Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 1, 131–134

NEW NIST-TRACEABLE STANDARDS FOR CALIBRATION AND VALIDATION OF DSC[*]

D. G. Archer[**]

Physical and Chemical Properties Division, National Institute of Standards and Technology, 100 Bureau Drive, MS 8380
Gaithersburg, MD 20899-8380, USA

Several reference materials and associated reference values have been recommended for the purposes of calibration and/or validation of differential scanning calorimetry (DSC). However, issues of available sample purity, reference-property value accuracy, and potential undesired reactions between reference materials and the materials used for sample pans have not been considered sufficiently in some of the recommendations of property values for the materials. These limitations attenuate greatly the usefulness of many of these reference material recommendations. Indeed, the state of uncertainty regarding true reference property values can be shown to be a limiting factor in the uncertainty of measurements made with DSC. NIST has certified the temperatures and enthalpies of fusion of two new Standard Reference Materials, SRMs 2234 and 2235, in order to help alleviate some of the difficulty.

Keywords: *bismuth, calibration, differential scanning calorimetry, gallium, indium, standard reference material, tin*

Introduction

Differential scanning calorimetry (DSC) is a relative method, in which all instrument responses must be calibrated relative to some standards, which are primarily reference materials. Because the instrument must be calibrated, one limitation to the method's accuracy could be the accuracy of the reference materials used to calibrate the instrument.

In earlier work on thermodynamic properties of highly supercooled aqueous solutions, we examined the accuracy with which we could obtain enthalpy and heat capacity data from a DSC [1]. We concluded from our own experience that the accuracy of the DSC method for transition enthalpies was limited by the accuracy of the reference materials that were available for the calibration.

Figure 1 shows the temperature calibration curve that we constructed from several materials [2]. The symbol β refers to scan rate and all results were extrapolated to zero scan rate. The organic materials at low-temperature required significant resources for purification and even after the purification, determination of the onset of the phase transition for the adamantane sample ($C_{10}H_{16}$) was difficult in both the DSC and the original adiabatic calorimetry.

Table 1 shows results that we obtained for enthalpies of transition for three substances after calibrating the DSC with properties for indium and synthetic sapphire [3]. From these results, the potential accuracy of enthalpy changes determined by DSC with this instrument was on the order of ±0.3%.

Table 1 Enthalpy of transition results

Substance	$\Delta_{trs}H_{literature}$/ J mol^{-1}	$\Delta_{trs}H_{measured}{}^{a}$/ J mol^{-1}	Δ^{b}/%
Adamantane	3376	3387±34	0.3
Mercury	2295	2288± 9	–0.3
Water	6009	5996±18	–0.2

[a] Quantities are average values from 3 replicates. The ± values are the sum of estimated uncertainties for both the measured and calculated quantities, and are not the uncertainties in the enthalpies measured with the DSC. The uncertainty in the value for adamantane is much larger due to factors that are discussed in the text; [b] $\Delta=100(\Delta H_{trs,exp}-\Delta H_{trs,lit})/\Delta H_{trs,lit}$

The problem though is how one chooses reference materials for calibration and validation of DSC. It is often not clear from published recommendations of calibration standards what the true uncertainties are in those recommended property values. As just one example, we consider the fusion temperature of cyclopentane, a substance which has been recommended by the German Society for Thermal Analysis (GEFTA) for calibration of DSC. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommended the use of commercial samples of cyclopentane of 99% or better purity and recommended that a fusion temperature of 179.71 K be used with those samples [4]. The ICTAC-recommended fusion temperature had been reported much earlier for samples of very high purities, purities which cannot be obtained commercially. We determined the fusion temperature of a commercial

---

[*] Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.
[**] donald.archer@nist.gov

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

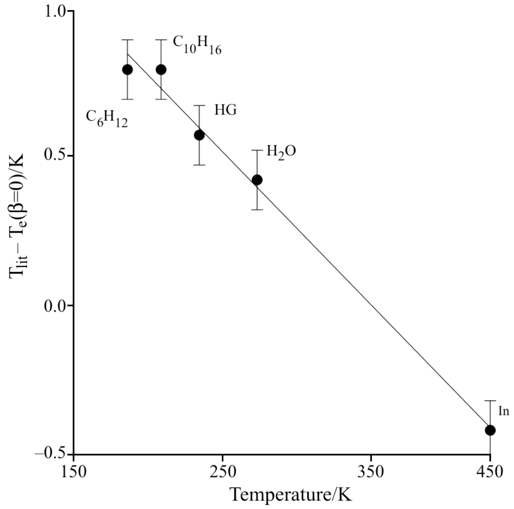

Fig. 1 Temperature calibration curve for a DSC

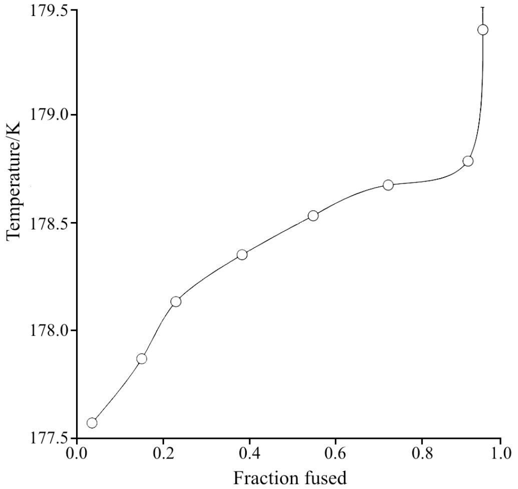

Fig. 2 Temperature *vs*. fraction fused for cyclopentane

sample that was determined to be 99.5% pure, the highest purity we could obtain commercially on a special order. The measured fusion temperature for that sample is shown in Fig. 2. The true fusion temperature of that sample, taken as the temperature of the 50% fused sample, was 1.2 K different from the value that the ICTAC recommended. Clearly, using the ICTAC's cyclopentane recommendation would introduce significant error into the calibration of the DSC. Considering the error due to the inaccurate fusion temperature recommendation, within the context of Fig. 1, one sees clearly that the reference material error would be larger than the native error in the instrument and that the use of the ICTAC recommended property value would make the instrument more inaccurate than if no calibration at all had been performed. Often, metals are recommended for calibrating and/or validating the temperature and enthalpy scales of the DSC. Unknown uncertainties also exist for recommendations of enthalpies of transition of metals used for calibration. Gmelin and Sarge [5] reviewed the literature and assessed uncertainties of the enthalpies of transition of metals commonly recommended for calibration. For metals covering the temperature range of approximately 30 to 275°C – gallium, indium, tin and bismuth – uncertainties of the recommended values were estimated to be 0.9, 0.4, 0.6 and 3.9%, respectively [5]. Clearly, the uncertainties in the enthalpies of transition of some of the commonly recommended calibration materials are significantly larger than the potential accuracy of the DSC, as demonstrated in Table 1. Obviously, calibration material recommendations have been a limiting factor in the uncertainty achievable with DSC.

Some of the uncertainty in these values may arise from chemical differences between samples, as in the above presented case of cyclopentane. It is often assumed that chemical differences must be less for metals. Indeed, metal samples with stated high purity are widely available. However, it must be cautioned that these stated purity levels are often given only on a 'metals' basis and might not include impurity determinations for some elements such as oxygen and carbon.

In addition to the problem of inaccuracy of DSC measurement arising largely from the uncertainties in reference material values, practitioners are faced with mounting pressures from quality auditors to assure traceability of calibration to National Measurement Institutes. The shortest chain of traceability, with the least compounding of uncertainty in the traceability chain, is achieved with certified reference materials available from a National Measurement Institute. The third issue with respect to reference materials relates to the concept of validation. Validation is the process by which the method is demonstrated as suitable for its use. Validation involves testing of the instrument and method and is best accomplished using a known reference standard that was not used directly for the calibration of the instrument. 'Official sources' of reference materials are often stipulated as the foremost choice for validation.

Certification of SRMs 2234 and 2235

Accurate primary determination of the enthalpy of transition is accomplished with adiabatic calorimetry. The most accurate adiabatic calorimetry depends on primary thermometry, comprising: platinum standard resistance thermometry, calibrated according to the International Temperature Scale of 1990 (ITS-90) at an NMI and measured with a high-accuracy ac inductance bridge that was calibrated with traceable Wilkins resistors of different resistances; measurement of voltages, times, and a standard resistance, all traceable to an NMI; and a demonstration of the accuracy of the calorimeter, usually achieved through measurement of the enthalpy increments for a sample of SRM 720, synthetic sapphire, also traceable to an NMI. Reference values for SRM 720 used at NIST are taken from the reference equation given by Archer [3], those being valid for the ITS-90.

An adiabatic calorimeter is one in which the heat leak from a sample to the environment is made as small as possible. Reduction of these unaccounted heat transfers is accomplished by maintaining a set of heat shields to be at the same temperature as the calorimetric sample and its container and through subtraction of the enthalpies of the calorimetric container when empty and when filled. It is assumed that most of the unaccounted heat transfers cancel when subtracting the measured enthalpy changes of the empty vessel from the measurements with the filled vessels, however, differences in the unaccounted heat transfers may exist when the calorimeter vessel is filled or empty and thus not be entirely canceled by this procedure. One type of unaccounted heat transfer arises from radiative energy transfer between the calorimeter proper and the surroundings due to small mismatches in the temperature differences between the calorimeter and the controlled adiabatic shields. Radiative energy transfer depends on surface area, therefore, for a given inaccuracy in matching the temperatures of the shields to that of the sample container, these unaccounted energy transfers become a decreasing percentage of the total measured enthalpy as the volume of the calorimeter vessel increases (surface area increases less rapidly than does volume). Additional unaccounted heat transfers can occur along electrical leads and mechanical supports, driven by temperature mismatch between the calorimeter and its surroundings. These heat transfers depend on the dimensions of the leads and supports, their materials of construction, and the temperature differences of the adiabatic shields. These conductive heat transfers do not depend strongly on the mass of the calorimeter and its contents. As such, conductive loss errors become a decreasing percentage error as the volume of the calorimeter increases. Therefore, the deleterious effects of the heat leak paths can be minimized by constructing calorimeters that hold larger amounts of sample than would be practical in more routine operations for which sample quantities might be much more limited. One such arrangement for a high temperature calorimeter is shown in Fig. 3.

We have determined the enthalpies and temperatures of transition of samples of bismuth and gallium for distribution as SRMs. For the bismuth SRM, SRM 2235, NIST obtained a 'low-oxide' sample of bismuth of 99.999% purity on a metal basis. The sample was in the form of shot, 1 to 2 mm in diameter. The gallium SRM, SRM 2234, was taken from a 30 kg lot of gallium used previously for distribution in fixed-point cells for thermometry calibration. The manufacturer's assay indicated that total detectable impurities were $1\cdot 10^{-7}$ or less, by mass, and that the residual resistance ratio was greater than 60000.

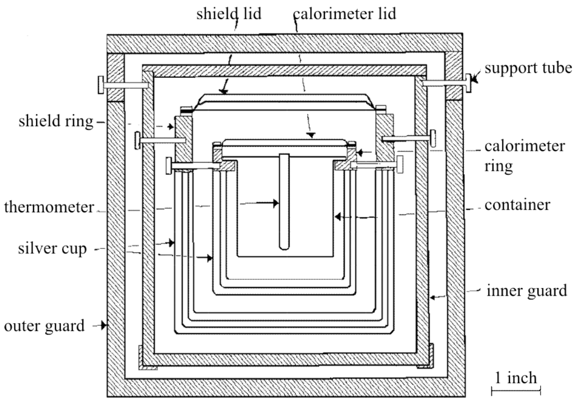

Fig. 3 Schematic drawing of the high temperature adiabatic calorimeter

The certified enthalpy of fusion of the gallium sample was determined to be 80.097±0.032 J g^{-1}, where the standard uncertainty value corresponds to a 95% confidence interval [6]. This uncertainty included uncertainties for the pre- and post-fusion enthalpy contributions; an uncertainty component that has been ignored in most other adiabatic-calorimetric determinations of the enthalpy of fusion of gallium. The triple-point temperature determined in the adiabatic calorimeter was 302.9146 K; this temperature is essentially within 2 mK of the ITS-90 fixed-point temperature.

The certified value of the enthalpy of fusion of the bismuth SRM was determined to be $\Delta_{\text{fus}}H$= 53.146±0.082 J g^{-1}, where the uncertainty corresponded to a 95% confidence interval [7]. The temperature of fusion of this sample was certified to be T_{fus}=544.556±0.005 K. Measurements of the fusion temperature *vs*. fraction fused are shown in Fig. 4.

Gallium alloys rather readily with aluminum, and this necessitates conditioning of aluminum pans used in DSC. A heat treatment for more than an hour in an oven in air at 843 K enables some aluminum pans to be resistive to chemical attack by gallium. These pans could be used for five or more fusions of gallium in one of our DSCs without noticeable drift in either the fusion temperature or the fusion enthalpy. Aluminum pans from some sources discolored during the heat treatment and these pans invariably lacked resistance to gallium.

Comparison of enthalpies of transition determined by NIST and PTB

NIST has determined the enthalpies of fusion of four different metals with three different calorimeters, all of which were capable of quite high accuracy. These four metals were gallium, indium [8], tin (SRM 2220), and

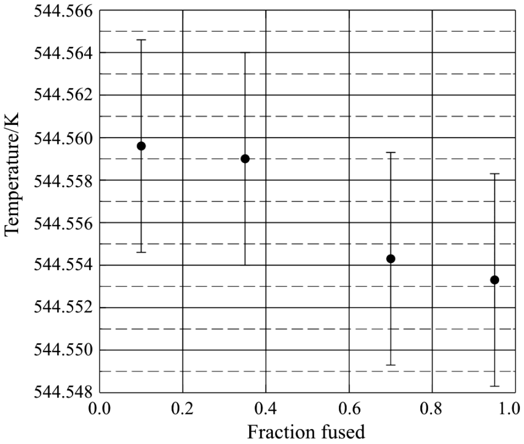

Fig. 4 Measured fusion temperatures of the bismuth sample *vs*. the fraction fused

bismuth. Two of the calorimeters were adiabatic enthalpy-increment calorimeters (colloquially called heat-capacity calorimeters) and the third was a Bunsen-type ice calorimeter. The German Physikalisch-Technische Bundesanstalt (PTB) recently retrofitted a commercial isothermal calorimeter with a special cell and electrical calibration unit [9]. Scientists at PTB used the retrofitted calorimeter to measure the enthalpies of fusion of several metals, including the four listed above. The goal in both institutes was to develop a set of enthalpy standards for calibration of differential scanning calorimetry and thermal analysis. Although the PTB apparatus could be used for measuring the enthalpies of fusion of the metals, it could not be used for enthalpy increment determinations and so the accuracy of the PTB calorimeter could not be determined by measurements on SRM 720. The PTB group, not having an adiabatic calorimeter of high accuracy, could obtain neither an independent nor a very accurate estimate of the uncertainty of their calorimetric method. Therefore, both laboratories – NIST and PTB – measured one of the metals (indium) in common, so as to eliminate sample purity effects from the determination of the uncertainty of the PTB calorimetric method. PTB measured the enthalpy of fusion of their sample of tin and also that of NIST's certified tin sample, SRM 2220, and found the two enthalpies of fusion for the two materials to agree to better than 0.1%. Additionally NIST and PTB have measured the enthalpies of fusion of different samples of bismuth and gallium. The determinations between the two NMIs for four well characterized metals, two of which were measured in common, allows now for an estimation of the accuracy of the PTB calorimeter and the methods used at PTB. Table 2 shows the NIST determinations of the enthalpies of fusion and their uncertainties for the certified reference materials, the PTB determinations of the enthalpies of fusion, and the differences between the two. Of the four metals listed, different samples were used between NIST and PTB for three of the four listed; NIST and PTB used the same sample of indium for the determinations made between the two institutes and PTB confirmed the NIST value for SRM 2220. The values determined between the two NMIs for all four metals agree substantially better than 0.1% with the root-mean-square difference for the four being approximately 0.05%. It is quite clear from Table 2 that the enthalpies of fusion of these four metals are now known quite well. The uncertainties of the now-established enthalpies of fusion of the four metals have been reduced by about an order of magnitude. A new generation of enthalpy calibration is now at hand.

Table 2 Comparison of NIST and PTB enthalpies of fusion of reference materials

Material	NIST $\Delta_{\mathrm{fus}}H$/J g^{-1}	PTB $\Delta_{\mathrm{fus}}H$/J g^{-1}	Difference/ %
Gallium	80.097±0.032[a]	80.136[e]	–0.05
Indium	28.6624±0.0076[b]	28.639[e]	+0.08
Tin	60.216[c]	60.238[e]	–0.04
Bismuth	53.146±0.082[d]	53.142[e]	+0.01

[a][6], [b][8], [c]SRM 2220 Certificate, [d][7], [e][9]

Conclusions

NIST has certified the enthalpies of transition and transition temperatures for two new SRMs (SRM 2234 and SRM 2235). SRM 2234 is a 1.5 to 2 g sample of gallium. SRM 2235 is a 1.5 g of bismuth packaged under argon. They are available from the Measurement Services Division at NIST. Information and on-line ordering of NIST's Standard Reference Materials are available at: http://ts.nist.gov/ts/htdocs/230/232/232.htm.

References

1 D. G. Archer and R.W. Carter, J. Phys. Chem. B, 104 (2000) 8563.
2 R. W. Carter and D. G. Archer, Phys. Chem. Chem. Phys., 2 (2000) 5138.
3 D. G. Archer, J. Phys. Chem. Ref. Data, 22 (1993) 1441.
4 R. Sabbah, A. Xu-Wu, J. S. Chickos, M. L. Planas Leitão, M. V. Roux and L. A. Torres, Thermochim. Acta, 331 (1999) 93.
5 E. Gmelin and S. M. Sarge, Pure Appl. Chem., 67 (1995) 1789.
6 D. G. Archer, J. Chem. Eng. Data, 47 (2002) 304.
7 D. G. Archer, J. Chem. Eng. Data, 49 (2004) 1364.
8 D. G. Archer and S. Rudtsch, J. Chem. Eng. Data, 48 (2003) 1157.
9 S. Rudtsch and S. M. Sarge, personal communication.

DOI: 10.1007/s10973-005-7356-6