Enthalpy of Fusion of Indium: 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 very pure sample of indium. The new value of the enthalpy of fusion was determined to be $\Delta_{\mathrm{fus}}H = (28.6624 \pm 0.0076)\ \mathrm{J{\cdot}g^{-1}}$, where the uncertainty corresponded to a 95% confidence interval. The temperature of fusion of this sample was found to not differ from the ITS-90 assigned value within the accuracies of the thermometry used in the present study. A comparison with previous determinations is made.

Introduction

Indium has been recommended as a material suitable for calibration of thermal analysis instruments.[1−3] One of these references recommended indium for calibration of the temperature scale of the thermal analysis instrument, and the other two recommended indium in a caloric calibration protocol. Additionally, indium serves as a heat flow calibration material in ASTM Standard Practice E968.[4] The temperature of fusion of indium is reasonably well determined for these purposes, and it serves as a fixed-point temperature on the International Temperature Scale of 1990.[5] The enthalpy of fusion of indium is less well-known.

Due to the importance of indium in the calibration of thermal analysis instruments, there are many "recommended" values in the literature. Recently, Sabbah et al.,[6] through the International Confederation for Thermal Analysis and Calorimetry (ICTAC), gave a series of recommended values for reference materials to be used for the calibration of calorimetric and thermal analysis instrumentation. In their section titled "3.1.3 $\Delta_{\mathrm{fus}}H$, indium", they recommended an enthalpy of fusion value for indium of $(3286 \pm 13)\ \mathrm{J{\cdot}mol^{-1}}$ and stated that "certified samples are available from NIST ... SRM 1971". (SRM is the acronym that the National Institute of Standards and Technology (NIST) uses for its Standard Reference Materials. NIST's SRMs are materials accompanied by NIST certifications that the materials have a particular property value.) Sabbah et al.'s description is incorrect on multiple counts. NIST's SRM 1971 is an indium freezing-point cell that has very pure indium sealed within the Teflon cell. NIST did not intend for this cell to be dissected so that the indium could be removed from it and subsequently used as an enthalpy of fusion reference material for caloric calibration of thermal analysis instruments. Second, the value given was not a NIST-certified value. Third, at the time of Sabbah's writing, NIST had not certified an indium enthalpy of fusion standard. Only later did NIST make available a certified SRM (SRM 2232), and it has a "certified" value different than that from Sabbah et al.[6]

There are several sources of "certified" indium available for calibration of differential scanning calorimeters (DSCs).[7] Unfortunately, each of these different materials has associated with it a "certified" enthalpy of fusion value different from the others. For example, the LGC (Laboratory of the Government Chemist, U.K.) sells two "certified" indium specimens for use in calibration of DSCs. One of these has the "certified" properties, $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = 3.296\ \mathrm{kJ{\cdot}mol^{-1}}$ $(28.71 \pm 0.078\ \mathrm{J{\cdot}g^{-1}})$ and a fusion temperature of 156.61 °C (429.76 K). The other specimen distributed by LGC is NIST's SRM 2232 with certified properties $\Delta_{\mathrm{fus}}H = (28.51 \pm 0.19)\ \mathrm{J{\cdot}g^{-1}}$ and 156.5985 °C (429.7485 K). Recently, the German Physikalisch-Technische Bundesanstalt (PTB) certified a sample of indium for calibration of DSCs. Their certified values are (156.598 ± 0.004) °C ((429.748 ± 0.004) K) and $(28.64 \pm 0.11)\ \mathrm{J{\cdot}g^{-1}}$ for the temperature and enthalpy of fusion of that sample.[8] Another certified sample is available from the National Research Center for Certified Reference Materials in China. Their certified values are (156.60 ± 0.01) °C and $\Delta_{\mathrm{fus}}H = (28.44 \pm 0.06)\ \mathrm{J{\cdot}g^{-1}}$. The discrepancies in these four "certified" enthalpy of fusion values (a range of 1%) could be taken to mean that calorimeters for which the enthalpy of fusion of indium is used for calibration cannot be calibrated more accurately than ±1%. Of course, decisions might be made as to which of these certified values was most likely determined with the most accurate equipment, and the assumed uncertainty of calibration could be considered reduced in this way. But such a decision might conflict with a requirement of traceability of calibration to a National Measurement Institute.

All of the uncertainties cited above corresponded approximately to 95% confidence intervals, obtained with different numbers of underlying measurements. Additionally, some of the cited uncertainties included somewhat arbitrary contributions for nonrandom errors. Without the estimated contributions from systematic biases and using

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[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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statistical tests, the differences between the two certified materials from LGC cannot be considered as arising from random variations.

High-accuracy adiabatic calorimetry and intercomparison with the same lot of material could serve to reduce the uncertainty of some of the certified materials and some of the methods used for certification. The present work presents new measurements of the enthalpy of fusion of one of the certified samples of indium (PTB's) with a highly accurate calorimeter at NIST, so as to improve the accuracy of the enthalpy of fusion value for indium and the confidence with which it can be used.

The present work arose through a Memorandum of Understanding signed between NIST, the PTB, and the Bundesanstalt für Materialforschung und -prüfung (BAM). The Memorandum of Understanding allows for cooperation between the signatory National Measurement Institutes for various purposes including, but not limited to, the mutual development and exchange of Certified Reference Materials and comparisons of national standards. The sample of material measured was supplied by PTB, and one of PTB's scientists (S.R.) visited NIST during the conduct of the measurements reported herein. The material was from the lot of material certified previously by PTB.

We note that NIST also distributes indium for calibration of differential scanning calorimetry as Standard Reference Material 2232, certified for temperature and enthalpy of fusion for calibration of differential scanning calorimetry. The enthalpy of fusion value reported on the SRM certificate is different from the value reported in the present work. The present value, although obtained with instrumentation of greater accuracy than that used for the SRM certification, cannot be considered a replacement value for the SRM because the present value was not obtained with the material that is distributed as NIST's SRM.

Experimental Section

The calorimeter used for the present work is based on the earlier work of West.[9−11] Those references can be consulted for approximate descriptions of the calorimetric shield construction and the principles considered for that particular design. The calorimeter vessel, the thermometry, and the instrument control and data acquisition packages are different from those described by West. These will be described in greater detail elsewhere.

The 25-Ω platinum-resistance capsule thermometer was specially constructed for this application by Hart Scientific and calibrated according to the ITS-90 at NIST. For the temperature range over which the present thermometer was calibrated, the ITS-90 specifies that the thermometer's resistance is to be determined at the triple point of water and at the freezing points of tin and zinc. These fixed-point temperatures of the ITS-90 are realized accurately in specially constructed cells that are carefully characterized for various effects, including lack of contamination of the reference material, pressure effects, and stem-length effects.

Other aspects of measurement of the resistance of the thermometer, time, voltage, and so forth are as described elsewhere.[12,13] Control of the adiabatic and guard shields are as described elsewhere.[13] The indium sample was contained in two seamless tantalum cylinders contained in the calorimeter. The automatic-balancing ac thermometry bridge was calibrated with Wilkins standard resistors of nominal resistances of (10, 25, and 100) Ω and which are suitable as resistance standards for the frequency used by the thermometry bridge. Each of these standard resistors had an uncertainty of calibration stated as $(3 \times 10^{-6})R$, where R is the resistance of the standard. Therefore, the systematic uncertainty in measurement of the absolute resistance of the thermometer was about $(1.7 \times 10^{-6})R$, which corresponds to approximately 0.7 mK in temperature. One junction of a thermocouple was placed between the walls of one of the tantalum cylinders and the concentric well in the calorimeter vessel in which the cylinder was placed; the other junction was placed in the top of the well in which the thermometer was placed. The voltage of this differential thermocouple was monitored with an isolated nanovoltmeter, as a function of time, with a partially fused sample of indium in the tantalum vessel in the calorimeter. The measurements were consistent with gradients of less than 1 mK between the thermometer well and the sample-containing well, when equilibrium was established. Therefore, the total uncertainty in the thermometer temperature was expected to be about 1 mK.

Table 1. Impurities Determined in the Present Sample of Indium

element[a]	impurity as $\mu g \cdot g^{-1}$	impurity as mole fraction $\times 10^6$
Al	4	17
Zr	1	1
Ti	0.08	0.2
Mg	0.06	0.3
Tl	0.06	0.03
Sc	0.07	0.2
Hf	0.07	0.04
Sr	0.02	0.03
Ag	0.01	0.01

[a] Elements analyzed but found to be less than 0.01 $\mu g \cdot g^{-1}$: Li, Be, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Y, Nb, Mo, Tc, Ru, Rh, Pd, Sb, Te, I, Cs, La, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Re, Os, Ir, Pt, Au, Hg, Th, U, Pu.

The sample of indium used for the present work was in the form of approximately spherical shot, each piece of which had a small tail that apparently arose from dropping of the molten indium at a temperature near the fusion temperature. The sample of indium was analyzed for several impurities at PTB. The results of this analysis are given in Table 1 and showed the sample to have total impurities of at least 2×10^{-5} mole fraction (i.e. purity ≤ 0.999 98 mole fraction) with several elements, most notably oxygen, having been not determined in the analysis. The largest apparent impurity was aluminum, constituting approximately 90% of the determined impurities. No attempt was made to purify further the indium prior to use. The mass of indium used in the present measurements was 36.6242 g, which is the buoyancy-corrected value. This sample was divided between two tantalum cylinders placed in the calorimeter. After six fusions in the calorimeter, the indium in the tantalum cylinders had not coalesced completely, evidenced by the appearance of partially joined, somewhat-spherical shapes with apparent voids between them. The failure to coalesce may have been due to the presence of a refractory coating on the indium shot. The failure of individual powder particles to coalesce was observed previously by Andon et al.[14] for a sample of indium powder that contained approximately 500 ppm of oxygen. However, we note that the lack of complete coalescence is not proof of the presence of impurity.

Preliminary enthalpy increment measurements for a sample of NIST's SRM-720, synthetic sapphire, were also made with the present calorimeter. This sample was taken from a larger sample of the material. The sample was calcined at 1273 K for 4 h. The mass of sapphire used was 124.8721 g, corrected for buoyancy. The temperature

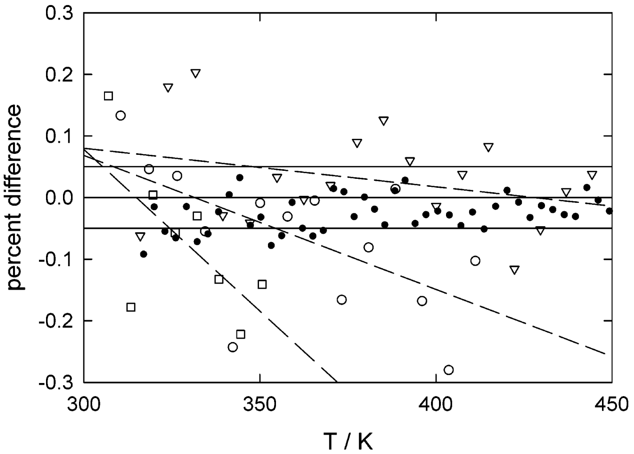

Figure 1. Comparison of new measured results for SRM-720 and results reported by Stølen et al.[18] for synthetic sapphire to values calculated from the equation given by Archer.[15] The small filled circles are for the present measurements. The open symbols are for different measurement series from ref 18. The dashed lines show trends of the individual measurement series. The rms deviation of the present results from the reference values was ±0.039%. The average deviation was −0.028%. The greater precision and accuracy of the calorimetric values obtained with the present calorimeter is obvious from the figure and from the rms and average differences for the respective measurements.

interval for the sapphire measurements was approximately 3 K.

In the determination of the enthalpy of fusion, 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 varying heat capacity in the region of the melting temperature and that 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 was satisfied.

The measurements for both materials were made with CO_2 gas in the calorimeter as described by West et al.[9−11]

Results

The sapphire enthalpy increment measurements were represented with a simple function. The root-mean-square (rms) deviation for the enthalpy increments was ±0.026%. This rms deviation corresponded to approximately ±0.0083% of the total measured enthalpy increment for the calorimeter and SRM 720. If this standard deviation were considered as arising entirely from the temperature measurements, then it would correspond to a standard deviation of ±0.17 mK in the temperature measurement. This value, ±0.17 mK, corresponds approximately to the resolution of the thermometry used in the present study. Comparison of the measured values with Archer's[15] representation of the thermodynamic properties for SRM-720 is shown in Figure 1. Agreement is well within the ±0.05% uncertainty claimed previously for the reference values for SRM 720.[15] The agreement demonstrates the accuracy achievable with the present calorimeter at these temperatures. Because all of the differences between the present measurements for SRM 720 and those upon which the reference values are based can be explained by the resolutions of the thermometry and differences in laboratory temperature scales, there is no need to invoke uncertainty components arising from unaccounted heat transfers within the present calorimeter.

Figure 2 shows the quantity $(\Delta q/\Delta T)$ obtained from individual measurements for the indium sample in the vicinity of the melting temperature, where Δq was the measured energy added to the calorimeter, in joules, and ΔT was the difference of the initial and final temperatures for the enthalpy increment. The quantity $(\Delta q/\Delta T)$ is only an approximation of heat capacity and is an approximation that becomes increasingly poor with increasing curvature of the heat capacity function, for constant ΔT. Figure 2b shows the values of $(\Delta q/\Delta T)$ very near to the fusion temperature. The horizontal bars show the temperature increment, ΔT, that corresponded to each of the values of $(\Delta q/\Delta T)$. The largest value of $(\Delta q/\Delta T)$ in Figure 2b, that is, the value closest to the fusion temperature, had values of T_1 and T_2 of 429.6946 K and 429.7390 K, respectively. In other words, the temperature increment was only 44.4 mK and the final temperature was within approximately 9.5 mK of the fusion temperature. Also shown in the figure is the premelting behavior predicted for a liquid-soluble/solid-insoluble impurity with mole fraction 1×10^{-8}; the calculated function is in quantitative agreement with the measured values of $(\Delta q/\Delta T)$. However, from the chemical analysis we know that the impurity mole fraction is at least

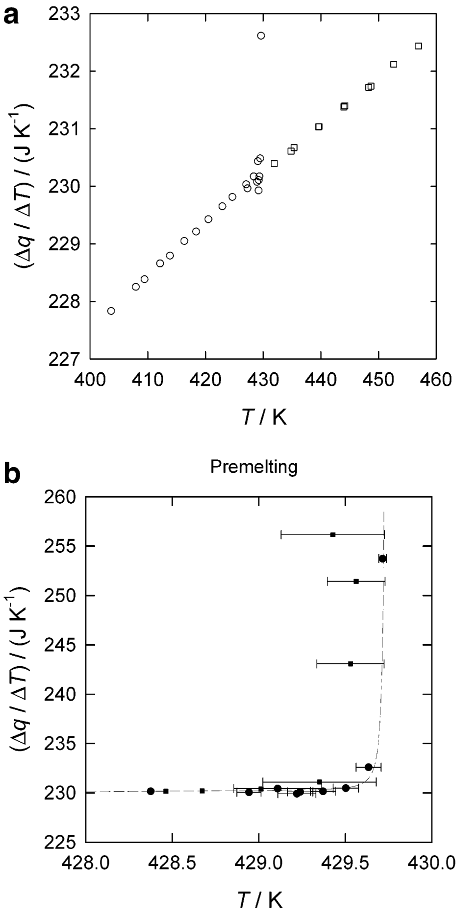

Figure 2. (a) Measured values of $(\Delta q/\Delta T)$ in the region of the fusion temperature of indium. Circles are for the solid phase, and squares are for the liquid phase. (b) Measured values of $(\Delta q/\Delta T)$ in the "premelting" region. The present values are for the addenda and the sample of indium. The results from ref 17 were recalculated to the same temperature scale basis and enthalpy basis (see text) to facilitate comparison. The horizontal lines represent the width of the temperature intervals used for the individual determinations. For the ref 17 symbols that have no horizontal bars, insufficient information was given for such a calculation. The dashed line is a calculated heat capacity effect for a liquid-soluble, solid-insoluble impurity of 1×10^{-8} mole fraction. The greater precision of the present measurements is obvious, despite the smaller sample size used for the present measurements, ~36.6 g (present work) vs ~250 g.[17]

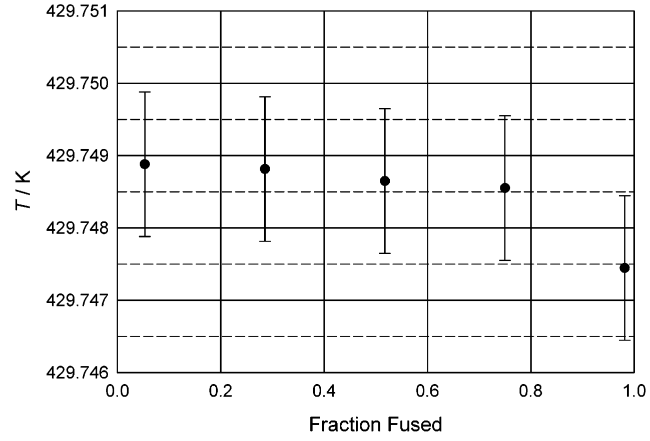

Figure 3. Measured equilibrium temperature vs fraction of the sample fused.

2×10^{-5}. Therefore, the fraction-fused method of determination of impurity greatly underestimated the impurity level for this sample of indium and we suggest that purities of other indium samples obtained solely on the basis of this type of fraction-fused calculation should probably be ignored.[16] A comparison with the same type of measured values, as reported by Grønvold,[17] after adjusting for differences of temperature scale, differences of mass of sample, and inclusion of a contribution for the present calorimetric addenda, is also shown in Figure 2b.

Figure 3 shows the temperature against fraction fused, *F*, for this sample of material. The temperature of fusion, in the middle range of fusion, was (429.7486 ± 0.001) K. This value compares well with the assignment of the indium fixed point temperature of 429.7485 K on the ITS-90.

Enthalpy increments spanning a range of nominal temperatures 401.5 K to 429.0 K ($n = 11$) were fitted with a function, linear in the parameters, obtaining

$$\Delta H_{\mathrm{cr}}(T_1 \rightarrow T_2)/H^\circ = (227.4938 \pm 0.019)(T_2 - T_1)/T^\circ + (0.093645 \pm 0.00108)[(T_2^{\,2} - T_1^{\,2})/2 - (400\ \mathrm{K})(T_2 - T_1)]/T^{\circ 2} \quad (1)$$

where H° was 1 J, T° was 1 K, and the uncertainties are 95% confidence intervals in the least-squares model calculation. Enthalpy increments for the liquid phase from 430.7 K to 459.1 K ($n = 11$) were fitted with a function, linear in the parameters, obtaining

$$\Delta H_{\mathrm{l}}(T_1 \rightarrow T_2)/H^\circ = (230.2168 \pm 0.027)(T_2 - T_1)/T^\circ + (0.082257 \pm 0.00174)[(T_2^{\,2} - T_1^{\,2})/2 - (430\ \mathrm{K})(T_2 - T_1)]/T^{\circ 2} \quad (2)$$

The rms deviation for the 11 measurements of the liquid phase was 0.0068%. The rms difference for the 11 solid-phase measurements was 0.0044%.

Determinations of enthalpy increments that spanned the fusion temperature are given in Table 2. The enthalpy of fusion was extracted from the measured quantities as

$$\Delta_{\mathrm{fus}}H = [\Delta H(T_1 \rightarrow T_2) - \Delta H_{\mathrm{cr}}(T_1 \rightarrow 429.7486\ \mathrm{K}) - \Delta H_{\mathrm{l}}(429.7486\ \mathrm{K} \rightarrow T_2)]/m \quad (3)$$

where m was the mass of indium in the calorimeter. The average of the four determinations was 28.6624 $\mathrm{J \cdot g^{-1}}$. The standard deviation (unbiased) based on the four measurements was ±0.0024 $\mathrm{J \cdot g^{-1}}$, and the standard deviation of the means was calculated to be ±0.0012 $\mathrm{J \cdot g^{-1}}$. A coverage factor of 3.2 was adopted to calculate the "uncertainty" of the enthalpy of fusion value, ±0.0036 $\mathrm{J \cdot g^{-1}}$; this corresponded to ±0.013% of the enthalpy of fusion. To this quantity, estimated uncertainties of the extrapolations of the crystal-phase enthalpy function, $\Delta H_{\mathrm{cr}}(T_1 \rightarrow 429.7486\ \mathrm{K})$, and of the liquid-phase enthalpy function, $\Delta H_{\mathrm{l}}(429.7486\ \mathrm{K} \rightarrow T_2)$, were added. To estimate these uncertainties, twice the rms deviation for the enthalpy increment measurements of the liquid and crystal phases was used as the estimate of the uncertainty of the two enthalpy increment contributions above and below the transition temperature. This quantity was approximately ±0.0040 $\mathrm{J \cdot g^{-1}}$ and corresponded to ±0.014% of the enthalpy of fusion. We summed these two error contributions to give ±0.0076 $\mathrm{J \cdot g^{-1}}$, which corresponded to a 95% confidence interval.

Comparison with Previous Values

Because of the importance of the enthalpy and temperature of fusion of indium for the calibration and validation of various types of calorimeters, there exist a large number of determinations in the literature. Many of these determinations were made with secondary instruments, for example, differential thermal analysis instruments and differential scanning calorimeters. However, these instruments require significant calibrations of the instrument response, and the thus obtained values for indium depend on values reported for some other materials, for example, tin or synthetic sapphire. Because of the dependence of those reported values for indium on properties of other materials, gleaned from other sources, and also their dependence on various calibration protocols, those values do not have the potential reliability that can accompany primary determinations, such as those from adiabatic calorimetry or Bunsen-type calorimetry. However, an important caveat is that these latter methods, although primary in nature, are not without the possibility of systematic error. It must be acknowledged also that not all adiabatic calorimeters are of equal accuracy. Figure 1 shows that the present measurements for SRM 720 agreed with the values tabulated by Archer for SRM 720 within the uncertainties assessed by Archer for the reference values, namely, ±0.05%.[15] Also shown in the figure for illustrative purposes are some contemporaneous values.[18] The values from ref 18 were obtained with temperature increments of 8 K, or 2.7 times larger than the increment used in the present work. The values from ref 18 obviously scatter about the established reference values[15] more so than do the present values. Additionally, each of the measurement series shown in the figure from ref 18 shows a small bias in the temperature dependency, shown in the figure as order one polynomial representations of each individual series. Only one measurement series was required for the present measurements for SRM 720. Figure 1 demonstrates the high degree of accuracy of the present calorimeter for this temperature range. Taking the differences in magnitudes of the temperature intervals into account, the present measurements were about an order of magnitude more accurate than the contemporaneous measurements.

There are reported determinations from three other different laboratories that used adiabatic calorimetry to determine the enthalpy of fusion of indium.[14,17,19,20] Two of those three laboratories were National Measurement Institutes.[14,19] The other laboratory was that of Grønvold at the University of Oslo.[17,20] There are second-hand reports

Table 2. Enthalpy of Fusion Determinations for Indium

T_i/K	T_f/K	q/J	q(prefusion)/J	q(postfusion)/J	q(fusion)/J	$\Delta_{fus}H$/J·g^{-1}	$\Delta_{fus}H_m$/J·mol^{-1}
427.798 73	433.224 55	2299.315	448.837	800.647	1049.831	28.6650	3291.26
427.952 03	433.379 12	2299.525	413.561	836.274	1049.690	28.6611	3290.82
427.509 48	433.351 24	2395.025	515.387	829.848	1049.788	28.6638	3291.13
427.487 98	433.330 94	2395.140	520.336	825.168	1049.636	28.6596	3290.65
					average	28.6624	3290.99
					standard deviation of population	0.0024	0.28
					standard deviation of means	0.0012	0.14

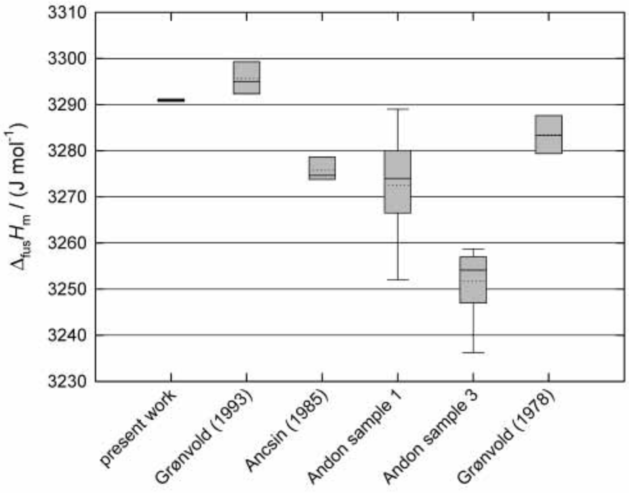

Figure 4. Box plot comparison of enthalpies of fusion determined with adiabatic calorimetry. The mean value of each set of determinations is shown as a dotted line in the box, the median value is shown as a solid line in the box, the 25th and 75th percentiles are shown as the ends of the box, and the 10th and 90th percentiles are shown as an error bar, if applicable.

of values having arisen from Bunsen calorimetry conducted at the National Institute of Standards and Technology (NIST) (for example, ref 21) and which have been cited only as coming from either a personal communication or an abstract of a presentation, or both. The present authors are not aware of those measurements having been published and do not suppose that they will be published as a NIST publication in the future. Therefore, those undocumented values are considered no further in this article.

Figure 4 shows a box plot comparison of the different determinations made with adiabatic calorimetry. A box plot shows the mean value, as a dotted line in the box; the median value, as a solid line in the box; the 25th and 75th percentiles, as the ends of the box; and the 10th and 90th percentiles, as an error bar, if applicable. Figure 4 is thus a visual depiction of the precisions, or reproducibilities, of the different adiabatic calorimetry studies. The better precision of the present study is quite obvious.

Two separate determinations of the enthalpy of fusion were obtained at the University of Oslo with an adiabatic calorimeter.[17,20] In the latter of the studies,[20] it was reported that the thermometer used in the calorimeter had been calibrated by means of fixed-point temperatures on the ITS-90; however, the thermometer was not calibrated within fixed-point cells of tin and zinc. Rather, samples of these metals were sealed in vessels that were, in turn, placed in the calorimeter, and the resistance of the thermometer was noted at the fusion points. They then determined a value for the triple-point temperature of indium, 429.7535 K, and compared it to the value 429.7436 K, which is the ITS-90 value less 4.9 mK for the change in pressure from ambient to the evacuated condition in the calorimeter vessel. Their determination of the fusion temperature of indium was 11 mK higher than the assigned ITS-90 fixed-point temperature. The enthalpy of fusion obtained with this version of their adiabatic calorimeter[20] had an uncertainty reported as ±9 J·mol^{-1}, or ±0.27% of the measured value. The uncertainty value was obtained as a combination of a 95% confidence interval based on five determinations, ±4 J·mol^{-1}, with an "estimated maximum systematic error (±8 J·mol^{-1})". The origin of the latter was not described. The later value (3296 ± 9 J·mol^{-1})[20] disagreed, using statistical tests, with their earlier value (3283 ± 7) J·mol^{-1},[17] where the uncertainty of the earlier value can be assessed by back-calculation to be the 95% confidence interval of the means.

Ancsin[19] used a device developed as a calibration facility[22] to measure the enthalpy of fusion of indium and melting curves for three samples of different purity. He obtained $\Delta_{fus}H = (28.53 \pm 0.02)$ J·g^{-1} and $T_{tr} = 429.7798$ on the IPTS-68 scale. Conversion of the triple-point temperature to the ITS-90 gave 429.743 ± 0.0005 K.[23] Conversion for the change in pressure to that of the ITS-90 fixed-point temperature gave 429.7492 K, which is only (0.7 ± 0.5) mK from the ITS-90 fixed-point temperature. The uncertainty stated in ref 19 is the standard deviation of the sample population and is not the standard deviation of the means. His value is 0.46% smaller than the present value. We did not find results measured with this instrument as a calorimeter for any calorimetric reference substance or any other substance, so it is not possible to assess objectively the true uncertainty of their instrument when it was used as a calorimeter. Within the precision of their instrument, their measurements did not detect a statistically valid dependence of measured enthalpy of fusion on the level of purity of the samples, the impurity contents of which supposedly ranged from 1×10^{-4} to 1×10^{-6}, presumably by mass fraction.

Andon et al.[14] also made enthalpy of fusion and triple-point temperature measurements for three samples of indium from different suppliers. The first sample, sample 1, had a manufacturer's claim of purity of 99.999%. Their sample 2 was a powder found to contain 0.0003 mass fraction of impurities, excluding oxygen, nitrogen, and carbon; oxygen was determined to be 0.0005 mass fraction. Their sample 3 was found to be very pure, the largest impurity being 2.5×10^{-6} mass fraction of silicon. It was found to contain less than 1×10^{-6} mass fraction of oxygen, nitrogen, and carbon. The adiabatic shields in their calorimetric apparatus were controlled manually for the measurements on samples 1 and 2 and automatically for the measurements on sample 3. Means, standard deviations of the measurements (i.e. of the populations), and the number of measurements for the three samples were $\Delta_{fus}H_m$ = (3273, 3247, and 3252) J·mol^{-1}; σ = (10.7, 12.8, and 7.6) J·mol^{-1}; and n = (9, 6, and 9), respectively. Andon assigned the measurements for sample 3 a weight of two, the measurements for sample 1 a weight of 1, and the measurements from sample 2 a weight of zero (because of the determined value of the oxygen content) to calculate an overall mean value. We note that there is not a statistical difference between the measurements for samples 2 and 3, at a 90% confidence level, despite their greatly different purities. We also note that the measurements for sample 1 show a statistically valid difference from the measurements for sample 3, despite both samples being believed to be of significantly greater purity that of sample 2. Therefore, at the level of uncertainty of Andon et al.'s calorimetric measurements, the evidence is that the measured enthalpies of fusion were not affected by the 0.03%−0.05% impurities present in sample 2.

PTB has also measured the temperature and enthalpy of fusion of the material used here.[8] They obtained the fusion temperature by comparison of the fusion temperature of the indium sample with an indium fixed-point standard by means of a 100-Ω thermometer used as a transfer standard. The transfer thermometer was calibrated in fixed-point cells of gallium, indium, and tin maintained at PTB. The transfer thermometer was not calibrated at the triple point of water and therefore cannot be considered a true ITS-90 device. The PTB-certified temperature, which is traceable to the ITS-90, of the indium sample was (156.598 ± 0.004) °C [(429.748 ± 0.004) K]. The PTB-certified value for the enthalpy of fusion was obtained with a modified commercial Tian−Calvet calorimeter in which the energy for the fusion was supplied electrically with a special resistance unit built into the sample cell. Their enthalpy of fusion was (28.64 ± 0.11) $J \cdot g^{-1}$, which is in very good agreement with the present value [(28.6624 ± 0.0076) $J \cdot g^{-1}$]. Therefore, the two PTB-certified values are in very good agreement with those reported here for a sample taken from the same lot of material. There is similar good agreement of the certified value of the enthalpy of fusion of gallium from NIST, 80.097 $J \cdot g^{-1}$, obtained with a high-accuracy adiabatic calorimeter[12] and PTB's certified value, 80.135 $J \cdot g^{-1}$, obtained with the same calorimetric arrangement used for their indium measurements. The agreement for these two substances (0.05% and 0.07%) would seem to indicate that the calorimetric uncertainty of PTB's enthalpy of fusion measurements is about 0.1%, or smaller, which is far smaller than the 0.4% uncertainty value assigned. Most of the uncertainty value for the PTB enthalpy of fusion was an estimate of the maximum unaccounted heat transfers that could have occurred in their calorimetric operation. We now see that uncertainty component, based on the good agreements for indium and gallium, was probably too conservative.

The NIST SRM 2232 values were obtained as the defined fixed-point temperature on the ITS-90 and an enthalpy of fusion value, $\Delta_{\mathrm{fus}}H = (28.51 \pm 0.19)\ J \cdot g^{-1}$. The enthalpy of fusion value was obtained with a DSC that had been calibrated with NIST's SRM 2220, tin. The enthalpy of fusion of SRM 2220 was determined with a Bunsen-type ice calorimeter. Others have claimed the value for SRM 2220, used in the certification of SRM 2232, is too small by about 0.5%, due to comparison with the results from their calorimeter[20] and various hypotheses, one of which is "a quenching in of disorder"[21] that does not affect their calorimetric results. We note that PTB obtained $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7150 \pm 32)\ J \cdot mol^{-1}$ for tin with the same calorimeter that they used to determine the indium value noted above and which would likewise not be affected by quench effects. The PTB value is in very good agreement with the NIST value of (7147 ± 22) $J \cdot mol^{-1}$, where the uncertainty is a 3σ value. If we accept an uncertainty for PTB's enthalpy of fusion of tin obtained from the comparisons of PTB's and NIST's measurements of the enthalpies of fusion of indium and gallium, then the uncertainty of PTB's enthalpy of fusion of tin is about 7 $J \cdot mol^{-1}$. PTB's value, $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7150 \pm 7)\ J \cdot mol^{-1}$, would then strongly support the earlier NIST value for SRM 2220, tin, $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7147 \pm 7)\ J \cdot mol^{-1}$ (here we give the 1σ uncertainty of the NIST value for comparison with the PTB value) rather than the value reported in ref 20, $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = (7179 \pm 15)\ J \cdot mol^{-1}$. PTB also found differences of less than 0.1% between the enthalpies of fusion of their sample of tin and a SRM 2220 sample, when measured in their calorimeter.

Conclusion

Through measurement of enthalpy increments for synthetic sapphire, we have shown the present calorimeter to be more accurate than other contemporaneous calorimeters in the temperature range considered here. Statistical comparisons of the enthalpy of fusion of indium show the present calorimeter to be about an order of magnitude more precise than other adiabatic calorimeters that have been used for determination of the enthalpy of fusion of indium. The newly determined reference values for the enthalpy of fusion of indium are therefore the best currently available. The present work helps establish new, better, uncertainty limits for the calorimetric procedure used at PTB for certification of enthalpy of fusion materials.

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