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DSC: the importance of baseline calibration

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Abstract

The issue of the baseline in differential scanning calorimetry (DSC) is outlined. Experimental results demonstrated that incorrectly applied calibration, which is caused by performing experiments under different experimental conditions, can easily result in inaccurate experimental data. A critical factor is the introduction of thermal masses into the system. Therefore, it is imperative that a correct calibration be used for experimental measurements.

Keywords: Accuracy; Baseline; Calibration; DSC; Standard materials; Thermal mass

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1. Introduction

Differential scanning calorimetry (DSC) is widely used to investigate heat-related reactions of samples [1, 2]. The result obtained from DSC experiments is the temperature of the occurring event and its energy. Since only small amounts of sample are used in a typical experiment (the most common amount is between 2 and 20 mg), DSC is highly sensitive.

However, higher sensitivity does not always mean that better results will be obtained, since the baseline and heat capacity calibrations are contributing factors. The ideal baseline for a system is a straight line without any slope. In this case, any perturbation of heat and temperature will be easily seen on the DSC plots. But in real DSC experiments, the baseline is normally not a straight line (Fig. 1). In order to obtain the correct heat and temperature information, it is then necessary to perform a calibration.

DSC calibration normally consists of three elements: the temperature; the baseline; and the heat capacity. The temperature calibration will ensure the accuracy in

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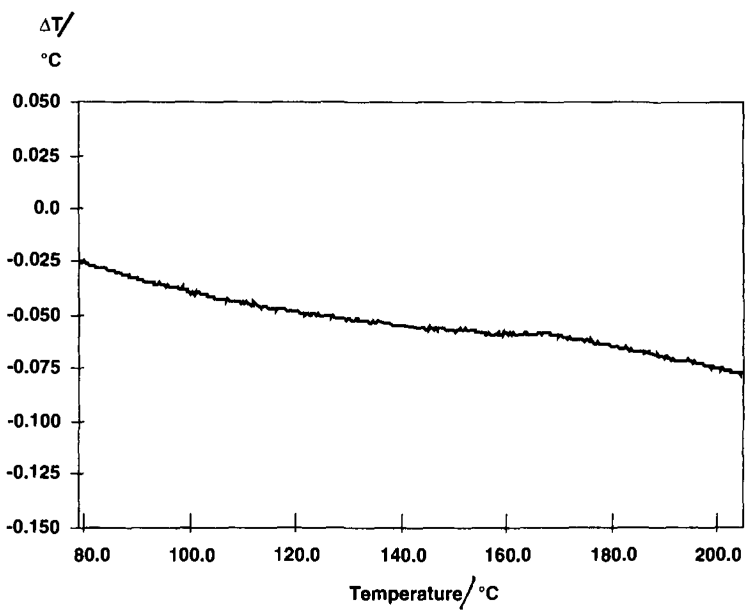

Fig. 1. Baseline curve.

measuring the temperature, which is related to the thermocouple. The baseline calibration will minimize the temperature variation in the heating process, while the heat capacity calibration takes care of the physical properties of the sample and crucible. The baseline and heat capacity calibrations together will ensure the correct conversion of temperature difference to heat capacity and heat flow. After the calibration, a set of calibration parameters can be saved and stored in the DSC unit or a calibration file.

During the sample experiments, however, the experimental conditions, such as the flow rate of reaction and purge gases, the flow rate of coolant and the contamination of DSC cells, can be different from those of the calibration runs. Therefore the corresponding experimental baseline and heat capacity calibration curves are different from those during the calibration runs. If the correct calibration is not performed for these experimental conditions, the observed heat and temperature results will be different from the correct values. In this situation, it is the same as applying a different calibration result, which used different baseline calibrations together with the same temperature and heat capacity calibration runs, to the experimental data. It is the purpose of this paper to demonstrate the effect of calibration on the final results.

2. Experimental

An ATI Cahn DSC unit was used for the study. It is a heat flux type DSC with a temperature range of – 150 to 600°C. Thermal sensors are chromel–alumel. Experiments were performed at a heating rate of 10°C min^{-1} from room temperature to 450°C. Indium (from Aldrich, 99.999%) and tin (from Aldrich, 99.999%) were utilized for two-point temperature calibration. Heat capacity calibration was performed with sapphire (Al_2O_3).

The unit can save the calibration results into files and apply the calibration results to the calibration mode data (in the ΔT vs. T format) after the experiment. Therefore it is possible to have different calibration results with different baseline calibration conditions, along with the same temperature and heat capacity calibration conditions. The variables in the baseline calibrations were flow rate and temperature of cooling water; empty cells and with two sample cups; DSC cell contaminated with and without water; and flow rates of purge and reaction gases. In this study, the conditions of cooling and reaction gas, dry air, were simplified as either on or off. Purge gas was off all the time. Table 1 lists the baseline calibration conditions.

Calibration runs for temperature and heat capacity calibrations were under the calibration condition #0 (control). Testing materials used were indium, lead (from Aldrich, 99.99%) and tin. Their melting behavior was analyzed. Sample sizes were about 10 mg. Experimental conditions were the same as those of control, which means that metals were put on the sample cup holder directly. Data were saved as the calibration data, which contained values of ΔT, temperature, and time.

3. Results and discussion

For the DSC unit, there are many criteria to evaluate the performance. No matter what criterion is utilized, the most important values are readings of temperature, heat flow, and heat capacity. Since heat capacity is intimately related to the heat flow, melting pure metals are widely utilized to evaluate DSC units by measuring the melting points and heats of fusion. Therefore, pure indium, tin, and lead were utilized.

It is believed that different calibration conditions will cause inaccuracy in the temperature readings. However, from the experimental results in this paper, it was found that the inaccuracy in temperature reading, caused by different calibration conditions, is within ±0.2°C. The following discussion and results are then focused on the amount of heat measured.

Table 1
Baseline calibration conditions

Calibration #	Cooling water	Reaction gas	Sample cups	Contamination
0 (control)	On	On	Without	No
1	On	On	Without	Yes
2	On	On	With	No
3	On	Off	Without	No
4	On	Off	Without	Yes
5	Off	On	Without	No
6	Off	On	Without	Yes

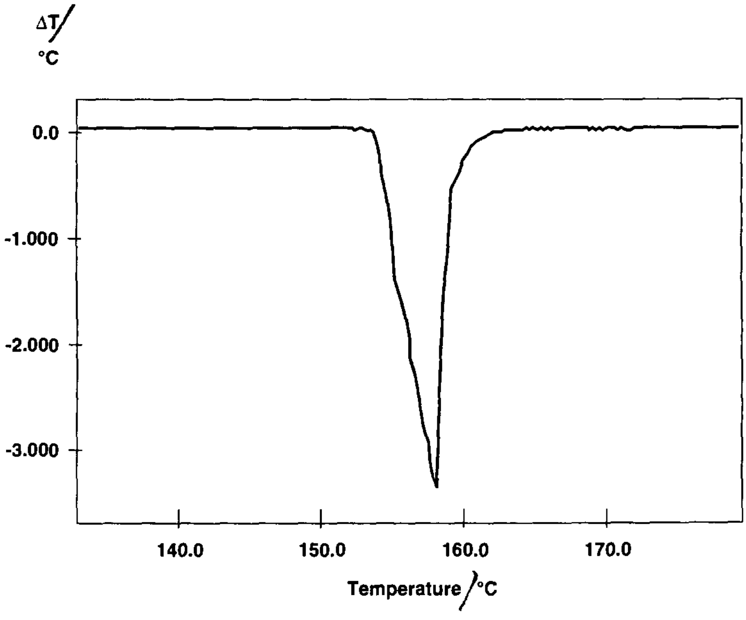

Fig. 2. Indium calibration curve, ΔT vs. T.

Fig. 2 shows the DSC curve for indium under the control condition. Similar experiments were performed for tin and lead under the control conditions. The heats of fusion for indium, tin, and lead under different calibration conditions are listed in Table 2.

Since the control conditions were the experimental conditions for indium, tin, and lead, theoretical heats of fusion should be observed. Results proved that it is true for indium and tin, but not so for lead. It is believed that there was a coating of oxidized lead on the lead sample's surface. From this result, it is recommended that lead should not be used as a standard material.

When the heat of fusion values at different calibration conditions are compared with those from the control condition, it can be seen that the biggest deviation from the

Table 2
Peak areas in J g^{-1} obtained after applying calibration[a]

	Control	Calib. #1	Calib. #2	Calib. #3	Calib. #4	Calib. #5	Calib. #6
Indium	28.4	32.1	22.7	28.5	30.1	30.8	30.0
Tin	59.2	59.8	47.2	57.7	58.7	61.8	62.2
Lead	21.4	23.4	17.2	19.8	21.1	22.5	20.9

[a] Theoretical values for the melting enthalpy are 28.4, 59.2, and 23.2 J g^{-1} for indium, tin, and lead, respectively.

correct value was under the calibration condition #2. The difference is that two sample cups were used in the calibration condition #2 and no cup was used in all of the rest of the calibration experiments. Introduction of thermal masses into the system shifted the baseline and heating pattern for the whole temperature range, and eventually the calibration parameters of heat capacity calibration. Such an effect is significant.

By comparing the heat of fusion measured under the calibration condition #1, which had water contamination, with theoretical values, it can be seen that the lowest temperature reaction, melting of indium (which occurred at 156.7°C), was affected to a larger extent. This is due to the large distortion of the baseline at the low temperature range caused by water. To the contrary, switching off the reaction gas (calibration conditions #3), had the least effect on the heat measurement of the low-temperature reaction. It is believed to be caused by changing of the heat sink created by the reaction gas during the heating process. Similar to calibration condition #3, switching off the cooling water, calibration condition #5, created deviations on the measured heats of fusion. However, the heat sink effect was different.

The combination of various calibration conditions, calibration conditions #4 and #6, had a joint effect on the heat measurement. However, the effect of introducing different thermal masses into the system had the largest effect.

4. Conclusions

Baseline calibration was proved to be very important in order to obtain correct heat information of samples. It is important to keep the experimental conditions the same as those of the calibration runs, or apply correct calibration results for the experiments. Results have shown that the largest influence was created by introducing thermal masses into the system. Smaller effects were observed on switching on/off reaction gas and cooling water. Contamination by water caused a larger effect on the low-temperature transition.

It is also concluded that lead is not a good standard material for testing heat of fusion on DSC, due to the oxidation which had occurred on the lead surface.

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