The Enthalpy of Fusion of Gallium

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An adiabatic calorimeter was used to measure the enthalpy of fusion of a very pure sample of gallium. The new value of the enthalpy of fusion was determined to be $\Delta_{\text{fus}}H = 80.097 \pm 0.032\ \text{J·g}^{-1}$, where the uncertainty corresponded to a 95% confidence interval. A comparison with previous determinations is made.

Introduction

Gallium has been recommended as a material suitable for calibration of thermal analysis instruments.[1−3] One of these references recommended gallium for calibration of the temperature scale of the thermal analysis instrument, and the other two recommended gallium in a caloric calibration protocol. For these purposes, the temperature of fusion of very pure gallium is reasonably well determined, and it serves as a fixed-point temperature on the International Temperature Scale of 1990.[4] The enthalpy of fusion of gallium is perhaps less well-known.

Berthelot[5] determined the enthalpy of crystallization of gallium at 13 °C to be 79.9 J·g^{-1}. Roth et al.[6] adjusted Berthelot's value to the melting temperature, taken as 29.75 °C, and obtained 80.21 J·g^{-1}. Roth et al. determined the enthalpy of crystallization calorimetrically and obtained $80.19 \pm 0.04\ \text{J·g}^{-1}$. Roth et al. believed their sample had a purity of 0.998 mole fraction, on the basis of the difference of their determined melting point from that determined by Richards and Boyer[7] and their measured enthalpy of fusion. Adams et al.[8] used an adiabatic calorimeter to determine the heat capacity and enthalpy of fusion of gallium. The sample used in the enthalpy of fusion measurements was supplied by the Aluminum Corporation of America, whose spectrographic analysis indicated no impurity greater than 0.001%. Adams et al. stated the purity to be less, reporting a mole fraction purity of 0.9998, solely on the basis of their "premelting" data. They obtained a value of $80.13 \pm 0.06\ \text{J·g}^{-1}$ for the enthalpy of fusion. More recently, Amitin et al.[9] determined the heat capacity and enthalpy of fusion of gallium in an adiabatic calorimeter. Amitin et al. stated that the impurity of their sample was $<1 \times 10^{-4}$, by mol fraction, as determined by melting temperature depression. The enthalpy of fusion that they reported was $79.63 \pm 0.01\ \text{J·g}^{-1}$. Amitin et al. did not discuss the 0.6% discrepancy between their enthalpy of fusion and all of the earlier calorimetric determinations. However, Amitin et al. did attempt to argue that the differences between their heat capacity values and those of Adams et al. were a direct result of the superior purity of their sample. Lavut and Chelovskaya[10] reported a value of $\Delta_{\text{fus}}H = 80.098 \pm 0.007\ \text{J·g}^{-1}$, which they obtained from isoperibol calorimetry. They stated that their sample had a nominal purity of 99.9999%. However, they sealed the sample in stainless steel cells. They did not describe an examination of the purity of the material during, or after, the measurements.

Of course, not all of the above values were obtained with calorimetric techniques of equal accuracy. Generally, adiabatic calorimetry is assumed to be most accurate, and the two more recent adiabatic calorimetry studies mentioned above were those from Adams et al.[8] and Amitin et al.[9] The discrepancy between the more recent value of Amitin et al. and the earlier value by Adams et al. has led to an unnecessarily large uncertainty in the values of the enthalpy of fusion of gallium recommended for calibration of the heat flow of differential scanning calorimeters. For example, Sarge et al.[1] recommended a value for the enthalpy of fusion of $79.88 \pm 0.72\ \text{J·g}^{-1}$ at the fusion temperature. The uncertainty of this value, ± 0.9%, is at least an order of magnitude greater than what can be determined by the more accurate adiabatic calorimeters.

More recently, Sabbah et al.,[11] through the International Confederation for Thermal Analysis and Calorimetry, gave a series of recommended values for calibration of calorimetric and thermal analysis instrumentation. In their section titled "3.1.2. $\Delta_{\text{fus}}H$, Gallium," they recommended an enthalpy of fusion value for gallium of $5569 \pm 50\ \text{J·mol}^{-1}$ and stated that "certified samples are available from NIST... (SRM 1968)." (SRM is NIST's abbreviation for Standard Reference Material. NIST's SRMs are materials certified by NIST to have a particular property value.) Sabbah et al.'s description is incorrect on several accounts. To date, NIST has not certified any enthalpy of fusion value for any sample of gallium. Second, NIST's SRM 1968 is a gallium melting-point cell that has very pure gallium sealed within the calibration cell. NIST did not intend for this cell to be dissected so that the gallium could be removed from it and subsequently used as an enthalpy of fusion reference material for thermal analysis and calorimetric instruments. Finally, the value given by Sabbah et al. for the enthalpy of fusion of gallium was that from Gmelin and Sarge,[3] who gave a weighted average of the values found in refs 8 and 9. That value is not a NIST-certified or NIST-measured enthalpy of fusion value for the gallium sample contained in the SRM 1968 melting-point cell.

Stølen and Grønvold[12] have reviewed the enthalpy of fusion of gallium and included some additional determina-

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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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tions of less accuracy than those enumerated above. They recommended a value of $\Delta_{\text{fus}}H = 79.974 \pm 0.27$ J·g^{-1} on the basis of their assessment.

To resolve the discrepancy in recommended values for the enthalpy of fusion of gallium and to improve the uncertainty assigned to the reference value, the enthalpy of fusion of a very pure sample of gallium was determined in a highly accurate adiabatic calorimeter.

Experimental Section

The National Institute of Standards and Technology (NIST) obtained a 30-kg lot of gallium from Rhodia Inc. The manufacturer's assay indicated that the total detectable impurities amounted to 1×10^{-7} g/g, or less, and that the residual resistance ratio was >60 000. NIST uses this material for Standard Reference Material 1751, the melting temperature of gallium standard. The total lot of this material was subdivided by the manufacturer into polyethylene bottles containing 200 g each. The sample used in the present work was taken from one of those polyethylene bottles.

The cryostat used in this work was the immersion cryostat described by Sterret et al.[13] A new calorimeter vessel was used for the present work. It had approximately the same dimensions and fabrication details as that described by Sterret et al., which was later used by Chang for a determination of the thermodynamic properties of NIST's Standard Reference Material 720, synthetic sapphire, from 9 to 360 K.[14] Exceptions to that general design were the following: A small stainless steel threaded hollow fitting of 1.27-mm i.d., which was to serve as an orifice to a calorimeter lid, was silver soldered to a lid that had been fabricated from oxygen-free high conductivity copper. The lid assembly was then gold plated. The threaded fitting terminated in a knife edge. A stainless steel cap was fabricated that would thread onto the fitting and compress a gold sealing disk against the knife edge. This lid assembly provided for two methods of entry into the calorimeter vessel. The first was removal and reattachment of the lid from the calorimeter body, accomplished by indium−tin soldering of the lid to the calorimeter body. The alternate method for introduction of material was through the small orifice of the threaded inlet. The thermometer used for these measurements was a miniature 100-Ω platinum thermometer (Minco) calibrated at NIST according to the ITS-90.[4] It was soldered into the center of the heater core, which was, in turn, soldered into the re-entrant well of the calorimeter vessel. A manifold for sealing the calorimeter with the screw cap was also designed and constructed. This manifold allowed for the admittance of either gas or liquid samples through the threaded inlet and under a controlled atmosphere. The electronic measurement instruments, data acquisition instruments, and instrument control methods, including the digital PID control of the shield temperatures, have been described previously.[15]

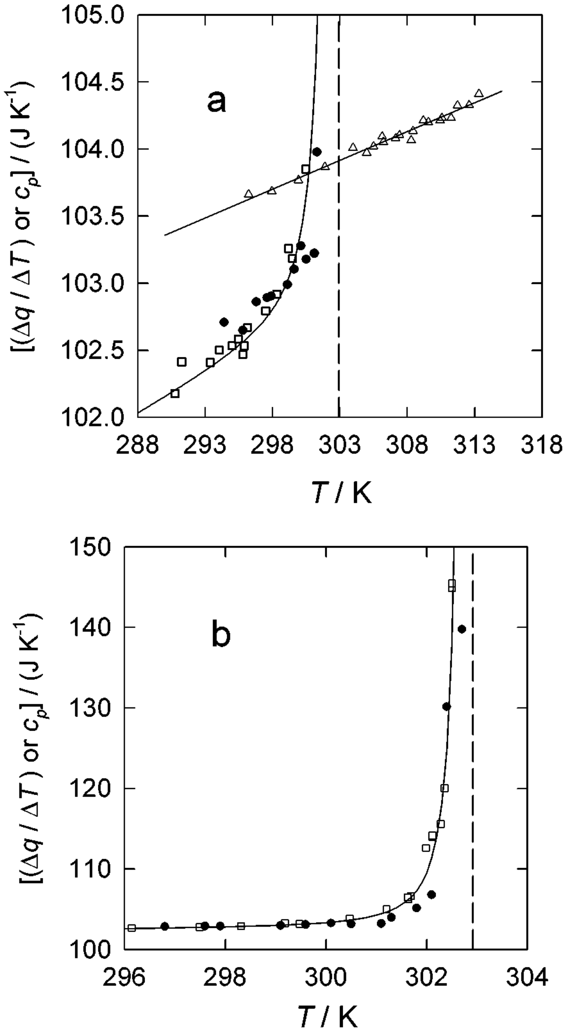

Figure 1. Values of $\Delta q/\Delta T$ or c_p vs temperature for gallium on different scales. The symbols are as follows: □, present measured values for the solid phase; ●, values calculated from Boitard et al.'s reported heat capacity values; △, present measured values for the liquid phase. The solid lines represent the heat capacities calculated from representations of the present measured values of $\Delta q/\Delta T$ for the solid and liquid phases. The triple-point temperature is shown as a dashed line. Parts a and b show different scales.

Gallium alloys fairly readily with gold, and so, the gallium could not be placed directly into the gold-plated calorimeter. Instead, the following procedure was used: Five seamless tantalum crucibles each with an outside diameter of 1.9 cm, a wall thickness of 0.25 mm, and a height of 5.08 cm were obtained. Inside each crucible was placed approximately 0.001 L of gallium, and the mass of gallium in the crucibles was obtained by weighing, correcting for buoyancy. The crucibles were placed inside the calorimeter, and the lid was soldered to the calorimeter body. The calorimeter was evacuated. Then, 0.002 MPa of helium (298 K) was sealed into the calorimeter to facilitate rapid attainment of thermal equilibrium. The mass of gallium used for the measurements was 31.9741 ± 0.0007 g, corrected for buoyancy. A small volume of gallium was used in each crucible to reduce strain resulting from the expansion of gallium upon freezing. The magnitude of this small volume of material did not negatively affect the uncertainty of the determination because of the large enthalpy of fusion of gallium per unit mass.

In determinations 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.

Results

Figure 1 shows the quantity $\Delta q/\Delta T$ obtained from individual measurements in the vicinity of the melting temperature, where Δq is the measured energy added to the calorimeter, in joules, and ΔT is the difference between the initial and final temperatures for the enthalpy increment. The quantity $\Delta q/\Delta T$ is only an approximation of the heat capacity, and it is an approximation that becomes increasingly poor with increasing curvature of the heat capacity function particularly so if ΔT is fixed in site (not the case here). Also shown in the figure is the true heat capacity calculated from a representation of the measured enthalpy increments. An increase in this quantity as the nominal melting temperature of gallium is approached from lower temperatures is evident. This effect was also seen by Boitard et al.,[16] who measured the heat capacity of a very pure sample of gallium (99.9999%) in a Calvet-type calorimeter. Their reported heat capacity values were adjusted to correspond to the mass of gallium in our calorimeter, and an approximation of the heat capacity of the empty calorimeter was added so that the values could be compared qualitatively with the present results in Figure 1. Their measurements were performed with nylon-lined sample cells. Thus, the effect observed cannot be attributed to a decrease in purity resulting from dissolution of some metal component of the vessel wall into their gallium sample. Their reported heat capacity values closely follow the heat capacity values calculated from a representation of the enthalpy increment measurements reported here for the solid phase.

One can construct the usual temperature vs inverse fraction melted relation to calculate a supposed impurity level, as in Figure 2a, which shows values for melted fractions, F, ranging from 8.7 to 47%. If one assumed that the effect observed was due to a solid-insoluble impurity, then an impurity level of 1×10^{-5} on a mole fraction basis (purity = 0.99999 mol fraction) and a triple-point temperature of 302.9146 ± 0.0001 K, where the uncertainties are the calculated 95% confidence intervals, would be calculated. The accepted triple-point temperature, 302.9166 K,[17] not the melting temperature, 302.9146 K, is the temperature with which we must compare our calculated result. The agreement was considered acceptable. The impurity value calculated from the difference of the observed triple-point temperature from the accepted value was 8×10^{-6} on a mole fraction basis, in agreement with that calculated from the slope of the line in Figure 2a. However, the sample was expected to be more pure than 0.99999 mol fraction. The ratio of the number of moles of helium to the number of moles of gallium in the calorimeter was 2.4×10^{-4}. Thus, there was sufficient helium in the calorimeter to have caused the impurity. However, it might be expected that the solid phase has a larger void volume, on account of its lower density, than does the liquid phase, resulting in some solubility of helium in both phases. The assumption of a solid-insoluble impurity is probably not justified for most metal impurities dissolved in gallium, including any tantalum that might have dissolved from the crucibles, and so the calculation described above is immediately suspect for those reasons. If any tantalum did dissolve into the gallium, then it would appear that this low solubility was established rapidly, as no measurable change in the enthalpy of fusion was detected over a period of more than 30 days. At low fractions melted, the curve does not follow Raoult's law behavior.[18] This is shown in Figure 2b, where the Raoult's law line from Figure 2a is shown, as are additional temperatures and $1/F$ values for smaller fractions melted. An alternate explanation of the phenomenon might be sought in concepts of heterophase nucleation,[19] free-surface melting,[20] and intergranular melting.[20,21]

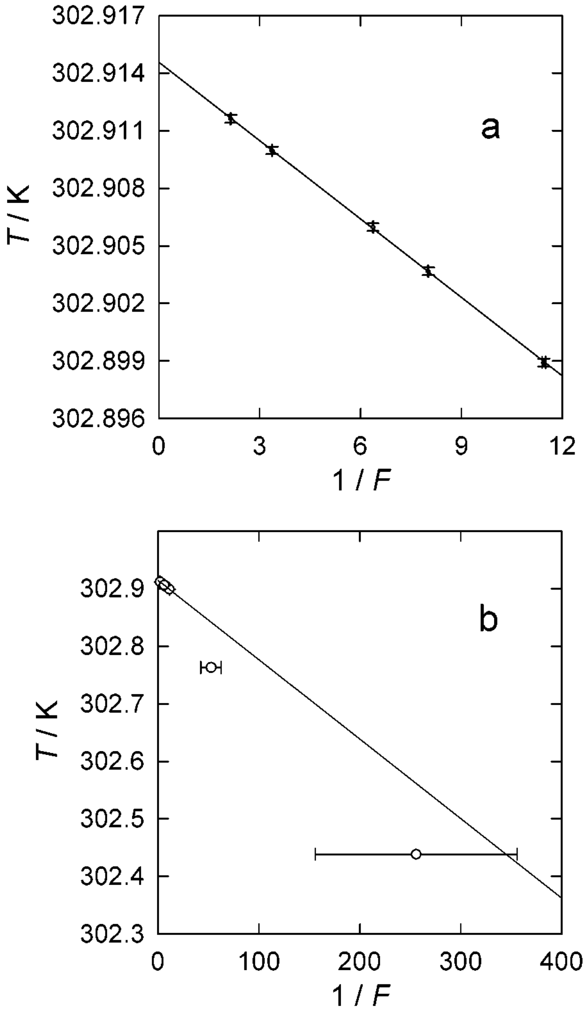

Figure 2. Values of the measured temperature vs $1/F$ for gallium, where F is the fraction of sample melted in the measurement. Bidirectional error bars representing the uncertainties of temperature and $1/F$ are shown. The solid line was calculated from the values shown in Figure 2a and is shown for comparison in both parts a and b.

Regardless of the source of the premelting effects, it is shown below that they do not have a significant impact on the measured enthalpy of fusion.

Enthalpy increments from 288.6 to 297.23 K (n = 10) were fitted with a linear model, yielding

$$\Delta H_{\mathrm{cr}}(T_1 \rightarrow T_2)/H^\circ = (102.543 \pm 0.056)(T_2 - T_1)/T^\circ + (0.078\,50 \pm 0.022)[(T_2^{\,2} - T_1^{\,2})/2 - (295\ \mathrm{K})(T_2 - T_1)]/T^{\circ 2} \quad (1)$$

where H° is 1 J, T° is 1 K, and the uncertainties are the calculated 95% confidence intervals in the least-squares model. Enthalpy increments for the liquid phase from 295.46 to 314.35 K (n = 22) were fitted with a linear equation to give

$$\Delta H_{\mathrm{l}}(T_1 \rightarrow T_2)/H^\circ = (103.567 \pm 0.046)(T_2 - T_1)/T^\circ + (0.043\,529 \pm 0.003\,56)[(T_2^{\,2} - T_1^{\,2})/2 - (295\ \mathrm{K})(T_2 - T_1)]/T^{\circ 2} \quad (2)$$

The root-mean-square (rms) deviation for the 22 measurements of the liquid phase was 0.03%. The rms difference for the 10 solid-phase measurements was 0.075%; ap-

Table 1. Enthalpy of Fusion of Gallium Obtained in the Present Work

T_1 (K)	T_2 (K)	Δq (J)	$\Delta_{fus}H$ (J·g^{-1})
296.34537	304.78646	3431.819	80.103
296.56201	305.06278	3438.108	80.096
296.64678	305.14039	3437.324	80.092
		average	80.097
		standard deviation (unbiased)	0.0057
		standard deviation of means	0.0033

proximately one-half of this rms error came from two measurements. Without these two values, the rms difference from the fitted eq 1 was 0.039% for the solid-phase measurements.

Determinations of the enthalpy increments that spanned the fusion temperature are given in Table 1. The enthalpy of fusion was extracted from the measured quantity by

$$\Delta_{fus}H = [\Delta H(T_1 \rightarrow T_2) - \Delta H_{cr}(T_1 \rightarrow 302.9146\text{ K}) - \Delta H_l(302.9146\text{ K} \rightarrow T_2)]/m \quad (3)$$

where m is the mass of gallium in the calorimeter. The average of the three determinations was 80.097 J·g^{-1}. The standard deviation (unbiased) calculated from the three measurements was 0.0057 J·g^{-1}, and the standard deviation of the means was calculated to be 0.0033 J·g^{-1}. A coverage factor of 4 was adopted to calculate the "uncertainty" of the enthalpy of fusion value, ±0.013 J·g^{-1}, which corresponded to ±0.016% of the enthalpy of fusion. To this quantity, estimated uncertainties of the extrapolations of the crystal-phase enthalpy function, $\Delta H_{cr}(T_1 \rightarrow 302.9146\text{ K})$, and of the calculated liquid-phase enthalpy increments, $\Delta H_l(302.9146\text{ K} \rightarrow T_2)$, were added. To estimate these uncertainties, twice the rms deviation for the enthalpy increment measurements of the liquid and crystal phases, ±0.07%, was used as the estimate of the uncertainty of the two enthalpy increments. This quantity was approximately ±0.019 J·g^{-1} and corresponded to ±0.024% of the enthalpy of fusion. The combination of these uncertainties gave ±0.032 J·g^{-1}, which corresponded to a 95% confidence interval.

Uncertainty components arising from the mass determination and from the calibration of the electronic instruments are approximately 1 and 2 orders of magnitude smaller, respectively, than the calculated 95% confidence interval and are considered no further. The last potential component of uncertainty to consider is that related to heat exchanges between the calorimeter and the calorimeter's environment. These heat exchanges can arise from a variety of sources including, but not limited to, offsets in measured thermocouple voltages, either intentional or not, by which the adiabatic shields are not at the same temperature as the calorimeter; heat exchanges along physical connections of the calorimeter body to other parts of the cryostat, including the suspension device and electrical connections; and incorrect apportionment of the heat generated in the electrical leads of the heater. All of these potential sources of uncertainty have been discussed previously; see, for example, the chapters by Ginnings and West, West and Westrum, and Westrum et al. in ref 22. Some portion of these heat fluxes does not vary with time at a particular temperature and is independent of whether or not the calorimeter is being heated. It is compensated by the determination of the time rate of change of the temperature of the calorimeter and subsequent calculation and therefore does not contribute to the uncertainty of the measurement. Another portion of these heat fluxes can be transient but independent of whether or not the calorimeter is being heated, meaning that it is not reproducible from one enthalpy increment measurement to the next. This irreproducibility is contained within the variance of the measurements. Therefore, it should not be considered as a separate component of uncertainty, over and above that of the variance of the measurements themselves. Finally, there are potential components of uncertainty that do depend on whether or not the calorimeter is being heated. These uncertainty components can potentially lead to bias of the measured values from the true values. This component of error is perhaps the most difficult error to evaluate in calorimetry and has often been handled simply by adding an arbitrary value to the standard deviation, or another statistic, of the measured values. The magnitude of the arbitrary value, with a few notable exceptions, has been rarely discussed by those following that practice. We consider the potential magnitude of this effect for the present calorimeter.

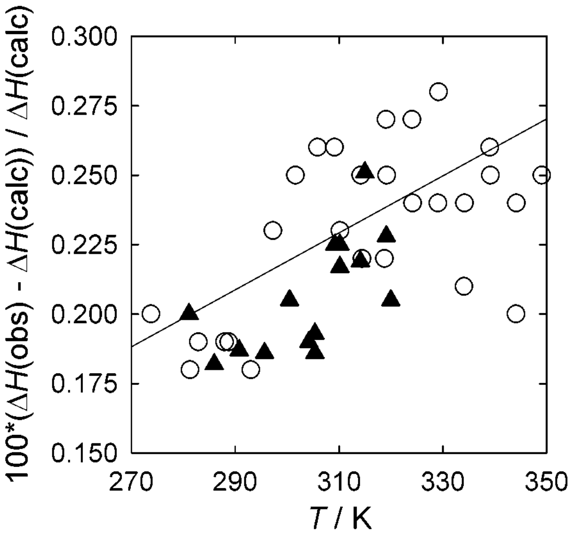

Figure 3. Differences of measurements made with a small-sample calorimeter for Standard Reference Material 720 from the reference equation given by Archer[23] (circles) and for Research Material 5 from the reference values from Martin[24] (triangles).

Archer measured enthalpy increments of NIST's SRM 720, synthetic sapphire, and NIST's Research Material 5, a special high-purity copper, in a small-sample calorimeter.[15] In that comparison, reference values from Archer's reference equation for synthetic sapphire[23] and the values that Martin[24] had determined with his "tray" calorimeter for a high-purity single crystal of copper were used. The reference equation for SRM 720, in the temperature range to be considered here, relies heavily on the calorimeter used for the present measurements for gallium, albeit with different electronics, different shield control systems, and different thermometry. This comparison, if biases in the small-sample calorimeter are assumed to be independent of the nature of the sample within the calorimeter, could show a degree of disagreement between the reference values for those two standards. In other words, the small-sample calorimeter might provide a comparison between the two standards and thus between the two very different calorimeters on which they were based. The magnitude of this disagreement, if one exists, could perhaps be used to infer a magnitude of unaccounted heat transfers in either of those two calorimeters. Figure 3 shows this comparison for the temperature range of interest here. The differences between the measured enthalpy increments for SRM 720 and the reference values obtained with the calorimeter used in the present work are shown as circles. A line has been fitted to the differences between the measured values and the reference values for synthetic sapphire. The differences between the measured values for copper and Martin's reference equation are shown as solid triangles. The average deviation of the copper residuals from the line representing the sapphire residuals was −0.017%. This difference, again with the caveat that there is an assumption that sample characteristics do not create a bias in the small-sample calorimeter, is a measure of the differences between the calorimeter used in the present work, albeit with different electronics and thermometry than that used for the SRM 720 work, on one hand and Martin's "tray" calorimeter on the other hand. This difference, −0.017%, is statistically significant using the usual analysis of variance (ANOVA) test. It could represent a real difference of this magnitude between the reference values for the two reference materials, and thus, it could represent a real systematic difference between the two calorimeters.

Is this difference, 0.017%, obtained from the comparison of measurements from two very different calorimeters, a measure of unaccounted heat transfers that should be added to the present uncertainty budget? The answer is that such a conclusion would not be a certainty, and not highly probable, because other potential differences between the two calorimeters could have given rise to the difference. We consider just two of these possibilities. First, the properties of the reference materials from the two different calorimeters were obtained as differences between enthalpy (or heat capacity) values determined for the empty calorimeter vessel or addenda and the calorimeter vessel or addenda containing some amount of one of the reference materials. Between two, or more, such determinations, there could have been very small differences in the enthalpy content of the calorimeter vessel that arose from the opening, resealing, and reassembly processes. A very small bias thus could have arisen from the assumption that the enthalpy contents of the calorimeters (or addenda) were identical for the empty and filled calorimeters (or addenda). Thus, some portion of the observed difference in the reference values from the two different calorimeters might have been due to a reassembly error. This small reassembly error might also have been present with the multiple determinations made with the small-sample calorimeter for the comparison. However, this type of reassembly error would not be relevant to the present gallium measurements because no separate determination of the empty calorimeter vessel was used in the determination of the enthalpy of fusion. Another potential source of the observed 0.017% difference could have been small differences in the thermometry used by Chang[14] and Martin.[24] Such a difference would not be relevant to the present measurements for gallium, because of the differences in our thermometry from that used by Chang. Therefore, because the source of the 0.017% difference is not known, it is not possible to ascribe the 0.017% difference solely to unaccounted heat transfers in Chang's calorimeter and cryostat design. Finally, the comparison discussed here is not sufficient to attribute the statistically significant differences observed in Figure 3 entirely to either one or the other of the two calorimeters, which is what would be required to include an additional 0.017% to the uncertainty budget for the present measurements. Therefore, all we can say from the excellent agreement of the reference values shown in Figure 3 is that unaccounted heat transfers for the present calorimeter are, in all likelihood, less than 0.017% and are, most probably, less than that value. However this conclusion, and its underlying comparison, cannot quantify any particular value of uncertainty due to unaccounted heat transfers that is <0.017%, at any particular probability.

In summary, thermodynamic property values obtained from a high-accuracy calorimeter with a very different design from that of the present calorimeter were compared to earlier thermodynamic property values obtained using the present calorimeter, albeit with different thermometry and instrumentation than that used here. A statistically significant difference of only 0.017% was observed in the comparison. It is not possible to attribute that difference solely to unaccounted heat transfers within the present calorimeter, as the difference could have arisen, in part, from reassembly errors that did not affect the present work and because the difference could have arisen, in part, from differences between the thermometry used previously in the other studies, which also did not affect the present work. It is also not possible to attribute with certainty the observed difference to the present calorimeter because the systematic bias might have been present instead in the other calorimeter; or it might have been divided between the two calorimeters; or it might have arisen because of a lack of validity, to some small degree, of the assumption used in the comparison made with the small-sample calorimeter. Nonetheless, the comparison and the observations above all indicate that unaccounted heat transfers for the present work were most probably much less than 0.017%, but that they cannot be quantified further with the present information. Therefore, an arbitrary value for unaccounted heat transfer between this particular calorimeter and its environment was not included in the uncertainty budget, and it is recognized that such effects were probably smaller than the 95% confidence interval calculated above. The above comparison and conclusion are also supported by preliminary new measurements on SRM 720 obtained with yet a third calorimeter of very different design.

Our measured value, 80.097 ± 0.032 $J\cdot g^{-1}$, agrees with the values obtained by Adams et al., 80.13 ± 0.06 $J\cdot g^{-1}$, and Roth et al., 80.19 ± 0.04 $J\cdot g^{-1}$, to within 2 or 3 times their own estimates of imprecision. The value from Lavut and Chelovskaya,[10] 80.098 ± 0.007 $J\cdot g^{-1}$, agrees with our value within our 95% confidence interval. Lavut and Chelovskaya did not describe what comprised their uncertainty value or how it was calculated. The uncertainty in their mass determination alone, at a 95% confidence interval, would contribute 0.014 $J\cdot g^{-1}$ to the uncertainty in the enthalpy of fusion, which is larger than the entire uncertainty claimed. The agreement of all of these different determinations is satisfying, particularly when one considers that the estimates of the purity of the gallium samples ranged from 99.8% to at least 99.999%. The differences in the measured values are therefore more likely to be representative of differences in systematic calorimetric biases than representative of purity effects. The result from Amitin et al.,[9] 79.63 ± 0.01 $J\cdot g^{-1}$, does not agree with the present measurement within either estimated uncertainty, the difference being 0.59% of their value; we note that Amitin et al. provided no description as to what their uncertainty included or how it was estimated. As stated above, the Amitin et al. value also does not agree with any of the earlier calorimetric measurements enumerated above, and it does not agree with the present determination on a sample of at least equal, or probably greater, purity. We can now safely rule out impurity level as the source of the discrepancy between the Amitin et al. value and the earlier values. Rather, the differences now appear to be indicative of significant systematic calorimetric errors in Amitin et al.'s measurements.

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