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Enthalpy of Fusion of Bismuth: A Certified Reference Material for Differential Scanning Calorimetry[†]

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An adiabatic calorimeter was used to measure the enthalpy of fusion of a sample of high-purity bismuth. The new value of the enthalpy of fusion was determined to be $\Delta_{\text{fus}}H = (53.146 \pm 0.082)\ \text{J·g}^{-1}$, where the uncertainty corresponded to a 95% confidence interval. The temperature of fusion of this sample was found not to differ with previous accurate determinations within the accuracy of the fusion-temperature determination made in the present study. A comparison with some other enthalpy of fusion determinations is made.

Introduction

Differential scanning calorimetry (DSC) requires calibration of both the temperature and the enthalpy responses of the calorimeter. Temperature calibration is accomplished by determining the instrument's response for two or more enthalpic events that are characterized by well-defined temperatures. As such, onset temperatures observed for first-order phase transitions are often recommended for temperature calibration protocols; for an example, see the ASTM International Standard Practice E967.[1] Temperature-calibration protocols generally require two or more transitions to be determined where these temperatures either bracket or span across the desired temperature range of interest, the former in the case where only two calibration temperatures are used, the latter if more than two calibration temperatures are used.

Some calibration protocols require calibration of the heat-flux signal of the calorimeter by means of multiple known enthalpies of transition,[2] while other calibration methods require calibration with one known enthalpy of transition combined with the known heat capacity of synthetic sapphire. Synthetic sapphire is a material with a very well-known enthalpy−temperature function.[3] An example of the latter type of calibration protocol is ASTM International Standard Practice E968.[4]

Validation of measurement protocols is becoming more important. Validation of enthalpy determinations made with differential scanning calorimeters can be achieved with materials that possess well-known enthalpies of transition.

There are many materials that possess first-order phase transitions and may be considered as candidates for calibration and validation purposes. The most often recommended of these are the fusions of pure metals. These recommendations reflect the facts that metals of apparently high purity are readily available and their transition temperatures are highly reproducible and fairly well known. Here we describe certification of the enthalpy of fusion and the fusion temperature of a sample of bismuth for distribution as a Standard Reference Material for DSC.

Experimental Section

The National Institute of Standards and Technology (NIST) purchased a "low-oxide" sample of bismuth of 99.999% purity on a metals basis. The sample was in the form of shot, 1 mm to 2 mm in diameter. The several sealed glass ampules were opened in an inert atmosphere in a glovebox and combined in a single vessel. The sample used in the certification measurements was taken from this larger sample of combined material. After completion of the measurements, the calorimetric sample was removed from the calorimeter. Inspection showed that the test sample was clearly still in the form of shot; in other words, despite being fused in the calorimeter several times, the individual shot pieces did not fully coalesce.

The high-temperature adiabatic calorimeter used in this work was that described by Archer and Rudtsch.[5] The thermometer used for these measurements was a specially constructed 25-Ω platinum thermometer (Hart Scientific) that was calibrated at the NIST according to the ITS-90.[6] The ITS-90 calibration specified determination of the thermometer's resistance at the triple point of water and at the freezing points of tin and zinc. The electronic measurement instruments, data acquisition instruments, and instrument control methods, including the digital PID detector control of the shield temperatures, have been described previously.[5,7]

The bismuth sample was contained in a seamless tantalum crucible that was in turn inserted into the aluminum calorimeter housing. The mass of bismuth in the tantalum crucible was determined by weighing, correcting for buoyancy. The mass of bismuth in the calorimeter was 26.8142 g. The inert gas used in the calorimeter was argon.

In the determination of the enthalpies and temperatures of transition, it is unnecessary to determine separately the enthalpy of the empty calorimeter vessel as a function of temperature, provided that the vessel has a monotonically

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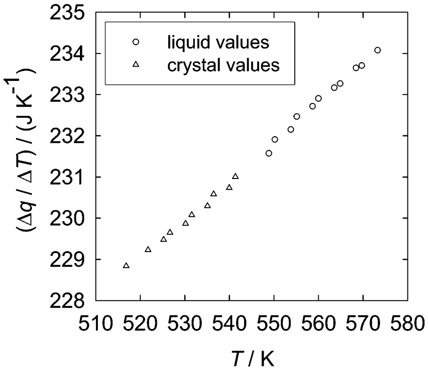

Figure 1. Values of $(\Delta q/\Delta T)$ calculated from measured quantities for the crystal and liquid phases of the sample of bismuth.

or gradually varying heat capacity in the region of the melting temperature, i.e., no component of it undergoes a transition in the temperature range of interest. Preliminary checks of the enthalpy of the empty calorimeter showed this condition to be satisfied.

Results

Enthalpy of Fusion. We observed significant supercooling of the bismuth sample; the sample did not show freezing until temperatures more than 25 K below the fusion temperature were achieved. Cooling to a few kelvins below the temperature at which the freezing effect was observed resulted in erratic and low values for the subsequently determined enthalpy of fusion, indicating that the entire sample did not freeze at that temperature. Ultimately, a process was instituted in which the calorimeter was cooled to $T < 400$ K between fusion determinations. This cooling procedure allowed reproducible determinations of the enthalpy of fusion.

Figure 1 shows the quantity $(\Delta q/\Delta T)$ obtained from individual measurements from 514 K to 576 K for the crystal and liquid phases of bismuth plus the calorimetric addenda (where q is heat and T is temperature). The quantity $(\Delta q/\Delta T)$ is only an approximation of heat capacity, and it is an approximation that becomes increasingly poor with increasing curvature of the heat capacity function. Thus, we treat these measurements as what they are, enthalpy increment measurements.

The enthalpy increment for changing the temperature of the calorimeter and its contents from T_1 to T_2 is $\Delta H(T_1 \rightarrow T_2)$. The enthalpy increments for the calorimeter containing all crystallized material or all liquid material are specified by subscripts cr and l, respectively. The enthalpy increments for the two cases of calorimeter + solid bismuth and calorimeter + liquid bismuth were represented by linear functions. Ten enthalpy increment measurements for the crystal phase plus the calorimeter for the temperature range of 514.4 K to 543.8 K were fitted with a function, linear in the parameters, obtaining

$$\Delta H_{\mathrm{cr}}(T_1 \rightarrow T_2)/H^0 = (229.931 \pm 0.049)(T_2 - T_1)/T^0 + (0.08685 \pm 0.0065) [(T_2^{\,2} - T_1^{\,2})/2 - (530\ \mathrm{K})\,(T_2 - T_1)]/T^{-2} \quad (1)$$

where H^0 was 1 J, T^0 was 1 K, and where the uncertainties are the calculated 95% confidence intervals in the least-squares model. The standard deviation of the residuals was 0.028%.

Eleven measured enthalpy increments for the liquid phase and the calorimeter from 546.3 K to 575.7 K were fitted with a function, linear in the parameters, obtaining

$$\Delta H_{\mathrm{l}}(T_1 \rightarrow T_2)/H^0 = (231.840 \pm 0.094)(T_2 - T_1)/T^0 + (0.09755 \pm 0.0072) [(T_2^{\,2} - T_1^{\,2})/2 - (550\ \mathrm{K})\,(T_2 - T_1)]/T^{-2} \quad (2)$$

The standard deviation of the residuals was 0.033%.

Determinations of the enthalpy increments that spanned the fusion temperature are given in Table 1. The enthalpy of fusion was extracted from the measured heat, $\Delta q(T_1 \rightarrow T_2)$, by

$$\Delta_{\mathrm{fus}}H = [\Delta q(T_1 \rightarrow T_2) - \Delta H_{\mathrm{cr}}(T_1 \rightarrow 544.556\ \mathrm{K}) - \Delta H_{\mathrm{l}}(544.556\ \mathrm{K} \rightarrow T_2)]/m \quad (3)$$

where m was the mass of bismuth in the calorimeter and 544.556 K was the fusion temperature determined here. The second and third terms within the square brackets are the pre-fusion and post-fusion heats, respectively, that are listed in Table 1. The standard deviation (unbiased) of the fusion enthalpies and the standard deviation of the means, calculated from the three determinations, are given in Table 1.

Uncertainties were calculated as described previously.[5] The standard deviation of the means was multiplied by a coverage factor of 3. To this quantity, twice the standard deviation for the pre- and post-transition enthalpy increments was added. This quantity clearly overestimates the uncertainty from this source, if different initial and final temperatures are used for the enthalpy increments, as was the case here. The resultant uncertainty value, 0.082 J/g, corresponded approximately to a 95% confidence interval for the enthalpy of fusion.

Uncertainty components that arose from the mass determination and calibration of the electronic instruments were at least 2 orders of magnitude smaller than the calculated 95% confidence interval, respectively, and are considered here no further.

Temperature of Fusion. Measurements were performed in which known fractions of the sample were fused and temperatures determined simultaneously. The partially transformed systems approached equilibrium only slowly. Examples taken from two different partial fusion equilibrations are shown in Figure 2. Even after several hours of elapsed time, the system was not completely in equilibrium. Therefore, temperature data for each of the partial transformations were collected over time and were corrected for the nonadiabaticity of the calorimeter. We obtained values of the equilibrium temperature from the temperature curves of the type shown in Figure 2 by fitting the last 15 to 25 determinations of each curve against the inverse square of time

$$T(\text{observed}) = T(\text{equilibrium}) + a/(t/t^0)^2$$

where t was the time elapsed and t^0 was 1 s. The equilibrium temperatures from four different fractions fused are shown in Figure 3. The error bars are estimates of uncertainty that incorporate judgment as to contributions that arise from model bias effects on the determination of the equilibrium temperature.

The certified temperature of fusion was obtained by averaging the four values shown in Figure 3, giving $T_{\mathrm{fus}} =$ 544.556 K. The unbiased standard deviation of the four values is 0.0032 K, which leads to a standard deviation of the means of 0.0019 K. Adopting a coverage factor of 3 gives an uncertainty of 0.0054 K. The certified temperature of

Table 1. Enthalpy of Fusion Determinations for Bismuth

T_i/K	T_f/K	q/J	ΔH(pre-fusion)/J	ΔH(post-fusion)/J	q(fusion)/J	$\Delta_{fus}H$/J·g^{-1}
542.2484	555.1614	4416.851	533.281	2458.614	1424.955	53.1418
542.6908	555.5986	4416.605	431.063	2560.203	1425.339	53.1561
542.3649	555.2662	4414.244	506.362	2482.956	1424.927	53.1407
					average	53.1462
					standard deviation of population	0.0086
					standard deviation of means	0.0050

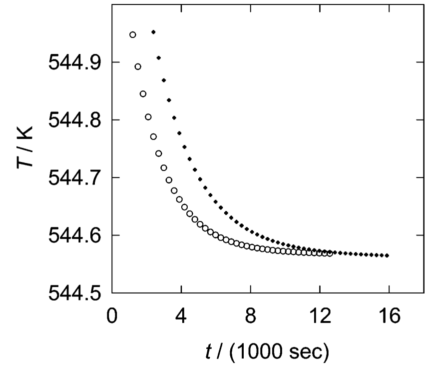

Figure 2. Temperature against time determinations following the heating periods for two partial fusion measurements. The symbols were calculated from linear representations of 300 measurements taken at 1 reading per second.

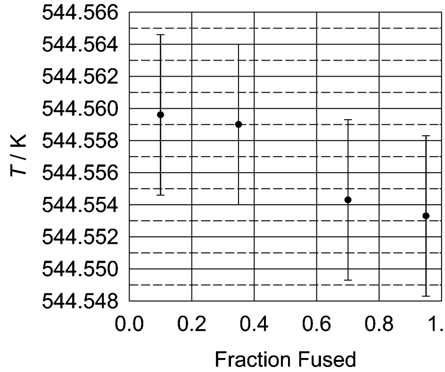

Figure 3. Values of the measured fusion temperature against the fraction fused, F, for the sample of bismuth.

fusion is thus $T_{fus} = (544.556 \pm 0.005)$ K. This value agrees within its uncertainty with other values in the literature, described next. We note that we cannot declare whether the difference between this certified value and that described below is due to small differences between our sample and those in the laboratory of Murdock, which would be a real effect, or due to error in our extrapolations of our temperature decays to equilibrium, which would be an artifactual effect.

McLaren and Murdock[8] determined carefully the temperatures of fusion of several samples of bismuth using several different platinum-resistance thermometers. Their recommended fusion temperature value was 271.375 °C on the International Practical Temperature Scale of 1948 (IPTS-48). Applying to their recommended fusion temperature an adjustment of +0.067 °C for conversion to the International Practical Temperature Scale of 1968 (IPTS-68) and then applying an adjustment of −0.039 °C for the conversion from the IPTS-68 to the ITS-90 gives a fusion temperature of 544.553 K on the ITS-90. The uncertainty of this value should include propagation of the nonuniqueness of the IPTS-48, of the IPTS-68, and of the ITS-90.

Ancsin and Murdock[9] used several different thermometers to determine temperatures of fusions of several metals including bismuth. The context of their work was, in part, to examine nonuniqueness of the IPTS-68 and the ITS-90, and to examine the reliability of the temperatures assigned to fixed points. Their average fusion temperature value for bismuth, on the ITS-90, was 544.553 K with a reported nonuniqueness of 1 mK.

Discussion

Two recent examinations of the previously published enthalpy of fusion values for bismuth were made in order to recommend an enthalpy of fusion value for bismuth for use in calibrations.[2,10] The literature basis from which to draw a recommendation did not change significantly between those two examinations of the literature, yet the recommended values and their recommended uncertainties were quite different. Sarge et al.[2] recommended $\Delta_{fus}H = (53.83 \pm 2.1)$ J·g^{-1}, which they obtained by averaging three literature values, whereas Stølen and Grønvold[10] recommended (53.33 ± 0.26) J·g^{-1}, which was nearly identical to Grønvold's[11] determination of the value but with a significantly larger assigned uncertainty. The differences between these two contemporaneous recommendations reflected the wide variance in published values for the enthalpy of fusion of bismuth, specifically, and this is the case also with many other metals.

A further example of the wide variation in previously reported enthalpies of fusion of metals is found with the most commonly recommended metal for calibration of differential scanning calorimetry, namely, indium. It was noted previously[5] that certified enthalpy of fusion values for indium, i.e., values distributed as “traceable” to a National Measurement Institute (herein NMI), spread across approximately 1%. It was also observed that values of the enthalpy of fusion of indium solely from adiabatic calorimeters also spread across approximately 1%. The limitations in accuracies of previous determinations of the enthalpies of fusion of metals required a concomitant recognition that the enthalpy response of differential scanning calorimeters could not be calibrated to better than 1% because the calibration protocols all stipulated calibration with at least one enthalpy value for a transition of a metal, usually that for the fusion of indium.

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,[7] indium,[5] tin,[12] and the present value for bismuth. Two of the calorimeters were adiabatic enthalpy-increment calorimeters (colloquially called heat-capacity calorimeters)[5,7] and the third was a Bunsen-type ice calorimeter.[12] The German Physikalisch-Technische Bundesanstalt (PTB) recently retrofitted a commercial isothermal calorimeter with a special cell and electrical calibration unit. Scientists at PTB used the retrofitted calorimeter to measure the enthalpies of fusion of several metals, including the four listed above.[13] The goal in both institutes was to develop a set of enthalpy standards for calibration of differential scanning calorimetry and thermal analysis. The PTB group, not having an adiabatic calorimeter of high accuracy, could not obtain a very accurate estimate of the uncertainty of their calorimetric method.

Table 2. Comparison of NIST and PTB Values for the Enthalpies of Fusions of Metals

material	$\Delta_{fus}H/(J \cdot g^{-1})$ NIST	$\Delta_{fus}H/(J \cdot g^{-1})$ PTB	% 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] Reference 7. [b] Reference 5. [c] Reference 12. [d] Present work. [e] Reference 13.

Both laboratories measured one of the metals (indium) in common. PTB measured the enthalpy of fusion of their sample of tin and also that of NIST's certified tin sample, which is 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 essentially 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 ~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 materials is now at hand.

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