity changes slowly with temperature, the second term is not zero, but can be corrected for [1] :

$$mc_p = K\Delta T/q + C_s d\Delta T/dT \tag{3}$$

The correction for the remaining asymmetry is made by measuring the instrument response over the temperature range of interest with two identical empty pans. The resulting heat flow is used as baseline for the subsequent calibration run with sapphire and the final sample run. These three runs should be made in close succession and inspected, to assure that there had been no change in the instrument in the time interval of the three measurements, as would be indicated, for example, by close to identical initial and final isotherms for the three runs. The evaluation of the sample specific heat capacity is then done by calibration at each temperature of interest:

$$mc_p = m_{Al_2O_3}c_p(Al_2O_3)\frac{a_s - a_b}{a_c - a_b} \tag{4}$$

where the a represent the heat flow or temperature difference of the sample run (s), the calibration run (c, usually with sapphire, Al_2O_3), and the baseline run (b, with two empty Al pans).

Introduction of temperature modulation [4–6] permits an additional evaluation of the heat capacity out of the response of the periodic change in sample and reference temperatures [7], the reversing heat capacity. The sample and reference temperatures are now represented by:

$$T_r - T_0 = qt - \frac{qC_r}{K} + A_{T_r}\sin(\omega t - \varphi) \tag{5}$$

$$T_s - T_0 = qt - \frac{qC_s}{K} + A_{T_s}\sin(\omega t - \varepsilon) \tag{6}$$

where A_T indicates the maximum modulation amplitudes; ω, the modulation frequency ($=2\pi/p$ with p indicating the modulation period in s); ε, the phase lag of the sample calorimeter relative to the heater; and φ the corresponding phase lag of the reference calorimeter. Inserting Eqs (5) and (6) into Eq. (2) permits the evaluation of the reversing heat capacity for the condition that $q=0$. This condition can be achieved either experimentally by quasi-isothermal measurement [8, 9], i.e. an oscillation about the constant temperature T_0 of experiments that cover the temperature range of interest in steps, or mathematically by evaluation of the pseudo-isothermal response of a standard TMDSC run by eliminating the effects due to the underlying, linear temperature-change by averaging over full modulation periods p and subtracting this average from the modulated temperatures [7]. The resulting basic equation for heat capacity is then:

$$|(C_s - C_r)| = \frac{A_\Delta}{A_{T_s}}\sqrt{\left(\frac{K}{\omega}\right)^2 + C_r^2} \tag{7}$$

where A_Δ is the maximum-heat-flow or temperature-difference amplitude. Note that the square root may be positive or negative. For a given A_{Ts}, ω, and empty reference calorimeter with identical mass to the empty sample pan, one might be tempted to use Eq. (4) with the recorded maximum heat-flow or temperature-difference amplitudes to calculate the heat capacity. This is, however, only valid if in all three runs $C_s - C_r$ has the same positive or negative sign. Particularly for the base-line runs with two empty pans this may not be so, leading to the possibility of errors of the magnitude of $\pm 2a_b$.

Experimental

The cell asymmetry tests were performed on four different instruments from three different instruments manufacturers by measuring the heat flow in various baseline runs. An artificial asymmetry was introduced by changing the masses of the sample and reference pans. Standard aluminum pans from the various instrument suppliers were used. All DSC measurements covered the temperature range from 240 to 320 K at heating rates of 10 K min^{-1}. Both heating and cooling experiments were performed with one minute isothermal segments every 20 K. Only representative results on heating at 320 K are displayed in the basic figures.

A commercially available Mettler-Toledo DSC 820 module, ADSC$^{\text{TM}}$, equipped with a ceramic sensor, was used in this research. Dry nitrogen gas with a flow rate of 10 mL min^{-1} was purged through the cell. The temperature dependence of the cell asymmetry over a wider temperature range was also investigated with the Mettler-Toledo DSC 820 with both heating and cooling segments from 170 to 480 K.

Two commercial Modulated DSCs (MDSC™), 2910 and 2920, of TA Instruments were used for the cell asymmetry estimation. The 2910 system was equipped with the liquid nitrogen cooling accessory. In the 2920 MDSC system cooling is accomplished to 193 K with a refrigerated cooling system (RCS). Dry nitrogen gas with a flow rate of 20 mL min^{-1} was purged through the DSC. The initial and final isotherms were 2 min. To confirm the heat capacity of the aluminum pans, the heat capacity of an aluminum pan of about 30 mg was also measured with the MDSC 2910.

Finally, the cell asymmetry tests were performed on a Perkin Elmer DSC 7/DDSC™ equipped with the intracooler II, a dry box assembly, and a nitrogen purging gas flow rate of 20 mL min^{-1}.

Mass determinations were done with a Cahn C-33 electrobalance with a sensitivity of 1.0 μg and an overall accuracy of ±0.001% for the sample and pan load of ca. 50 mg. The samples for temperature calibration were: indium (429.7 K), naphthalene (353.42 K), *n*-octane (116.4 K), acetone (177.9 K), cyclohexane s/s (186.09 K), cyclohexane s/s1 (297.7 K), cycloheptane (265.1 K), tin (505.05 K). The heat flow was calibrated using sapphire (41.535 mg).

Results

Figures 1 to 4 show the heat flow of the baseline runs as a function of mass difference between the sample and reference pans, $\Delta m = m_{(\text{sample})} - m_{(\text{reference})}$. This choice makes the heat flow endothermic (negative) for the cases where the mass on the sample side is larger than the mass on the reference side, permitting a direct comparison with standard DSC experiments, where larger mass leads to more endothermic signals.

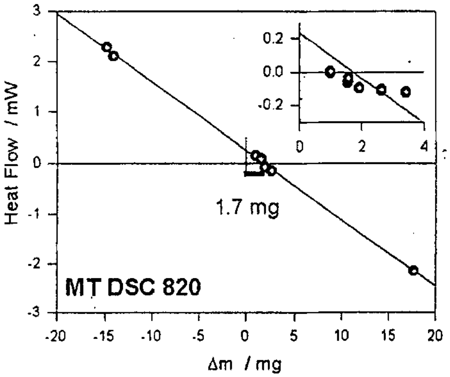

Fig. 1 Cell asymmetry of the DSC 820 (Mettler-Toledo) from baseline runs with Al pans of different weights at 320 K

In Fig. 1 the data points of the Mettler-Toledo DSC 820 are presented. The linear fit function intersects the zero-heat-flow line at a +1.7 mg inherent asymmetry. The range outside the ±4 mg mass difference is linear, while inside this margin a significant curvature is observed. Overall, the fit to a linear equation shows a slope of -0.136 W g^{-1} with a correlation coefficient of 0.999. The insert shows an expanded view of a separate series of experiments with mass-differences about zero, using a different reference pan.

Figures 2 and 3 are for the MDSC of TA Instruments. In the range from -4 to $+4$ mg mass-difference the least squares fit to a linear function intersects the zero-heat-flow line at +0.6 mg in the DSC 2910 and at -0.4 mg in the DSC 2920 cell. The slope of the linear fit in the 2910 cell is -0.132 W g^{-1} with a correlation coefficient of 0.896. The fit in the 2920 cell is -0.104 W g^{-1} with a correlation coefficient of 0.972. The slope from the heat capacity measurement with 30 mg difference in Al mass, measured with the DSC 2910, was -0.140 W g^{-1}, in good agreement with -0.138 W g^{-1} calculated from the measured heat capacity of the pan alu-

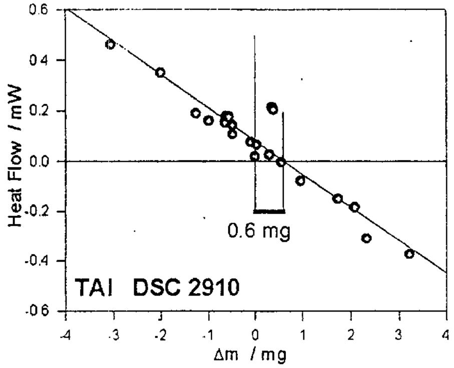

Fig. 2 Cell asymmetry of the DSC 2910 (TA-Instruments) as in Fig. 1

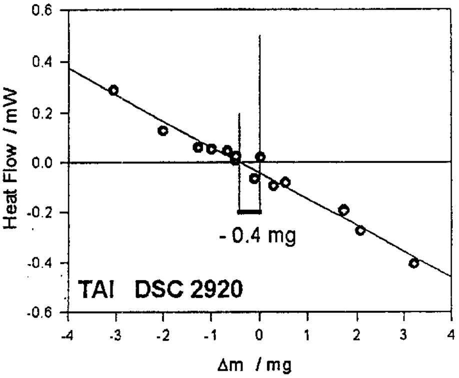

Fig. 3 Cell asymmetry of the DSC 2920 (TA-Instruments) as in Fig. 1

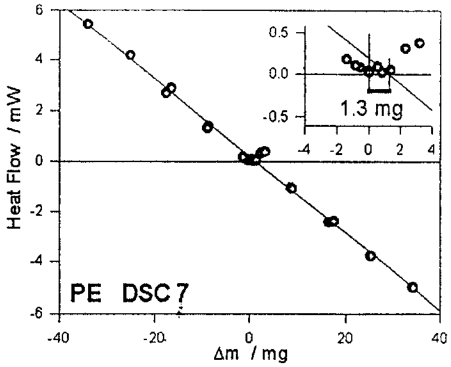

Fig. 4 Cell asymmetry of the DSC-7 (Perkin-Elmer) as in Fig. 1

minum. Because of this agreement, no additional data were taken for the intermediate masses, as for the other two instruments which show distinct deviations from linearity in the small mass-difference range, while in Figs 2 and 3 only a somewhat larger scatter is observed.

Figure 4 displays the Perkin-Elmer DSC-7 data. The linear fit intersects the zero-heat-flow at +1.3 mg. The overall fit to the linear equation shows a slope of –0.152 W g^{-1} with a correlation coefficient of 0.991. The insert shows the non-linear behavior in the vicinity of the zero-heat-flow line.

The uncalibrated, reversing heat capacities measured with the MDSC 2910 operating under quasi-isothermal conditions are shown in Fig. 5. A minimum for the apparent heat capacity exists at around 0.5 mg, in agreement with the A1 equivalent of the cell asymmetry shown in Fig. 2.

In Fig. 6 the temperature-dependence of the cell asymmetry is illustrated. The heat flow for heating (H) and cooling (C) runs is shown for the mass differences of

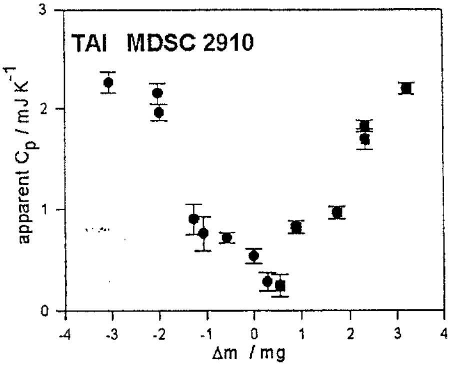

Fig. 5 Uncalibrated data for the heat capacity measured by MDSC 2910 in the quasi-isothermal mode. The error bars correspond to the standard deviation of the apparent heat capacity averaged over 10 min. From baseline runs with Al pans of different weights at 320 K

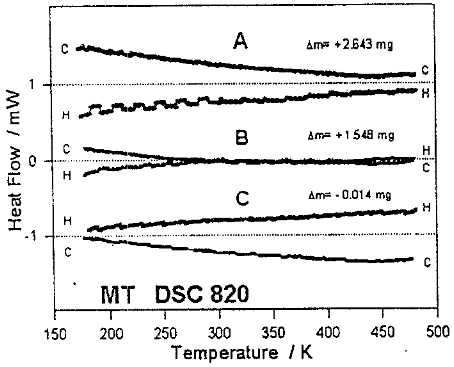

Fig. 6 Temperature dependence of the heat flow for baseline runs with Al pans of mass-difference Δm to illustrate the change of cell asymmetry of a DSC 820 with temperature (H on heating, C on cooling). The top and bottom curves are shifted by ±1 mW, respectively

–0.014 mg, +1.548 mg, and +2.643 mg. The heat flow curves are corrected for zero-heat-flow in the intervening isothermal segments. The curve for the mass differential of +1.548 mg is shown on the absolute heat-flow scale, while the other two curves are shifted by ±1 mW. The asymmetry at 320 K is close to the value of Fig. 1, but it can be seen that the asymmetry is a function of both, mass difference and temperature.

Discussion

The experiments of Figs 1–4 illustrate that each individual calorimeter tested has a unique asymmetry that can be eliminated at any given temperature by compensation of the pan weights. For DSC this compensation is not necessary since Eq. (4) corrects for asymmetry by including the proper sign with the amplitudes of a_b. The TMDSC data shown in Fig. 5 illustrate the magnitude of the error introduced by Eq. (7) which does not discriminate between positive and negative deviations. It will be shown in a subsequent paper that the sign of the correction can be determined by finding the phase shift between sample and baseline runs [11]. Finally, compensation of the asymmetry by choosing a deliberate imbalance at one temperature is not, as one might think, a suitable correction recipe because of the temperature dependence of the asymmetry shown in Fig. 6.

Absolute calculations of the heat capacities due to the difference in mass of Al needs evaluation of the calibration constants. This was not done because of the rather large error that is involved in the measurement with small mass differences and actual slope changes close to zero (Figs 1 and 4). This uncertainty had resulted in our laboratory to suggest many years ago to try to match the Al pans rather than to correct for remaining mass differences with the known heat capacity of Al [1] .

The experiments lead to the following recommendations for TMDSC:

- If only the amplitudes of the response signal of Eq. (7) are used for measurement, a calibration of the individual cell is necessary because of missing phase information [11].
- In order to avoid problems with the temperature dependence of the cell asymmetry, a sample pan of larger mass than the reference pan is to be chosen, sufficient to overcompensate the aluminum equivalent of the asymmetry at all temperatures. A reference pan which is lighter than the sample pans by at least three times the aluminum equivalent of the cell asymmetry should be sufficient. The sample pans should then be within 0.01 mg for all three measurements (baseline, calibration, and sample runs) in order to use Eq. (4).
- If the baseline correction is performed in the time domain, i.e. before calculation of the maximum amplitudes for both the calibration and the sample runs, cell asymmetries can be detected as in DSC and automatically corrected for. This correction is not available for all commercial TMDSC instruments.

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