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Enthalpy Increment Measurements from 4.5 to 318 K for Bismuth(cr). Thermodynamic Properties from 0 K to the Melting Point[†]

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Enthalpy increments for bismuth(cr) were measured from 4.5 to 318 K with an adiabatic calorimeter. The calorimeter's performance was demonstrated through comparison of measured enthalpy increments for copper and aluminum oxide to literature values. The effect that different temperature scales had on these comparisons for copper at low temperatures was discussed. The new enthalpy increments for bismuth(cr) were combined with previously measured thermodynamic properties for temperatures below 4 K and above 300 K in order to generate the thermodynamic properties of bismuth(cr) from 0 K to the melting point.

Introduction

Recent analysis of the thermodynamic properties of bismuth compounds performed for the U.S. Navy showed that discrepancies of heat capacity values for bismuth(cr) given in the literature, upon which were based the reference values of the thermodynamic properties, were on the order of 2−10% and were systematic between different laboratories (Neumann, 1994). As an example, where they overlapped from 200 to 300 K, the heat capacities given by Anderson (1930) were 1.5−2% smaller than values given by Bronson and MacHattie (1938).

There are also problems with previous determinations of the thermodynamic properties of bismuth(cr) found in some reference works. Figure 1 shows a comparison between measured values of heat capacity and the "selected values" given by Hultgren et al. (1973, 1963). (The heat capacity values from Franzosini and Clusius (1964) were published between publication of the two Hultgren references; however they were not listed among the measurements considered for the more recent version of Hultgren et al. (1973).) For 80−100 K, the more recent Hultgren et al. (1973) values were 1−2% larger than the measured values and were smaller than any of the measured values near 300 K, except for the rather imprecise values from Anderson (1930). Indeed, the earlier version of Hultgren et al. (1963) appeared to give more reasonable heat capacity values than the more recent version.

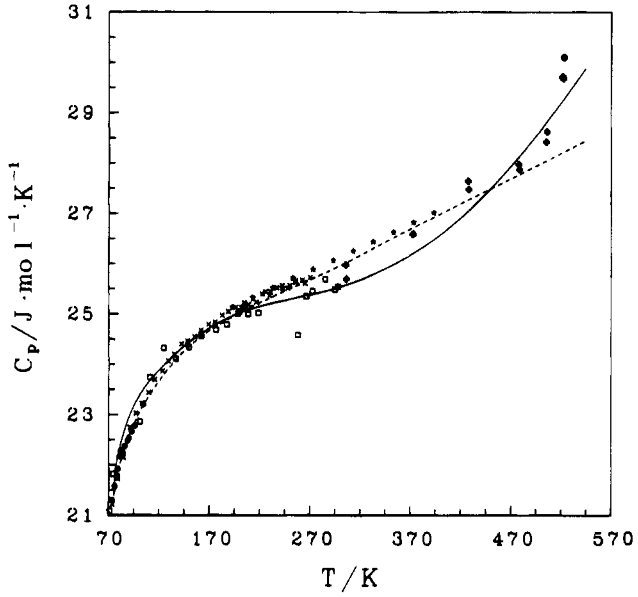

Figure 1. Symbols represent measured values of the heat capacity of bismuth(cr), and the lines are "selected values". Symbols: (□) Anderson (1930); (★) Bronson and MacHattie (1938); (●) DeSorbo (1958); (+) Carpenter and Harle (1932); (×) Franzosini and Clusius (1964). The solid line is from Hultgren et al. (1973), and the dashed line is from Hultgren et al. (1963).

The difference of the 298.15 K entropy given earlier by Hultgren et al. (1963) from the more recent Hultgren et al. (1973) value should have been related to the differences of the heat capacities given in those two works. From the difference in the two sets of heat capacity values one can calculate that the more recent Hultgren et al. value of the 298.15 K entropy should have been larger than the earlier value by no more than 0.04 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$; however, the more recent value is larger by 0.21 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$. This discrepancy puts the thermodynamic consistency of the more recent Hultgren et al. values in doubt. Of further interest is that the 298.15 K values of heat capacity, entropy, and enthalpy relative to 0 K, given by Hultgren et al. (1973), are all the same as those given by Wagman et al. (1982). Notes found at the National Institute of Standards and Technology (the successor to the National Bureau of Standards) indicated that Wagman et al.'s 298.15 K values of the heat capacity, entropy, and enthalpy relative to 0 K for bismuth(cr) were not obtained from their own examination of heat capacity measurements. Rather, Wagman et al. apparently took the 298.15 K values from three different treatments of different sets of measurements. Wagman et al.'s value of the 298.15 K heat capacity was taken from Anderson's (1930) treatment of his own measurements, the 298.15 K entropy value was from DeSorbo's (1958) treatment of literature results and the $H_\mathrm{m}(298.15\ \mathrm{K}) - H_\mathrm{m}(0\ \mathrm{K})$ value was taken from Stull and Sinke's (1956) different treatment of a different set of measurements. Thus, there is no reason to expect

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[†] Certain commercial materials 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.

that Wagman et al.'s values of the thermodynamic properties for bismuth(cr) are thermodynamically consistent with each other. There appears to be no reason to doubt the thermodynamic consistency of the earlier Hultgren et al. (1963) values. So apparently the thermodynamic inconsistency was introduced in order to bring the more recent values from Hultgren et al. (1973) into agreement with the values from Wagman et al. (1982).

All of these things considered, it was reasonable to expect that the uncertainty in the often reported values of the entropy of elemental bismuth(cr) could be 1.5%, perhaps larger, for 300 K. This uncertainty introduced an unnecessary 250 $J{\cdot}mol^{-1}$ minimum uncertainty into thermodynamic calculations involving the Gibbs energy of bismuth(cr).

The present work provides new thermodynamic measurements and thermodynamic functions for bismuth(cr). The measurements are enthalpy increments measured for small differences in temperature, on the order of 1.5–5 K, with an adiabatic calorimeter. In the past, these enthalpy increments were usually divided by the difference of the higher and lower temperatures for the increment and referred to as a "heat capacity". Sometimes, a so-called "curvature correction" was added to these "heat capacity" values. This "curvature correction", in its most often used form, required assumption of a model. The model assumed for the curvature correction usually did not match the model used for the subsequent treatment of the "heat capacities". While the "heat capacity" approach presented certain simplicities in handling of the experimental data quite some time ago, today's low cost of computation severely reduces this benefit. Considering the problems of model assumption for the "curvature corrections", and the frequent loss of experimental information that occurs from reporting only the average temperature for the measurement, the present author sees little beneficence associated with this "heat capacity" approach. As such, the experimental results are reported and treated here as what they are, namely, enthalpy increments.

Experimental Section

Calorimeter. The cryostat used for this work was that originally constructed by Osborne et al. (1972). It was obtained from a now defunct Department of Energy calorimetry program at Argonne National Laboratory (ANL). The present work utilized a calorimeter vessel, of 6 cm^3 internal volume, recovered with the cryostat. The cryostat and calorimeter vessel have been described previously (Osborne et al., 1972; Johnson et al., 1982; Price et al., 1986). Several changes have been made to the calorimetric system prior to the measurements reported here.

An encapsulated miniature 25 Ω platinum thermometer (Minco Inc.) was used for measurement of the temperature of the calorimeter. This thermometer was calibrated at the National Physical Laboratory (NPL) of the United Kingdom on the International Temperature Scale of 1990 (ITS-90) by a comparison method. Measurements of the thermometer's resistance at 4.2 and 7.2 K were also made at the NPL and were used in an interpolatory function for temperatures below 13.8 K, the lowest defined ITS-90 value for platinum thermometers. A new heater core was machined to accommodate the new thermometer. The heater core had the general appearance of the heater core described by Sterrett et al. (1965). The heater core was bifilarly wound with approximately 150 Ω of 32 gauge Evanohm wire, which was subsequently varnished in place.

A computer was used for data acquisition and control of the calorimeter measurement circuitry. The resistance of the thermometer was measured with a self-balancing bridge (Tinsley Co.). Power to the calorimeter heater and an in-series standard resistor was supplied by a general-purpose-interface-bus (GPIB) programmed, regulated power supply. The output of this power supply was switched between a "dummy" resistor and the calorimeter circuit by a high-speed mercury-wetted relay. This relay was controlled by a separate multiplexor. The multiplexor also performed the switching necessary to measure voltages across the standard resistor and the calorimeter heater. Voltages were measured with a $7^1/_2$ digit voltmeter with internal calibration. Time was measured with a 1 MHz counter for voltages impressed across the calorimeter heater greater than 0.3 V. For smaller voltages, time was measured with the computer's internal clock. Both of these timers were periodically checked aqainst a rubidium frequency standard.

Temperature control of the adiabatic shields was performed with a second computer. This computer used the thermoelectric voltages of the shield thermocouples to control the temperatures of the individual shields. The side-, top-, and bottom-shield thermocouple voltages were measured with nanovoltmeters, the outputs of which were obtained by the computer over a GPIB. Thermocouples for the less-critical shields, in the present case a tempering ring, were measured with nanovoltmeters which did not have a GPIB interface. The chart-recorder output from these nanovoltmeters was digitized by an analog-to-digital converter (12 bit) installed in the computer.

The digitized thermocouple voltages were used in algorithms that utilized proportional, integral, and derivative control actions. The algorithm outputs were converted to analog voltage signals by buffered, latching, 12-bit, digital-to-analog converters. The outputs from these converters drove voltage-programmed dc power supplies that were connected to the shield heaters. During the interval between calorimeter heatings the computer changed the proportional, integral, and derivative coefficients on the basis of the calorimeter temperature. In this way, the adiabatic shields were always near optimum control regardless of the calorimeter temperature and without an operator present. The two computers communicated with each other over an RS-232 bus. This permitted the computer that performed the shield control to obtain the calorimeter's temperature from the other computer. Incorporation of the RS-232 communication was necessitated because the commercial software used to construct the instrument control programs did not incorporate IEEE-488 slave-controller characteristics. Digital control of the adiabatic shields also allowed for rapid experimentation with shield control strategy. It was found that significantly better control of the shields was obtained by feeding the square root of the PID output to the power supplies.

Communication of the two computers over the RS-232 bus also allowed each computer to poll the other computer for problems and, if found, to shut down power supplies controlled by the other computer. This prevented the possibility of an excessive temperature increase that could result from malfunction of either the hardware or software. Power to computers, measurement instruments, and power supplies was supplied with an uninterruptible, isolated power supply in order to overcome the short-term random power outages in the laboratory.

The adiabatic shields were previously controlled at ANL by a simultaneous combination of manual control and analog PID controllers. Characteristics of the adiabatic-shield construction complicated conversion to fully automatic control. In order to prevent the top- and bottom-shield controllers from driving-off the side-shield control, it was necessary to sum the side-shield thermocouple voltage to the top- and bottom-shield thermocouple voltages

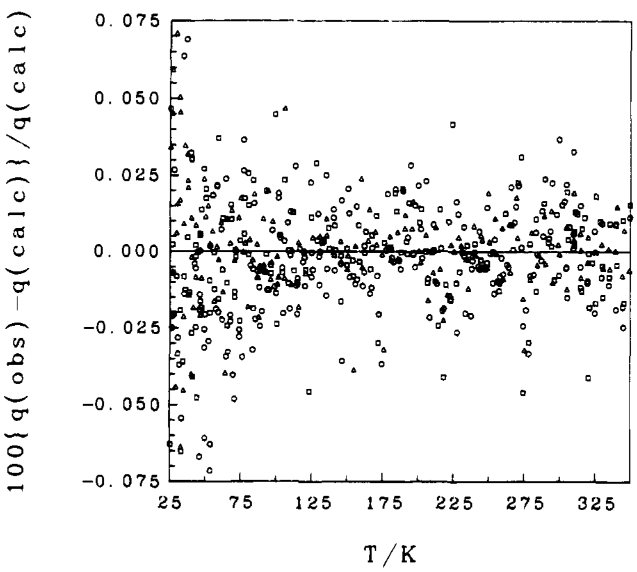

Figure 2. Difference of measured enthalpy increments for the empty calorimeter from the fitted equations for temperatures from 25 to 350 K. The three symbols each represent different determinations.

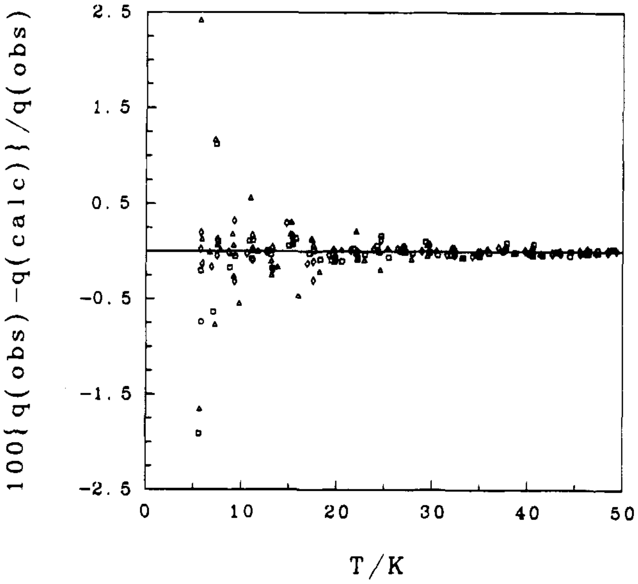

Figure 3. Difference of measured enthalpy increments for the empty calorimeter from the fitted equations for temperatures from 4 to 50 K. The three symbols each represent different determinations.

for the input to the digital PID routines. This allowed the PID algorithms to operate on the difference of temperature of the top and bottom shields from the calorimeter rather than on the difference of the top- and bottom-shield temperatures from the side-shield temperature. Additionally, for temperatures less than 200 K, there was insufficient loss of heat from the bottom shield to allow good control of the temperature of the shields. In order to alleviate that problem, a set of copper wires was attached so that one end contacted the center of the bottom shield and the other end, which was weighted, was allowed to rest on the bottom of the first passive shield. The first passive shield attached to the lower refrigerant reservoir and thus provided a heat-leak path from the bottom shield.

Figures 2 and 3 show the difference of measured enthalpy increments for the empty calorimeter from fitted equations. Three separate determinations of the enthalpy content of the calorimeter are shown. Figure 2 shows that the calorimeter's enthalpy is determined with a standard deviation of about 0.015% for temperatures greater than 50 K. A small systematic difference between the measured and calculated values is seen for all enthalpy increments that span 273.15 K, whether the calorimeter is empty or full. The standard deviation for the determination of the enthalpy of the empty calorimeter for temperatures of 4−5 K is about 1 to 1.5%; however the standard deviation attenuates rapidly with increasing temperature, reaching about 0.2% at 10 K and 0.1% at 20 K.

No significant discrepancies in enthalpy determinations for the empty or full calorimeter were found for different heater currents. The range of investigated heater current corresponded to approximately −50% to +20% about the value of the heating current chosen to be that for routine measurement. What was found to have a significant affect in determination of accurate enthalpy increments was the time allowed for equilibration after an energy input to the calorimeter. In many determinations, nonequilibration of the filled calorimeter could still be observed 30 min after the end of a 600 s heating interval that spanned a temperature difference of 2.5−4.5 K. Because of this, no equilibration period was ever taken to be less than 35 min, even if the program's criteria for determination that equilibrium had been reached was satisfied.

The performance of the calorimetric system was demonstrated by comparison with values for two calorimetric reference substances, synthetic sapphire and copper. Such a comparison was deemed particularly important because of the small volume for this calorimeter.

Materials. Performance of the calorimetric system was demonstrated using synthetic sapphire (α-aluminum oxide) and copper. The aluminum oxide sample was taken from batches previously used to obtain calorimetric values for the National Institute of Standards and Technology's (NIST) Standard Reference Material 720. The aluminum oxide was in the form of single-crystal rods that were approximately 2−2.5 mm in diameter and 5−6 mm in length with a purity greater than 99.98%. This material, previously calcined, was loaded into the calorimeter and the calorimeter evacuated. Approximately 8 kPa (pressures of He are for 300 K) of helium was then introduced into the calorimeter. The mass of the aluminum oxide in the calorimeter was 9.8710 g and corresponded to approximately half of the internal volume of the calorimeter.

Copper, NIST's Research Material 5, was in the form of polycrystalline rods with a purity greater than 99.999%. A single rod was machined to fit, not snugly, the calorimeter's internal cavity. After machining, the copper sample was heavily acid-etched, dried, and then loaded into the calorimeter with approximately 16 kPa of helium. The mass of the copper specimen was 46.9073 g and corresponded to approximately 90% of the internal volume of the calorimeter.

Bismuth was obtained from Aldrich Chemical as 99.9999% pure (metals basis). Due to the high affinity of bismuth for oxygen, all sample handlings were performed in an argon-filled drybox. The calorimeter was sealed with 8 kPa (300 K) of helium in addition to the bismuth. The inside of the calorimeter was not gold plated. Bismuth oxide and copper metal are more thermodynamically stable than copper oxide and bismuth metal. In order to determine if the bismuth metal would contaminate itself with oxygen from the internal copper wall of the calorimeter, a sample of bismuth shot was put in contact with an old piece of copper sheet for a period of 3 months. No reduction of the copper sheet was observed, indicating a probable kinetic barrier to the oxygen-transfer reaction. The mass of the bismuth sample was 23.0013 g (0.110 065 mol).

All enthalpy increments measured for the loaded calorimeter were corrected for differences in the amounts of helium and Apiezon grease between the empty and loaded calorimeter determinations.

Calorimeter Performance. The enthalpy increments for copper and aluminum oxide utilized separate determinations of the enthalpy content of the empty calorimeter; i.e. the same determination of the enthalpy content of the empty calorimeter was not used for both reference substances. This gives a better measure (more strenuous) of the performance of the calorimeter than does using the same empty calorimeter determination for both reference-substance determinations.

For temperatures greater than 50 K, the measured enthalpy increments were compared to values calculated from the equations for aluminum oxide and copper given by Archer (1993) and Martin (1987a), respectively. Archer's equation for aluminum oxide, for temperatures less than 300 K, is based primarily on the heat capacities given by Chang (1977). The values from the equation for temperatures above 300 K are in excellent agreement not only with Chang's values but also with the heat capacities from West and Ginnings (1958) and from Andrews et al. (1978) and with the enthalpy increment measurements from Ditmars and Douglas (1971), indicating excellent agreement of all of these measurements. Martin's equation for copper is based entirely on his own values. Martin showed good agreement of his equation with the heat capacity values given by Robie et al. (1976) and by Martin and Downie (1980) except at the lowest temperatures where Martin and Downie's precision was degraded.

Martin's (1987a) measurements for copper were based on a thermometer calibrated on the International Practical Temperature Scale of 1968 (IPTS-68). Martin's equation was used here as he reported it. Some might say that his equation corresponds to the IPTS-68 and a comparison of the present measurements obtained with an ITS-90 calibrated thermometer to Martin's IPTS-68 equation is fallacious. It is also common to find this sort of statement in calorimetry papers: "The changes in heat capacity, enthalpy increment, and entropy resulting from the conversion from IPTS-68 to ITS-90 have been shown to lie within the experimental error of the measurements over the range from $14 \leq (T/\mathrm{K}) \leq 2150$" accompanied with citation of a paper from Goldberg and Weir (1992) (see Appendix I). These two points are dealt with here.

In addition to his measurements for copper, Martin (1987) also measured the heat capacity of silver and gold with the same calorimeter and thermometer used for the copper measurements. For all three metals, Martin (1987) compared the difference of his measurements from his equations that had been fitted to those measurements (i.e. the residuals) in his Figure 6. A systematic pattern of bias which was similar for all three metals was observed in the residuals from 15 to 70 K. Martin then superimposed the difference in experimental heat capacity that would be caused by the difference of the IPTS-68 from a magnetic thermometry scale (Cetas, 1976). The calculated effect of the difference of IPTS-68 from the magnetic-salt temperature scale matched the systematic differences of the experimental measurements from the fitted equations extremely well from 20 to 70 K. Temperatures from the IPTS-68 oscillated about temperatures from the magnetic-salt temperature scale which Martin had chosen for comparison. (It is outside the scope of the present paper to describe all magnetic-salt thermometry results. It will suffice to observe that the differences in temperature between different magnetic-salt thermometers and different laboratories vary smoothly with thermodynamic temperature whereas the differences for a platinum thermometer calibrated on different international scales have not in the past.)

Martin's (1987) Figure 6 shows a couple of things. The first is that his fitting process removed most of the difference in heat capacity that would result from the difference of the IPTS-68 from the chosen magnetic-salt temperature scale. This is another demonstration of Archer's (1993) conclusions regarding the effect of model-fitting on the rapid fluctuations of temperature scale differences relative to thermodynamic temperature. Because most of the difference in thermodynamic measurement that would have resulted from the difference of the IPTS-68 from the magnetic-salt scale was contained in the fitting residuals, this portion of the difference could not also have been contained in the fitted equation. Thus, Martin's equation for temperatures up to 80 K was more related to the magnetic-salt temperature scale than to the IPTS-68. Martin's equation could be converted to the ITS-90 by the mathematical method described by Archer (1993); however, it will be used here with the recognition that its temperature basis is essentially that of the chosen magnetic-salt temperature scale.

Another thing shown by Martin's (1987) Figure 6 is that the change in his measured heat capacities that would result from the conversion of the IPTS-68 to a magnetic-salt temperature scale was not significantly smaller than the other known sources of uncertainty of his measurements. It will be shown below that an effect arising due to the difference of the ITS-90 from the same magnetic-salt temperature scale used by Martin was observed in the present results for copper for temperatures less than 70 K. Both of these cast doubt on the quoted statement presented above.

Figure 4 shows the percentage differences of the calorimetrically determined enthalpy increments for aluminum oxide and copper obtained with the present calorimetric system from the two equations (Archer, 1993; Martin, 1987a) for temperatures greater than 50 K. Above 150 K, the measured values for copper are more precise than those for aluminum oxide because of improvements in thermometer-lead shielding made subsequently to the aluminum oxide measurements. The apparently random scatter of the differences for aluminum oxide about those for copper indicated that the poorer electrical shielding did not introduce a systematic bias into the results. The differences of the measured values from the fitted equations for the two reference materials showed excellent agreement with each other, attesting to the accuracy of the previous thermodynamic measurements used to generate the reference-material equations. Figure 4 also showed that the calorimetric results obtained with this calorimeter exhibited a small systematic bias which was linear in temperature from 100 to 350 K. Because of the large dissimilarities of the two standard material samples, this systematic bias appeared to be independent of the nature of the measured specimen. As such, a correction for this bias will be applied to further measurements obtained with this calorimeter. The correction will be

$$\epsilon \Delta H_{\mathrm{m}} = -[\{(T_2 + T_1)/2\} - 100\ \mathrm{K}]\cdot 0.00001\ \mathrm{K}^{-1}\ \Delta H_{\mathrm{m}} \tag{1}$$

where T_2 and T_1 are the two temperatures for the enthalpy increment and $\epsilon\Delta H_{\mathrm{m}}$ is added to the substance's measured enthalpy increment, ΔH_{m}.

Below 100 K, the contribution from the aluminum oxide became a decreasingly small percentage of the total measured enthalpy increment and so aluminum oxide was somewhat less useful as a calorimetric standard below 50 K. Figure 5 shows comparison of the measured enthalpy increments for copper from literature equations for temperatures less than 80 K.

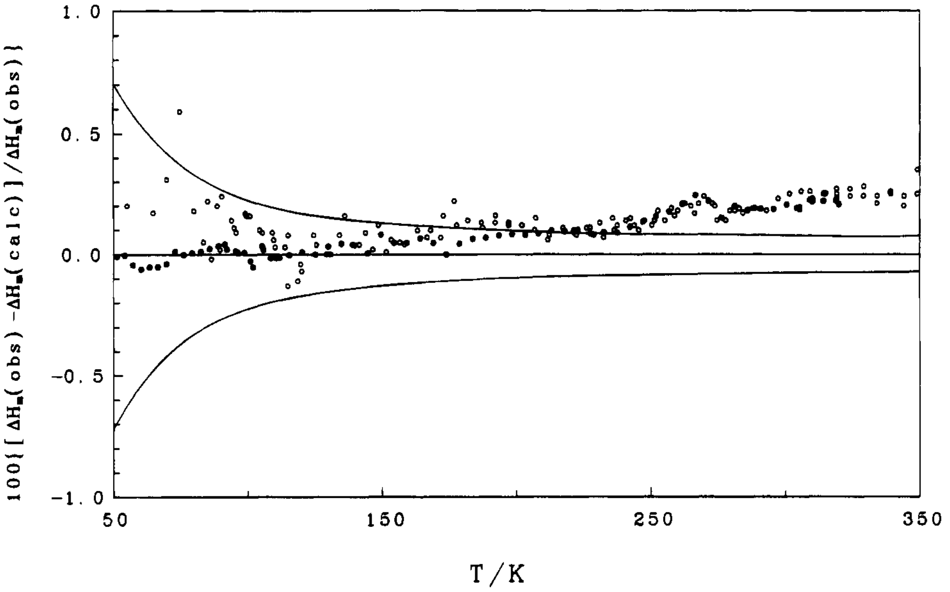

Figure 4. Differences of measured enthalpy increments from reference values for (○) synthetic sapphire (SRM-720) and (●) copper for temperatures greater than 50 K. The two lines were calculated from ±0.03% of the total measured enthalpy increment for synthetic sapphire and the addenda; they have no relation to the copper determinations.

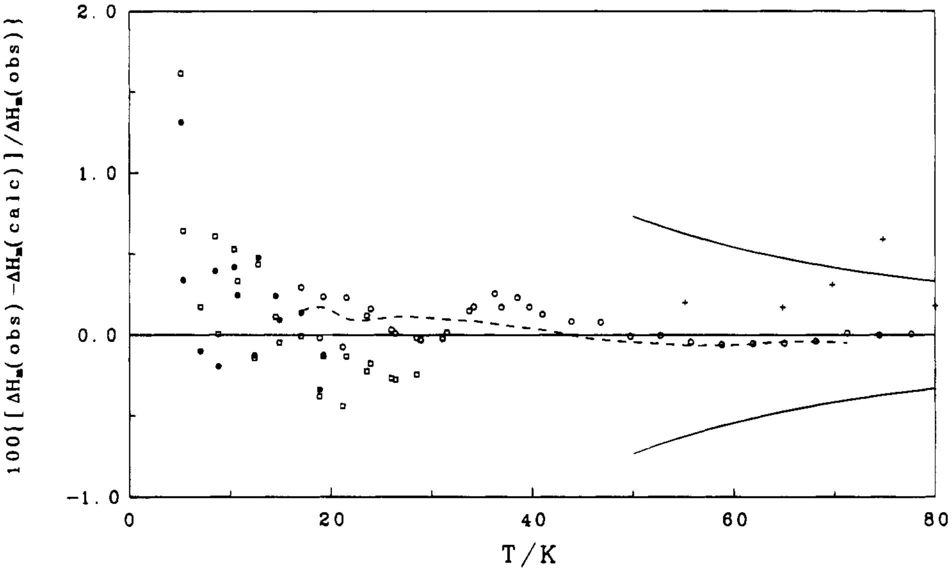

Figure 5. Differences of measured enthalpy increments from reference values (+) for synthetic sapphire (SRM-720), (○) for copper from the equation given by Martin (1987a), (●) for copper from the equation given by Osborne et al. (1967), and (□) for copper from the equation given by Holste et al. (1972). The dashed line is the difference of the present enthalpy increments on a magnetic-salt temperature scale from the enthalpy increments on the ITS-90 (see text). The two solid 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.

Comparison of the present enthalpy increments with values calculated from Martin's (1987a) equation is shown for temperatures above 15 K. As stated above, the temperature basis of Martin's equation can be considered to be a particular magnetic-salt temperature scale. The differences of the present enthalpy increments relative to Martin's equation, $100\{[\Delta H_m(\text{present, ITS-90}) - \Delta H_m(\text{Martin, magnetic-salt scale})]/\Delta H_m(\text{ITS-90})\}$, are represented as open circles. This quantity showed an average positive deviation for temperatures less than 40 K and an average negative deviation for temperatures from 40 to 70 K. Also shown in the figure is a dashed line which is the difference of the present enthalpy increments using temperatures on the ITS-90 from the same enthalpy increments using temperatures calculated on the same magnetic-salt scale considered by Martin. In other words, the dashed line is $100\{[\Delta H_m(\text{ITS-90}) - \Delta H_m(\text{magnetic-salt scale})]/\Delta H_m(\text{ITS-90})\}$. This quantity also showed a positive deviation from 15 to 40 K and a negative deviation from 40 to 70 K. Below 50 K the ITS-90 is an average of approximately 6 mK less than the magnetic-salt scale. This difference caused the bulk of the average positive deviation of the dashed line shown in Figure 5. From 40 to 80 K, the ITS-90 changes from 8 mK less than the magnetic-salt scale to 8 mK greater than it. This rapid change of temperature relative to the magnetic-salt temperature scale caused the average negative deviation above 50 K shown in the figure. These differences of the ITS-90 from the magnetic-salt scale are much larger in magnitude than were the differences of the IPTS-68 from it.

Again, the dashed line is $100\{[\Delta H_m(\text{present, ITS-90}) - \Delta H_m(\text{present, magnetic-salt scale})]/\Delta H_m(\text{ITS-90})\}$ and the open circles are $100\{[\Delta H_m(\text{present, ITS-90}) - \Delta H_m(\text{Martin, magnetic-salt scale})]/\Delta H_m(\text{ITS-90})\}$, and so a comparison of these two objects is a comparison of the present measurements with Martin's equation on the same temperature basis. There are two conclusions to be drawn from the comparison of the dashed line and open circles of Figure

5. The first is that when the present enthalpy increments are brought onto the same temperature basis as Martin's equation, the differences in calorimetry produce differences in these thermodynamic values of no more than 0.03% from 50 to 80 K, and no more than 0.15% from 15 to 50 K. These values are representative of the present instrument's calorimetric uncertainties, including the imperfections in the thermometer calibration (e.g. the nonuniqueness of the temperature scale) but not including the uncertainty introduced by the *definitions* of the international temperature scales. The second conclusion is that the *definition* of the international temperature scales introduces an additional, nontrivial, uncertainty comparable in magnitude to, or larger than, the other sources of uncertainty in the calorimetric measurements, as evidenced by the temperature-dependent systematic nature of the average deviations shown by the dashed line in Figure 5. Also, because Martin showed that the differences of the IPTS-68 from a magnetic-salt temperature scale were observed in his results and because the present measurements showed an effect due to the difference of the ITS-90 from the same magnetic-salt temperature scale and because the two effects were not at all the same, the difference of the ITS-90 from the IPTS-68 would also be observed in *either* calorimeter. This shows the effect of changing from the IPTS-68 to the ITS-90 on low-temperature thermal-property measurements is not, generally, "negligible" or "within the experimental error of the measurement". Rather, the difference of international temperature scales is large enough that its neglect can interfere with determination of true calorimetric uncertainties below 70 K.

Reference values for copper for temperatures less than 30 K were significantly more uncertain than for higher temperatures, mostly due to differences in temperature scales, both international and laboratory. Because of this, enthalpy increments from the present calorimeter for temperatures less than 30 K were compared to three different literature sources in Figure 5.

Comparisons with Holste et al.'s (1972) equation for temperatures below 30 K and with Osborne et al.'s (1967) equation for temperatures below 20 K are also shown in Figure 5. Comparison with Osborne et al.'s equation above 20 K was not made for the reasons given by Martin (1987a). Differences due to the choice of equation were clearly visible in the figure.

For temperatures from near 30 K to near 15 K, the true enthalpy increments for copper are probably not known better than ±0.2%, including the uncertainty due to *definition* of the international temperature scales, or ±0.1% without the uncertainty due to *definition* of the temperature scales. For temperatures less than 15 K they do not appear to be known to better than ±0.3%. Despite the differences in the literature values there appeared to be a small systematic bias in the present results (0.25% large) for temperatures less than 13 K. This was not surprising in that the internationally-adopted temperature scales have not defined an interpolatory resistance-temperature relation for platinum thermometers below 13.8 K and that the bias introduced due to the differences of the ITS-90 and the IPTS-68 was on the order of 0.15% at 13–15 K. Accordingly, further enthalpy increments obtained with the present instrument for temperatures less than 13.8 K will be reduced by 0.25%. This correction can be considered a correction for both calorimetric and temperature errors in this temperature region.

Results

Enthalpy Increment Measurements for Bismuth(cr). The measured enthalpy increments for bismuth(cr) are given in Table 1. Above 50 K, the measurements for this sample are expected to be uncertain by ±0.05 to ±0.1%. Below 50 K, the results must be considered less accurate, due to limits in accuracy of platinum resistance thermometer temperature scales below 50 K. The contribution of the bismuth to the total measured enthalpy increment was a minimum of 20% at the highest temperatures and increased in percentage with decreasing temperature. The sample contributed 79% of the total enthalpy increment for the lowest temperature measurement. The increasing contribution of bismuth to the total enthalpy increment as temperature decreased from 300 K was a result of bismuth having a much smaller Debye temperature than copper, which comprised the bulk of the calorimeter.

Representation of Thermodynamic Properties. Thermodynamic properties for bismuth were calculated from a least-squares representation of the enthalpy increments from Table 1. The present measurements do not span the whole temperature range of existence for the crystalline state. In order to obtain thermodynamic properties for the full range of temperature some previous measurements were selected and included in the least-squares representation. The present enthalpy increments as well as some previously reported heat capacities were fitted using a cubic-spline method described previously (Archer, 1992). That method was altered in the present case to allow incorporation of the effect of electrons that occupy a conduction band.

Briefly, a function $f(T)$ was used, where

$$f(T) = [T\{(C_{p,\mathrm{m}} - \gamma_{\mathrm{el}}T)/C_p^\circ\}^{-1/3} - bT]/T^\circ \qquad (3)$$

and where T was temperature, T° was 1 K, $C_{p,\mathrm{m}}$ was the molar heat capacity, C_p° was 1.0 J·K^{-1}·mol^{-1}, γ_{el} was the contribution from the conduction electrons, and b was chosen to be 0.35 for the present case. The function $f(T)$ of eq 3 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \qquad (4)$$

where the subscript i refers to the polynomial that contains the specified value of T and spans the temperature range T_i to T_{i-1}. A particular (T_i, d_i) pair is referred to as a "knot". "Natural spline" end conditions (i.e. second derivative equal to 0) were imposed at the two end knots. (For the purpose of calculation: $T_{i-1} > T > T_i$). The calculated heat capacity is thus

$$C_{p,\mathrm{m}}/C_p^\circ = \left(\frac{T}{T^\circ f(T) + bT}\right)^3 + \gamma_{\mathrm{el}}T/C_p^\circ \qquad (5)$$

Equation 5 was integrated numerically to obtain the enthalpy. The model was fitted to the experimental values with a nonlinear least-squares program. The vector of residuals was calculated using eq 5 for the heat capacity or numerical integrations of eq 5 to obtain the enthalpy increments.

Krishna and Srivostava (1973) calculated the electronic contribution to the low-temperature heat capacity from a one-electron ellipsoidal nonparabolic model of the density of states at the Fermi level. Their value, 8.28 × 10^{-6} K^{-1}, was used as $\gamma_{\mathrm{el}}/C_p^\circ$.

For the range of temperatures greater than that of the present measurements (~318 K) the heat capacities given by Grønvold (1975) were included and assigned square roots of the variance of ±0.3%. Two sources of values were used for temperatures less than 4.2 K. Collan et al. (1970) gave experimental values for temperatures from 0.074 to

Table 1. Enthalpy Increment Measurements for Bismuth(cr)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	$100\sigma/\Delta H_m(T_1 \rightarrow T_2)$[a]	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	$100\sigma/\Delta H_m(T_1 \rightarrow T_2)$[a]
4.571	5.734	0.3071	2	138.5934	143.1904	111.510	0.1
5.706	7.134	0.8363	1	143.1819	147.7927	112.247	0.1
9.073	11.238	4.8636	0.5	147.7834	152.3911	112.589	0.1
11.235	13.7247	8.6498	0.5	152.3814	156.9901	112.959	0.1
13.7199	16.0137	10.9737	0.5	156.9796	161.5779	113.047	0.1
16.0059	18.6466	15.9584	0.5	161.5663	166.1711	113.549	0.1
18.6480	21.0994	17.9734	0.25	166.1590	170.7600	113.572	0.1
21.0974	23.6374	21.6619	0.25	170.7473	175.3632	114.399	0.1
23.6331	26.2466	25.3849	0.2	175.3496	179.9628	114.616	0.1
26.2416	28.9027	28.9299	0.2	179.9484	184.5571	114.837	0.1
28.8965	31.5935	32.2874	0.1	184.5420	189.1521	115.306	0.1
31.5861	34.3003	35.3411	0.1	189.1372	193.7369	115.339	0.1
34.2941	37.3175	42.5479	0.1	193.7220	198.3190	115.330	0.1
37.3103	40.3649	45.9769	0.1	198.3042	202.9085	115.758	0.1
40.3572	43.4282	48.9561	0.1	202.8925	207.4840	115.516	0.1
43.4201	46.5469	52.4168	0.1	207.4672	212.0682	115.997	0.1
4.484	5.871	0.3777	2	212.0505	216.6456	116.082	0.1
5.860	7.464	1.0739	1	216.6269	221.2138	116.084	0.1
7.465	9.403	2.6809	0.5	221.1954	225.7939	116.525	0.1
9.399	11.843	6.0832	0.5	225.7741	230.3641	116.526	0.1
11.842	14.4823	10.1908	0.5	230.3426	234.9324	116.656	0.1
14.4780	17.0623	13.5891	0.5	234.9094	239.4918	116.716	0.1
17.0584	19.4585	15.6757	0.5	239.4663	244.0469	116.776	0.1
19.4585	21.9632	19.3849	0.25	244.0198	248.6107	117.402	0.1
21.9637	24.5433	23.0711	0.25	248.5813	253.1753	117.475	0.1
24.5429	27.1766	26.6560	0.2	253.1409	257.7296	117.564	0.1
27.1736	29.8146	29.7532	0.2	257.6979	262.2899	117.775	0.1
29.8106	32.5020	33.2023	0.1	262.2525	266.8407	117.885	0.1
32.4972	35.2276	36.5274	0.1	266.8017	271.3940	118.109	0.1
35.2221	37.9949	39.7821	0.1	271.3559	275.9341	117.738	0.1
37.9888	40.7893	42.6129	0.1	275.8939	280.4677	118.087	0.1
40.7819	43.8073	48.5747	0.1	280.4250	285.0034	118.366	0.1
43.8010	46.8402	51.208	0.1	284.9580	289.5363	118.490	0.1
46.8336	49.8966	53.802	0.1	204.4619	209.1323	117.668	0.1
49.8897	52.9964	56.568	0.1	209.1116	213.6887	115.320	0.1
52.9893	56.0952	58.362	0.1	213.6683	218.2559	115.897	0.1
56.0881	59.2404	60.814	0.1	218.2328	222.8103	115.995	0.1
59.2325	62.3896	62.453	0.1	222.7885	227.3666	116.081	0.1
62.3821	65.5562	64.159	0.1	227.3402	231.9318	116.654	0.1
65.5480	68.7386	65.716	0.1	231.9066	236.4923	116.668	0.1
68.7309	71.9390	67.213	0.1	236.4659	241.0465	116.777	0.1
71.9300	75.1499	68.442	0.1	241.0155	245.5981	116.916	0.1
75.1406	78.3826	69.874	0.1	245.5680	250.1454	117.073	0.1
78.3732	81.6242	70.934	0.1	250.1137	254.6940	117.278	0.1
81.6148	84.8595	71.584	0.1	254.6564	259.2320	117.413	0.1
84.8504	88.1154	72.795	0.1	259.1980	263.7793	117.634	0.1
88.1085	91.3641	73.184	0.1	263.7429	268.3202	117.816	0.1
91.3568	94.6289	74.150	0.1	268.2814	272.8628	118.072	0.1
94.6216	97.8829	74.474	0.1	272.8217	277.4037	117.970	0.1
92.9362	97.4915	103.699	0.1	277.3609	281.9464	118.380	0.1
97.4894	102.0211	104.185	0.1	281.9004	286.4862	118.577	0.1
102.0182	106.5589	105.304	0.1	286.4390	291.0232	118.781	0.1
106.5556	111.1151	106.558	0.1	290.9724	295.5438	118.485	0.1
111.1112	115.6807	107.509	0.1	295.4900	300.0680	118.839	0.1
115.6763	120.2392	108.055	0.1	300.0099	304.5884	118.999	0.1
120.2344	124.8258	109.264	0.1	304.5265	309.1105	119.413	0.1
124.8192	129.4049	109.827	0.1	309.0442	313.6278	119.456	0.1
129.3981	134.0008	110.718	0.1	313.5549	318.1448	119.865	0.1
133.9934	138.6014	111.350	0.1				

[a] σ is the expected 95% confidence interval for the measured sample.

0.77 K. From these values was subtracted $0.0064T^{-2}$ J·K·mol^{-1}, which Collan et al. believed was "undoubtedly associated with nuclear contributions to the heat capacity from the addenda". These adjusted heat capacity values were assigned square roots of the variance of ±10% for $T < 0.3$ K and ±3% for $T > 0.3$ K. Also used were values for 1−4.2 K given by Cetas et al. (1969) in their Table 3. Those values were obtained from their least-squares fitting to their values. They gave neither the measured values nor the fitted functions. Their values were assigned square roots of the variance of ±3%. The present values were assigned square roots of the variance for the least-squares procedure calculated from twice the irreproducibility for a full calorimeter determination and the percentage of the observed enthalpy due to the bismuth sample. These values, given in Table 1, actually corresponded to an approximately 95% confidence interval rather than the square root of the variance.

Representation of the experimental results, over the full range of temperature, required 14 variable knot positions. The optimized knot positions are given in Table 2. The number of digits in Table 2 was given for calculation of thermodynamic properties and was not meant to be representative of any statistical assessment. The optimized knot position for the 0 K knot yielded a value of 120.9 K for the Debye temperature. The root-mean-square (rms) difference of the present measurements from the fitted model was approximately 0.05% for temperatures greater than 50 K. Calculated thermodynamic properties of bismuth(cr) are given in Table 3. The melting point, 544.56

Table 2. Least-Squares Estimated Knot Positions and γ_{el}

T_i/K	d_i	T_i/K	d_i
0	9.686 982	40	2.075 271
1	9.269 905	60	1.227 325
2	8.791 534	100	0.164 420
5	6.367 506	190	−1.524 217
9	4.477 692	280	−3.271 058
15	3.621 904	380	−5.964 892
25	2.951 995	560	−14.843 97

$\gamma_{el}/C_p^\circ = 8.28 \times 10^{-6}\ \mathrm{K}^{-1}$

Table 3. Calculated Thermodynamic Properties of Bismuth(cr)

T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	$H_m(T) - H_m(0\ \mathrm{K})$/kJ·mol^{-1}	S_m/J·K^{-1}·mol^{-1}
0.5	0.000143	0.000	0.000
1	0.001132	0.000	0.000
2	0.00937	0.000	0.003
4	0.1003	0.000	0.029
6	0.4575	0.001	0.125
8	1.177	0.002	0.347
10	2.155	0.005	0.711
15	4.833	0.023	2.095
20	7.392	0.054	3.839
30	11.885	0.151	7.716
40	15.41	0.288	11.643
50	17.92	0.455	15.37
60	19.67	0.644	18.80
70	20.91	0.847	21.93
80	21.82	1.061	24.78
90	22.49	1.283	27.39
100	23.00	1.510	29.79
120	23.74	1.978	34.05
140	24.25	2.458	37.75
150	24.44	2.702	39.43
160	24.61	2.947	41.02
180	24.89	3.442	43.93
200	25.11	3.942	46.57
250	25.58	5.210	52.22
298.15	25.98	6.451	56.76
300	25.99	6.499	56.92
350	26.45	7.810	60.96
400	27.01	9.146	64.53
450	27.69	10.513	67.75
500	28.48	11.917	70.71
544.56	29.26	13.203	73.17

K, was the value given by Grønvold (1975), after adjustment from the IPTS-68 to the ITS-90.

Comparison of Representation with Previous Measurements. Comparison of the fitted equation results with the fitted values, as well as with other literature values, is shown in Figures 6–8. Figures 6 and 7 show the comparison for the lowest temperatures. Agreement of the representation with the measurements from Collan et al. (1970), from Cetas et al. (1969) taken from their Table 3, and the present results, all of which were included in the least-squares representation, is good. The heat capacity values given by Cetas et al. (1969) for temperatures from 3.8 to 30 K in their Table 4, after reduction by 0.4% for a calorimetric error (Holste, 1972), are also in excellent agreement with the representation. Holste (1972) also stated that a better matching of their thermometer scale to the thermodynamic temperature (Holste et al., 1972) was made subsequent to the bismuth measurements. No correction of either the Table 3 or Table 4 heat capacity values from Cetas et al. (1969) was made for their reported change in temperature scale. This was because only values calculated from fitted equations were given; the original measurements were not given. Archer (1993) showed the method by which such fitted models can be adjusted for the effect of the changes of the temperature scale. However, Cetas et al. did not give the form of their fitted equation and so that method could not be used. Values of the heat capacity taken from Phillips's (1960) fitted equation *sans* the "nuclear" term agreed with those from the fitted equation within 2–3% for temperatures from 0.75 to 2 K and can be considered in good agreement. For temperatures less than 0.75 K, the values from Phillips diverged from the representation. This divergence was representative of the difference in the value of γ_{el}/C_p° that Phillips obtained from his fitting of his measurements, 21 × 10^{-6} K^{-1}, and the value obtained from the Fermi-based calculation, 8.28 × 10^{-6} K^{-1}. Agreement of the heat

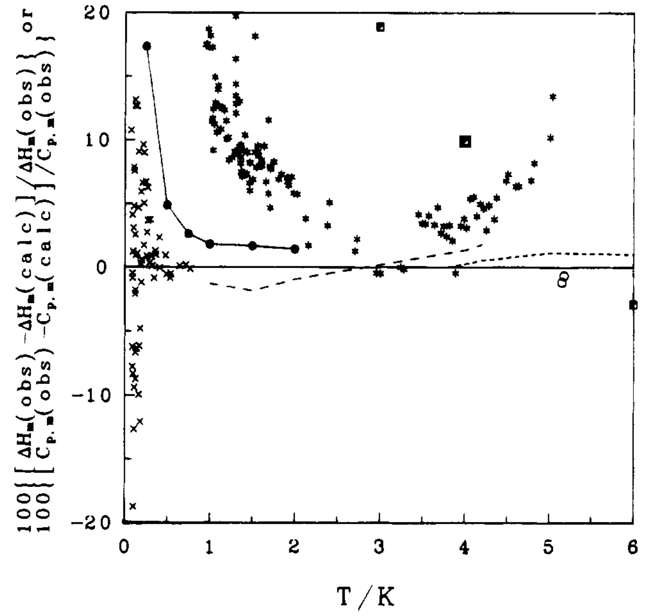

Figure 6. Differences of the present enthalpy increments and of literature values of the heat capacity of bismuth(cr) from the fitted equation for temperatures less than 6 K. Symbols: (×) Collan et al. (1970); (—•—) Phillips (1960); (*) Keesom and Pearlman (1954); (■) Keesom and van den Ende (1931); (○) present results. Lines: (– –) Cetas et al. (1969), Table 3; (- - -) Cetas et al. (1969), Table 4.

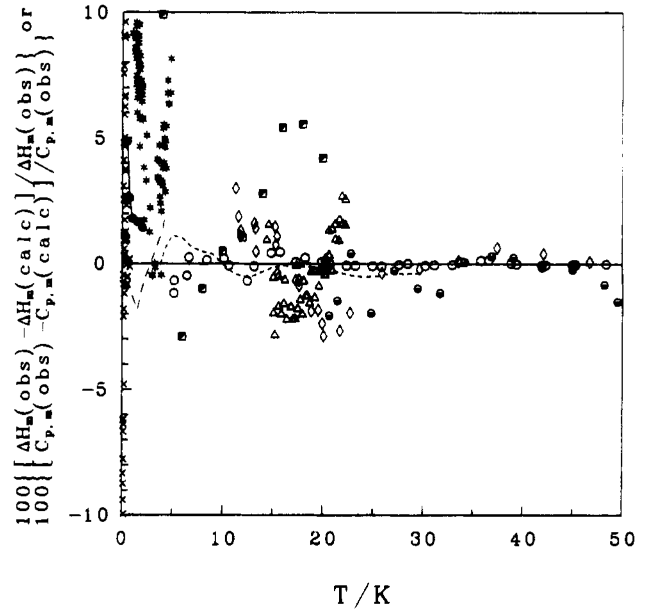

Figure 7. Differences of the present enthalpy increments and of literature values of the heat capacity of bismuth(cr) from the fitted equation for temperatures less than 50 K. Symbols: (×) Collan et al. (1970); (—•—) Phillips (1960); (*) Keesom and Pearlman (1954); (●) DeSorbo (1958); (△) Armstrong and Grayson-Smith (1949); (■) Keesom and van den Ende (1931); (◇) Franzosini and Clusius (1964); (○) present results. Lines: (– –) Cetas et al. (1969), Table 3; (- - -) Cetas et al. (1969), Table 4.

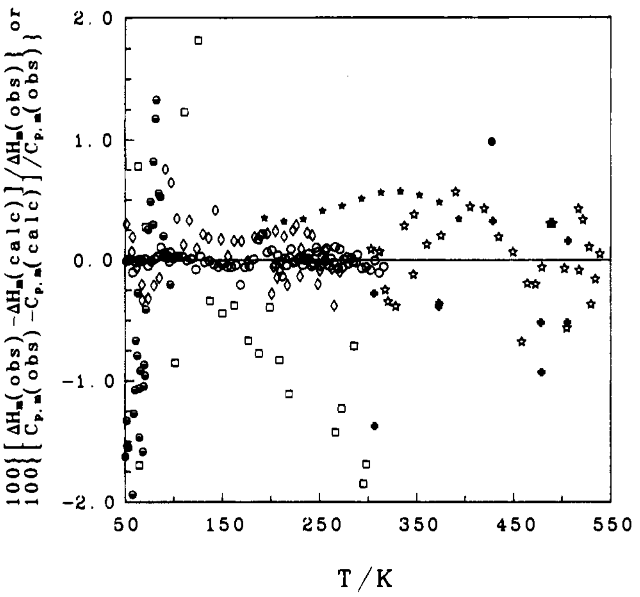

Figure 8. Differences of the present enthalpy increments and of literature values of the heat capacity of bismuth(cr) from the fitted equation for temperatures greater than 50 K. Symbols: (□) Anderson (1930); (★) Bronson and MacHattie (1938); (◇) Franzosini and Clusius (1964); (◒) DeSorbo (1958); (+) Carpenter and Harle (1932); (☆) Grønvold (1975); (○) present results.

capacity values from Keesom and Pearlman (1954) was poor.

Agreement with the low-temperature results of Armstrong and Grayson-Smith (1949) was acceptable; their values crossed the representation, and the present measurements, at two different temperatures (see Appendix II). The values from Keesom and van den Ende (1931) disagreed with the representation. The results from DeSorbo (1958) agreed with the present results within ±2% and crossed the present values at four different temperatures. From 25 to 273 K, the heat capacity measurements from Franzosini and Clusius (1964) were in very good agreement; differences were always within twice the precision of their measurements. The high-temperature heat capacities from Grønvold (1975), included in the least-squares representation, overlapped very well with the present results at 300 K. There was also agreement, an average deviation of 0.4%, of the values given by Bronson and MacHattie (1938) with the present results. The high-temperature heat capacities from Carpenter and Harle (1932) scattered about the representation generally by less than 1%, after exclusion of those values that contained a component of enthalpy from the premelting due to sample impurity.

There was poor agreement with the values given by Anderson (1930). Both Wagman et al. (1982) and Hultgren et al. (1973) took the values from Anderson as superior to the values from Bronson and MacHattie with no explanation and in spite of the obviously large scatter in Anderson's values.

The two heat capacity measurements reported by Kano (1989) for bismuth(cr) for temperatures near 450 K were about 0.8% larger. The recent heat capacity measurements from Badawi et al. (1987) were larger than the representation by 3% for 330 K and 2% for 400 K and were near agreement for temperatures greater than 500 K. Also larger by 2−3% were the recent heat capacities for 350 K to the melting point from Ichikawa and Matsumoto (1983). They claimed no more than ±2% uncertainty.

Iitaka's (1911) enthalpy increment measurements from 375 to 526 K (lower temperature = 293 K) were in good agreement with the present values. They possessed a root-mean-square deviation of 1.3% but an average deviation of only −0.2%, remarkably good considering the date of publication, 1911. Umino's (1926) enthalpy increment measurements (upper temperatures from 323 to 523 K) showed a systematic bias relative to the representation. Umino's values were smaller than the representation for upper temperatures less than 450 K and were larger for upper temperatures greater than this. The enthalpy increment determinations (upper temperatures from 385 to 541 K) from Kubaschewski and Schrag (1940) scattered about the present values with a rms deviation of 3.8%.

Comparison of the present values of the 298.15 K thermodynamic properties to values from Wagman et al. (1982) and from Hultgren et al. (1973) would have been meaningless, as those values are probably not thermodynamically consistent, as discussed in the Introduction. Due to the performance of the present calorimeter, as demonstrated by the results for the two calorimetric reference substances, the present values of the thermodynamic properties are believed, by the author, to be more accurate than previous assessments.

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Appendix I

The meaning of "experimental error of the measurements" can be equivocal (in the logical sense). Consider the appropriate combination of all sources of random error and systematic bias, except that due to the differences of temperature scales, and refer to this combination as δx, which is positive. Call the absolute value of the systematic bias caused by a difference of temperature scale δy. It seemed most probable that the quoted statement was equating "experimental error of the measurements" with δx and was thus stating that $\delta y \ll \delta x$. This was what I believed the authors to have meant.

However, it could subsequently be argued that the authors meant "experimental error of the measurements" to include the component of uncertainty that resulted from the difference of temperature scales and was actually $\delta y + \delta x$. In this case, the quoted statement would have meant $\delta y < \delta y + \delta x$, which must always be true and thus there would not have been any good reason to have stated it. This interpretation of "experimental error of the measurements" would give the quoted statement the meaning "The uncertainty of the measurement including the component of uncertainty due to the temperature scale differences was larger than the uncertainty of the measurement when not including the uncertainty due to the temperature scale differences." This statement then would have introduced a logical fallacy because it would have in no way been related to the need to correct the reported measurements for differences in temperature scales, which was the context within which the statement appeared. Thus, this was not taken to be what the authors meant.

Appendix II

Simple calculus applied to the finite-difference heat capacity,

$$C_{p,\mathrm{m}} = \Delta H_{\mathrm{m}}/(T_2 - T_1) \qquad (6)$$

gives the effect of temperature scale change on such values. This effect is

$$\delta C_{p,\mathrm{m}} = C_{p,\mathrm{m}} - C_{p,\mathrm{m}}' = -C_{p,\mathrm{m}}\{(T_2 - T_2') - (T_1 - T_1')\}/(T_2 - T_1) \quad (7)$$

$$\delta T_\mathrm{m} = T_\mathrm{m} - T_\mathrm{m}' = \{(T_2 - T_2') + (T_1 - T_1')\}/2 \quad (8)$$

where $\delta C_{p,\mathrm{m}}$ and δT_m are the differences in heat capacity and midpoint temperature, respectively, T_1 and T_2 are the initial and final temperatures for the finite-difference heat capacity, and the new and old scales are indicated with a prime and its absence, respectively. Clearly, the correct adjustment of a finite-difference heat capacity measurement requires, among other things, knowledge of the initial and final temperatures used for the measurement. Because none of the previous heat capacity reports included these values, no attempt was made to change the temperature scales. Adjustment of an enthalpy increment for a change in temperature scales involves merely adjusting the upper and lower temperatures, and no correction to the enthalpy is required.

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