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NIST and standards for calorimetry

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Abstract

The present article describes briefly some of NISTs more recent work on calorimetric standards. New reference-quality measurements of the enthalpy of solution of aqueous sodium chloride, obtained with an adiabatic solution calorimeter, are presented and compared to a previous equation of state for NaCl(aq). Other calorimetric standards that are discussed are potassium chloride used for solution calorimetry and reference materials used for calibration of enthalpy-increment and heat-capacity calorimeters, namely synthetic sapphire (α-Al_2O_3) and copper. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetric standards; Sodium chloride; Potassium chloride; Copper; α-aluminum oxide

1. Introduction

There are two different philosophies regarding calibration of any instrument, in general, and calorimeters, in particular. The first of these is the *consensus* philosophy. The consensus philosophy is recognized by words like ‘round robin’, ‘pooled results’ and others. In the consensus philosophy, several laboratories measure, often with commercial instruments, a property of a material selected to be the calibrating substance or a reaction involving the calibrating substance(s). The results from these laboratories are then averaged together and this average value for the property is declared to be the standard value for the calibrant. This philosophy can also be extended to the standard deviation of the population of the measured values, or of the mean, by which such a standard deviation is declared the uncertainty of the standard value. But the commercial calorimeters might have systematic biases and so the standard value obtained in the round robin, or other procedure, may be systematically biased from the true value of that property for the reference material. That a so-obtained standard value may have little relation to the true value of the property has no impact on the consensus philosophy or those who advocate it. As a result, instruments of greater accuracy might be ‘calibrated’ to give values of lesser accuracy than they would have otherwise produced if the standard value was based on a population in which some of the measured values were similarly biased.

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The alternate philosophy is the *most-accurate-value* philosophy. In this philosophy, research instruments of the highest possible accuracy are used to establish the standard value, for the chosen reference substance, i.e. a truth-based standard. This accurate value is then used to calibrate commercial instruments and also research instruments of a lesser degree of accuracy. The accurate standard value in this philosophy might show measurements made with instruments of a particular design to be systematically biased. To advocates of the most-accurate-value philosophy, this concern is met with an 'As it should be' response. The only legitimate disadvantage of the most-accurate-value philosophy is the fact that the cost of producing the most accurate value is often not small and is borne by only those few laboratories (sometimes one laboratory) capable of executing the difficult measurement.

An excellent example of the potential problem that could arise from a consensus standard can be obtained from results shown previously by Grolier [1]. His Figure 4.19 [1] showed four sets of heat capacity measurements for the $CCl_4 + C_6H_6$ system. Three of those sets were obtained with Picker-type mass-flow calorimeters and one was obtained more recently with a Setaram instrument. In that figure, the measurements from the three Picker-type calorimeters were in good agreement with each other, but all differed by approximately the same amount from those obtained with the Setaram instrument. One could average the values from the three Picker-type instruments and that average value could be labeled as a consensus standard. Or one might average the values from the three Picker-type instruments and the one Setaram instrument and that average could be labeled as a consensus standard. However, the heat capacity calculated from the temperature derivative of enthalpy of mixing measurements agreed better with the measurements from the Setaram instrument than it did with those from the Picker-type instruments. A reasonable inductive conclusion is that the Picker-type instruments might have had a small calorimetric bias, similar in each of the three instruments and larger than that possibly present in that particular Setaram instrument. Equally reasonable is the realization that inclusion of biased values in the average used for the consensus value could result in a less accurate value for the standard.

NISTs primary interest in calorimetric calibration problems is the development of truth-based thermodynamic property values for substances suitable for use in calibration of calorimeters. Some of our recent work in establishing truth-based standards is described in the following sections.

2. Solution calorimetry

2.1. NaCl(aq)

There are several types of calorimeters intended for the measurement of the properties of solutions. Calibration of these calorimeters with sodium chloride solutions should be attractive for a number of reasons. Sodium chloride is inexpensive, readily available in highly pure form, and stable in aqueous solution at higher temperatures. Additionally, there is a plentiful base of data on the thermodynamic properties of aqueous sodium chloride. A comprehensive equation of state has been formulated for the $NaCl + H_2O$ system [2]. This equation of state was based on more than 5000 measured values that spanned the available composition range, and spanned temperatures from the freezing line to 623 K. This equation requires consistency of all thermodynamic relations. Therefore, a single calculated property value is based not just on the measurements of that property for the particular chosen conditions (i.e. T, p, and m), but also on measured properties that define higher and/or lower derivatives of that property. As an example, an enthalpy of solution value calculated from the equation for the conditions 308.15 K, 0.15 mol kg^{-1} and 0.1 MPa, is based not just on an enthalpy of solution measurement at those conditions (in fact no such measurement existed) but is based on other measurements also. The calculated value depends on enthalpy of solution measurements at other temperatures, on the difference in measured heat capacities for the aqueous solution and the crystal phase, on the dependence of measured component activities with respect to temperature, and on how the aqueous solubility of the crystal phase changes with respect to temperature. In other words, the calculated enthalpy of solution must be in reasonable agreement with all of these measured properties.

Keeping in mind the accuracy with which the properties of aqueous solutions of sodium chloride have been measured, it is widely recognized as both an isopiestic and calorimetric standard. As a calorimetric standard, it is often used for calibration of Picker-type mass-flow heat capacity calorimeters and as a check on the operation of, or as a calibration substance for, enthalpy of dilution calorimeters. Historically, there has been less interest in use of NaCl as an endothermic calibrant of enthalpy of solution calorimeters and for that purpose interest had been more focussed on potassium chloride as a check or calibrant for those calorimeters. This may have been due, in part, to scatter in some of the previously published direct measurements of the enthalpy of solution of NaCl. It also may have been due, in part, to sodium chloride having a smaller enthalpy of solution, in magnitude, than has potassium chloride. Fig. 1 shows differences of some of the previously measured values from the fitted equation for 298.15 K. A good deal of scatter is apparent for the previous measurements of the enthalpy of solution for NaCl(aq). The more reliable of the previous measurements, disregarding obviously inaccurate values, define a band of uncertainty of at least ±20 J mol^{-1}. Because the enthalpy of solution, in dilute solution for 298.15 K, is ≈4 kJ mol^{-1}, a reference value taken solely from the previous enthalpy of solution measurements would have been considered to have been no better known than ±0.5%. However, the enthalpy of solution that is calculated from the equation of state is determined not just by the previous measurements of enthalpy of solution but also by other measurements that are related through thermodynamic relationships. The end result is a more accurate value.

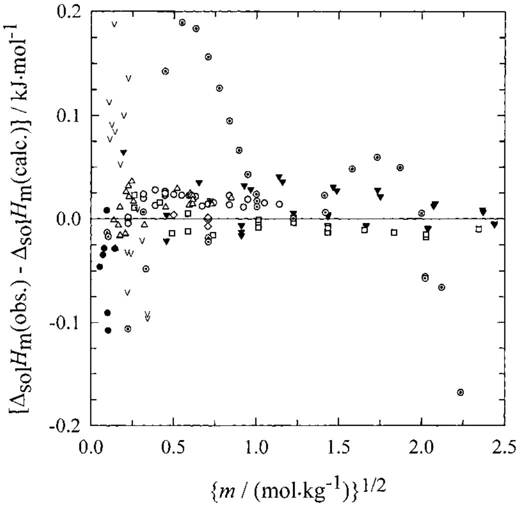

Fig. 1. Differences between measured enthalpies of solution of NaCl(aq) for 298.15 K, 0.1 MPa and values calculated from the equation of state. Each symbol represents a different set of measurements.

We have recently made measurements of the enthalpy of solution of sodium chloride in water with a high-accuracy, adiabatic, enthalpy of solution calorimeter. The mechanical construction of the calorimeter was described previously [3]. The thermometer used in the calorimeter was a 25 Ω, capsule, platinum-resistance thermometer, calibrated on the International Temperature Scale of 1990 (herein ITS-90) at NIST. The resistance of the thermometer was determined with a self-balancing AC inductance bridge. Voltages for electrical calibration of the calorimeter were determined with a 6-1/2 digit voltmeter. Data acquisition from the calorimeter and control of the adiabatic shields were implemented with computers. Additional detail of the calorimetric system will be presented elsewhere. Some of the sodium chloride samples were from Mallinckrodt and other samples were taken from optical crystals that were from the same lot used for previous measurement of enthalpy increments for NaCl(cr) [4]. The Mallinckrodt samples of NaCl were dried at 773 K for 24 h prior to use. The optical crystals were used as received, except for cutting and then grinding into smaller-sized crystals. Water was distilled and deionized.

Measurements of the enthalpy of solution of sodium chloride are endothermic and rapid. Electrical energy was supplied to the calorimeter's calibration heater during the solution process in order to compensate for the endothermic enthalpy of solution. The vessel and its contents therefore remained nearly isothermal during the process, thereby preventing shield control problems that would have resulted from a rapid decrease in temperature of the calorimetric vessel. Corrections to the observed enthalpy change were made for evaporation of solvent into the void volume of the sample cell, for changes in solvent activity due to the dissolution, for expansion of the vapor-space volume due to the change of volume upon mixing of the two condensed phases, and for any slight differences of the adiabatic-shield temperature from the calorimeter-vessel temperature.

Table 1
Enthalpy of solution of NaCl in H_2O

T (ITS-90) (K)	m (mol kg^{-1})	$\Delta_{sol}H_m$ (obs) (J mol^{-1})	$\Delta_{sol}H_m$ (obs) $-$ $\Delta_{sol}H_m$ (calc)[a] (J mol^{-1})
Mallinckrodt			
298.1584	0.1456	4221.3	−2.2
298.2805	0.1369	4205.0	−1.8
298.2909	0.1338	4196.3	−8.3
298.1546	0.1300	4212.7	−7.5
298.1170	0.1270	4225.3	+1.5
298.1765	0.1290	4217.4	+0.2
			average = −3.0 J mol^{-1}
			s.d. population (unbiased) = 4.0 J mol^{-1}
Optical crystal			
298.3366	0.1312	4190.3	−8.0
298.1641	0.1356	4220.8	+0.2
298.1654	0.1357	4226.1	+5.3
Mallinckrodt			
303.1363	0.1231	3623.8	−3.8
303.1214	0.1278	3628.4	−2.3
Optical crystal			
303.3100	0.13659	3604.9	−10.7
Mallinckrodt			
308.1444	0.1302	3068.2	−7.1
308.1556	0.1514	3081.6	−8.1

[a] Difference of the measured value from that calculated from the 1992 equation of state [2].

Measured values obtained recently with this calorimeter are given in Table 1, as are the differences of these values from the 1992 equation of state [2]. The equation for NaCl(aq) is in excellent agreement with the measured values. For temperatures near 298.15 K, the mean difference of the measured values from those calculated from the equation of state is −3.0 J mol^{-1}. The standard deviation of this mean value is 1.6 J mol^{-1}. These measurements therefore establish that values of the enthalpy of solution calculated from this equation of state at 298.15 K are accurate to within 3–4 J mol^{-1} or ca. 0.075–0.1% of the measured value.

Measured values of the enthalpy of solution for 308 K are slightly smaller (−8 J mol^{-1}) than values calculated from the equation of state. This difference may not be statistically significant when compared to the standard deviation of the measurement (4 J mol^{-1}). Additional measurements will be required to demonstrate whether this difference is real or due to random effects. If the difference is in fact real, then the −8 J mol^{-1} difference would be consistent with a bias of only −0.6 J K^{-1} mol^{-1} in the calculated values of $C_{p,\phi}$, for a nominal concentration of 0.13 mol kg^{-1}. This bias is well below that expected from uncertainty of individual measurements of the heat capacity of a solution of sodium chloride for this composition.

No statistically significant difference was found for sodium chloride samples taken from the sample of optical crystals when compared to that from the Mallinckrodt sample ($p = 0.1$; t-test).

As new, more accurate, results become available, including those described here, the equation of state for sodium chloride + water will be updated. Other recent measurements made at NIST that satisfy these conditions are heat capacities for NaCl(aq) as a function of temperature and composition for temperatures from <240 to 273 K; and new determinations of the low-temperature thermal functions, and hence a new determination of the entropy of NaCl(cr) [4].

2.2. KCl(aq)

An equation of state for the KCl + H_2O system has been prepared recently [5]. That work provided a new examination of an old problem, namely, reported discrepancies in the use of the enthalpy of solution of potassium chloride and their effect on the reliability of using KCl to calibrate calorimeters or as a check on their accuracy.

Previously Montgomery et al. [6] claimed that previous published claims of observed discrepancies in enthalpy of solution measurements for KCl were due to the presence of water-containing occlusions within many of the measured samples. They further hypothesized that these occlusions were not removed from samples unless they were dried at $T > 600$ K. In other words, Montgomery et al. were claiming that the samples had not been sufficiently dried for the majority of previous measurements.

The Montgomery et al. [6] analysis was examined in some detail during the preparation of the $KCl + H_2O$ equation of state. It was found that their conclusion was based on some faulty premises and statistical calculations. Archer [5] presented evidence that (1) the values of relative apparent molar enthalpy used by Montgomery et al. and by some others, were biased and the bias introduced errors into their comparisons of measured enthalpies of solution; (2) potassium chloride, when heated to a high enough temperature, may decompose to some extent; (3) when composition dependence of the measurements is handled properly, little or no dependence of measured enthalpy of solution on temperature of drying is observed; and (4) the only exceptions to (3) were samples that had been heated to such high temperatures that they may have decomposed to some extent.

Fig. 2 shows differences of measured enthalpies of solution from the fitted equation [5] where the measurements were taken from 37 different references, all but one of which had been considered by Montgomery et al. [6] The solid circles represent samples heated above 600 K and the open circles represent samples dried at temperatures <600 K. The four solid circles corresponding to a molality of 0.2775 mol kg^{-1} and that fall outside the ±20 J mol^{-1} band in the figure (one of the four circles partially superimposes one of the others) had been heated to temperatures near, or in excess of, 1000 K and we suppose them to have been contaminated by decomposition [5]. This supposition was supported by other reports of decomposition of KCl(cr) heated above 700 K in air. Fig. 2 shows that there was no real bias of the measurements based on the drying temperature. In fact, many of the measurements reported in the past were in good agreement with each other, within ±0.1%, if the concentration dependence of the enthalpy of solution was handled accurately. Many of the measurements shown in the figure were performed as 'a check on the calorimeter's performance' and thus were not necessarily of the same caliber as measurements undertaken to establish a standard value, such as those described by Kilday [7]. All of this considered, the agreement of so many of these measurements is vindication of the previous work of many of those laboratories and there is not substantial evidence that many of the measurements had been corrupted due to insufficient drying of the samples.

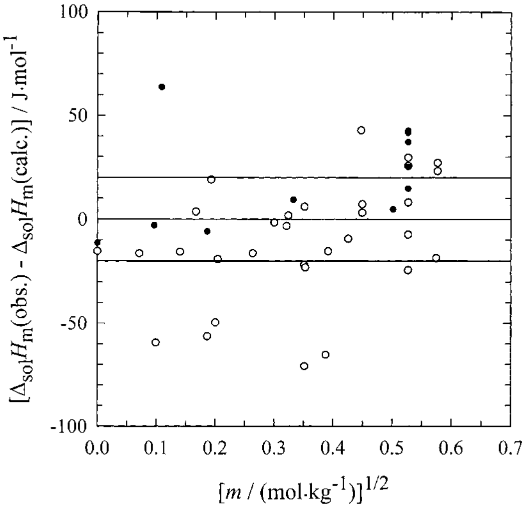

Fig. 2. Differences of measured enthalpies of solution of KCl(aq) from the fitted model. The filled circles are for potassium chloride samples heated above 600 K. The empty circles are for potassium chloride samples not heated above 600 K.

This work [5] demonstrated unequivocally that potassium chloride is suitable as a calibration material for enthalpy of solution calorimeters.

3. Enthalpy-increment calorimetry, heat-capacity calorimetry

There are several types of calorimeters that have been constructed for measurement of the thermal properties of condensed phases. Calorimeters of these types generally produce measurements of enthalpy increments or heat capacities. These instruments range from research-quality adiabatic cryostats to commercial thermal-analysis instruments. Previous work on development of standards for calibration of calorimeters that measure enthalpy increments or heat capacities has focussed on a small handful of materials. Of these, more recent efforts have concentrated primarily on synthetic sapphire (α-Al_2O_3) [8–11] and copper [4]. Because these types of calorimeters are used over significant ranges of temperature, one must consider also accuracies, or changes, of the temperature scales that were used in the generation of the thermodynamic properties of the standard materials.

3.1. Synthetic sapphire, α-Al_2O_3

The previously tabulated thermodynamic values for synthetic sapphire, NISTs Standard Reference Material-720 (SRM-720), were obtained by Ditmars et al. [8] from their fitting of different functions for different ranges of temperature to selected thermodynamic measurements. The measurements that had been included in the earlier representations from Ditmars et al. [8] were those given by Chang [9] who used an immersion-type adiabatic cryostat operating from 8.6 to 371.3 K; enthalpy increment determinations given by Ditmars and Douglas [10] using a Bunsen ice calorimeter with upper temperatures ranging from 323.15 to 1173.15 K; and enthalpy increment determinations given by Ditmars et al. [8] by means of an adiabatic enthalpy-increment calorimeter operating with upper temperatures from 1173.18 to 2257.11 K. Because of the nature of the equations fitted to these sets of measurements, there existed a small bias in the tabulated values for SRM-720, sapphire, from Chang's [9] measured heat capacities for temperatures from ca. 290 to 373 K. There was also a small bias of the tabulated values from West and Ginnings's [12] heat capacity measurements that had been obtained with an adiabatic calorimeter operating from near 300 to 700 K. The bias in the tabulated values was entirely an artifact of the method used for representation of the measurements and so could have been avoided had a better method been utilized.

In order to correct for this bias and also to answer other questions that had arisen regarding the Ditmars et al. [8] values for SRM-720, Archer [11] re-examined the measured thermodynamic properties for sapphire and applied a new method of representation to them. The new model of the properties of sapphire spanned the temperature range of 0 K to the melting point. The new representation did not show the systematic bias between the tabulated properties for SRM-720 and the heat capacity measurements for near-ambient and higher-temperature that had been present in the earlier tabulated values

Archer [11] not only corrected the systematic bias in the previous tabulated properties, but generated the new properties for sapphire on the basis of the ITS-90. In that article, the effect of the change of temperature scale from the International Practical Temperature Scale of 1968 (IPTS-68) on tabulated thermodynamic properties for SRM-720, specifically, and also on the general case of any least-squares generated equation, was examined. Comparisons and mathematical analysis [4,11] showed that a method described in an IUPAC Technical Report [13] on this subject was mathematically flawed and could result in unrealistic effects when applied to tabulated thermodynamic properties. This erroneous method had been recommended or suggested by other standards organizations (e.g. ASTM [14]) for adjustment or 'upgrad(ing)' the tabulated thermodynamic properties of sapphire for use in calibration of thermal analysis instruments. Alteration of previously tabulated values for calorimetric standards in that way would result in less accurate calibrations of calorimeters.

3.2. Copper

The Debye temperature of α-Al_2O_3 is rather high, $\sim$1000 K, and this limits the suitability of sapphire as a calibrant at lower temperatures. The lowest temperature at which sapphire will be useful for calibration will depend on the design and sensitivity of the particular calorimeter; however, for most applications sapphire's usefulness diminishes below ca. 50–80 K. Other materials have been sought for this low temperature range. One of those materials has been very pure copper (e.g. NISTs RM-5). Probably the most accurate set of measurements for copper was Martin's [15] measurements obtained with a 'tray' calorimeter and a vacuum-grown, single crystal of very pure copper that was ca. 180 g in mass. Martin made these measurements with a thermometer calibrated on the

IPTS-68. However, he did not publish his measured values, only a polynomial representation of them. Therefore, one could not adjust the measurements to make them more consistent with the ITS-90. (Equations for adjustments of measurements of heat capacities and enthalpy increments for changes in temperature scales are given in Ref. [16]). However, Archer [11] showed that one can adjust a linear least-squares generated equation for this change in temperature scale. Martin's polynomial equation was adjusted to be more consistent with the ITS-90 by the mathematical method described by Archer [11]. This ITS-90-compatible equation has been published elsewhere [4]. In that article, it was also noted that there was some cycling of Martin's polynomial about his measured values; this was established from comparison of new measurements obtained on the ITS-90 [4] with residual plots given by Martin [15].

We have described two equations for two calorimetric reference substances, α-Al_2O_3 and copper, that were based on measurements from different specially-constructed adiabatic calorimeters in different laboratories. A more stringent test of the accuracy of these reference materials could be had through additional measurements for both materials in the same calorimeter. Such a test could demonstrate systematic biases between the calibration values, so long as any calorimetric biases of the additional calorimeter were independent of the material being measured. This test has been made recently. Enthalpy increments for small temperature changes have been made recently for the calorimetric standards α-Al_2O_3 and copper in the same calorimeter [16]. The measured values were compared to values calculated from the equations given by Archer [11] and Martin [15], respectively, for temperatures from 50 to ca. 320 K. This comparison is shown in Fig. 3. The two lines were calculated from ±0.03% of the total measured enthalpy increment for the sample of synthetic sapphire and the calorimetric vessel; they have no relation to the copper determinations. The close agreement of the differences of the new measurements from the equations for both reference materials demonstrates the level of accuracy of values calculated from the reference equations, and consequently the measurements upon which they are based, and confirms the assumed premise that the calorimetric biases in this particular small-sample calorimeter were independent of the substance being measured. The agreement shown in Fig. 3 demonstrated that the thermal properties of these two materials had been previously determined to approximately ±0.03% for temperatures from 200 to 350 K and to approximately ±0.05% from 150 to 200 K [16]. Below 100 K, the measurements obtained with the small-sample calorimeter agreed with those from Martin to within ±0.05% for temperatures from ca. 30 to 60 K and to within ±0.03% for temperatures from 60 to 100 K, on the same temperature scale basis [4]. The reader is referred to references [4] and [16] for further details.

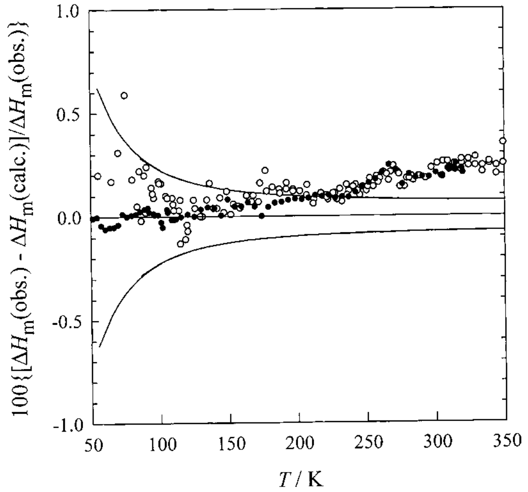

Fig. 3. Differences of measured enthalpy increments from reference values for: ○, synthetic sapphire (SRM-720) and ●, copper, for temperatures from 50 K to above ambient. The two lines were calculated from ±0.03% of the total measured enthalpy increment for synthetic sapphire and the addenda; they have no relation to the copper determinations.

4. Determination of accuracy of measurements of thermodynamic properties

Many of the equations for calorimetric standards discussed above were dependent upon a selection of some measurements from a larger subset of all measurements, or, in other words, some of the sets of measurements were removed or deweighted on the basis of perceived inaccuracies of those particular sets of data. Such a procedure could be argued by some to be such a non-objective enterprise that confidence in so-obtained values must be compromised. However, there are numerous objective thermodynamic tests to which various thermodynamic data can be subjected to establish their validity or to demonstrate a level of significant inaccuracy of the measurements. In other words, specific thermodynamic tests or comparison methods may establish bounds of uncertainties for particular sets of measurements and thereby reduce the subjectivity of assignment of weighting factors to sets of measurements. Some of these considerations are as follows. First, some measurement instruments are simply built to more exacting standards than are others. For example, measurement of the enthalpy change for a slow reaction, say, dissolution of quartz in hydrofluoric acid, should be expected to be more accurately determined with a carefully controlled adiabatic solution calorimeter than could be obtained with an isoperibol calorimeter that leaks heat to the constant-temperature surroundings. However, although not of high probability, even the most exactingly constructed calorimeter can be used improperly. Second, because of the relationships of thermodynamics, it is often possible to compare measurement of a particular property with a particular instrument to different properties obtained with other instruments. An example could be comparison of a set of solubility measurements against temperature with enthalpy of solution and enthalpy of dilution measurements. An example of the use of this test can be found in Ref. [2]. Disagreement outside of claimed inaccuracies would indicate that one or the other of the measurements, or both, are significantly less accurate than claimed. Third, internal consistency of a set of thermodynamic measurements can sometimes provide information on the inaccuracy of those measurements. A demonstration of an examination of internal consistency is described in the next paragraph.

In the example described here, a recently published set of thermal property measurements (reported as heat capacities) determined against temperature is examined for internal consistency in the absence of any other set of measurements. These measurements will be referred to as Set 1. The original authors of Set 1 described their 'probable errors in heat capacity' as 1% at 10 K and <0.2% for temperatures <30 K. A representation of the reported measured values could not be obtained with the root-mean-square (r.m.s.) deviations corresponding to the 'probable error' values without introducing physically-unrealistic behavior into the first derivative of the heat capacity with respect to temperature. Fig. 4 shows ($dC_{p,m}/dT$), labeled as Set 1, calculated from a representation for which the r.m.s. difference was still somewhat larger than the inaccuracy values claimed by the original authors (the method used for the representation has been described elsewhere [17,18]). There is no physical reason for the unusual behavior seen for this property. Reducing the r.m.s. difference for the representation to even smaller values, i.e. fitting the data more closely, only further increases the eccentricities seen in the first derivative. These eccentricities are a direct consequence of systematic errors in the reported measurements. Because most measurements contain some systematic error, we show for comparison purposes a similar treatment of a second set of measurements for a different, but chemically similar compound. This second set of measurements was similarly obtained from recent low-temperature enthalpy-increment determinations for a similar compound and obtained in a different laboratory than the first compound. This second set of measurements will

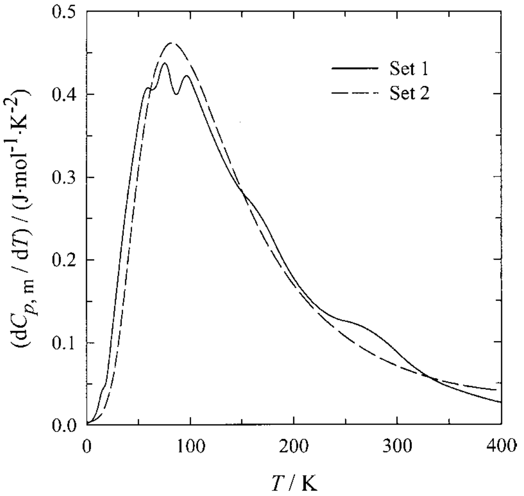

Fig. 4. The first derivative of heat capacity with respect to temperature for two similar, but nonidentical materials calculated from fitted models. The solid curve was calculated from a representation of the values for Set 1 for which it was attempted to reduce the r.m.s. difference to the authors' claimed 'probable error'. The resultant behavior is clearly physically unrealistic. The dashed curve was calculated from a representation of the measured values for Set 2. It does not show the physically-unrealistic eccentricities of the other curve.

be referred to as Set 2. Representation within expected calorimetric uncertainties (<|±0.1|% for $T > 30$ K) could be obtained for this set of measurements. Thus, the eccentricities observed for Set 1 are indicative of systematic errors significantly larger than for other contemporaneous measurements. Values of $(\mathrm{d}C_{p,\mathrm{m}}/\mathrm{d}T)$ calculated from this representation are also shown in Fig. 4. Returning now to Set 1, a more physically realistic representation of those measurements can be obtained by removal and readjustment of knot positions, as well as increasing the variance assigned to the measurements, until $(\mathrm{d}C_{p,\mathrm{m}}/\mathrm{d}T)$ had a more physically reasonable behavior similar to that shown for Set 2 in Fig. 4. The differences between the realistic fitted equation and the measured values for each of the two substances are shown in Figs. 5 and 6. The conclusion to be drawn is that the Set 1 measurements are not internally consistent within the author's claimed 'probable errors'. The method used for fitting Set 1 does not necessarily remove all systematic bias, rather, it removes only a portion of the bias, a portion which varies rapidly with respect to temperature for $T < 350$ K. Figs. 5 and 6 therefore show that the uncertainties for the first substance were not 1% at 10 K and not <0.2% for temperatures >30 K, but, instead, were more likely to be 5–10 times larger than the claimed uncertainties. The measured values for the second compound (Set 2) were obtained with less than half the sample used for the first compound, and thus the differences in inaccuracy between the two sets cannot be related to an advantage in sample size. This was a demonstration of the advantage of examining the derivative of a function fitted to a set of measurements to provide one clue as to whether uncertainties claimed by original authors were indeed reasonable, i.e. whether the measurements were internally consistent to this degree.

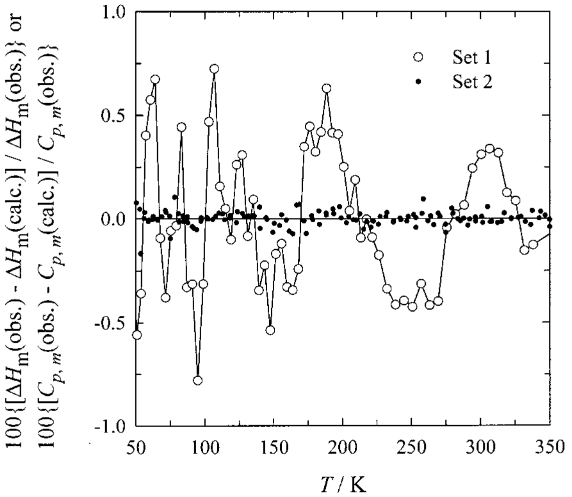

Fig. 5. Differences of the measured values from fitted models that possessed a physically reasonable behavior of $(\mathrm{d}C_{p,\mathrm{m}}/\mathrm{d}T)$. Temperatures range from 50 to 350 K. The symbols are: ○, Set 1; ●, Set 2.

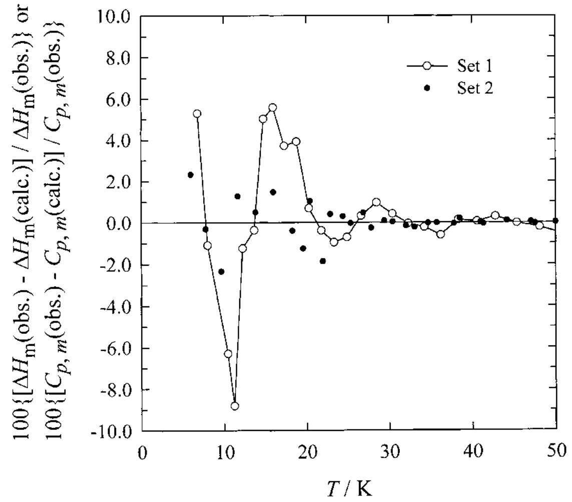

Fig. 6. Differences of the measured values from fitted models that possessed a physically reasonable behavior of $(\mathrm{d}C_{p,\mathrm{m}}/\mathrm{d}T)$. Temperatures range from 5 to 50 K. The symbols are: ○, Set 1; ●, Set 2.

The preceding material in this section showed that objective tools are often available to help establish the validity or inaccuracies of reported measurements of the thermodynamic properties of materials, including reference materials to be used for calibration of calorimeters.

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