Journal of Thermal Analysis, Vol. 45 (1995) 359-368

FUSION TEMPERATURES AND ENTHALPIES OF HIGH-TEMPERATURE MATERIALS DETERMINED BY DIFFERENTIAL THERMAL METHODS

Jane E. Callanan[*]

National Institute for Standards and Technology, Thermophysics Division, Boulder, Colorado 80303, USA

(Received August 2, 1994; in revised form September 15, 1994)

Abstract

The temperature and enthalpy of fusion of silver were measured in a differential thermal analyzer with gold and aluminum as reference materials. The measurement procedures and the data calibration (or correction) procedures used successfully in our laboratory for differential scanning calorimetry were applied. The experimental fusion temperature, (1233.9±1.0)K, and enthalpy, (108.4±3.3) $J\cdot g^{-1}$, are compared with the assigned value of temperature for the IPTS-68 scale, 1235.08 K, and with a value for enthalpy, 110.75 $J\cdot g^{-1}$.

Keywords: DTA, DSC, fusion temperature, high-temperature materials

Introduction

Instruments classified as differential scanning calorimeters (DSC) and differential thermal analyzers (DTA) require the use of correction procedures in order to measure the thermal properties of materials accurately. Because the data are not correct until such procedures have been applied, we call them data calibration procedures. These may involve evaluation of the behavior of the electronic components employed in the construction of the instrument [1] or concurrent measurements on reference materials [2]. This latter procedure is preferable for commercially available instruments.

---

[*] Retired. Present address: Royal Military College of Canada, Dept. of Chemistry and Chemical Engineering, Kingston, Ontario, Canada, K7K 5LO
Permanent address: Callanan Associates of Boulder, 2888 Bluff, #429, Boulder, Colorado 80301
Work done at the National Institute of Standards and Technology.
Not subject to copyright.

0368–4466/95/ $ 4.00
John Wiley & Sons, Limited
Chichester

The reference substances used must be well-characterized materials on which extensive measurements have been made. A certified reference material is one for which the property values have been certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body. Ideally, the property certified should be determined by two reliable and independent measurement methods. Since this is not a possibility for thermal properties, we must rely on an extensive, well-designed, series of measurements, often coupled with measurements made on the same material, by the same procedure, in a number of laboratories on instruments of different design (round-robin). The reference values so obtained apply only to material from the batch that has been certified; the same substance from a different lot or purchased from another supplier may not have the same values.

Several years ago, the US National Institute of Standards and Technology, formerly the National Bureau of Standards, had a program for the development of certified reference materials for DSC.This program was initiated after a feasibility study demonstrated that the procedures used resulted in reliable values for temperature and enthalpy [3]. The validity of these methods is reinforced by a comparison of results, recently obtained by drop calorimetry, on tin foil that had previously been measured by DSC. The values obtained by drop calorimetry and DSC, respectively, are (505.10±0.01)K and (505.11±0.14)K for temperature and $(60.22\pm0.19)\mathrm{J\cdot g^{-1}}$ and $(60.15\pm0.15)\mathrm{J\cdot g^{-1}}$ for enthalpy.

The increased interest in, and development of, new high-temperature materials has created an urgent need in industry for reference materials for both temperature and enthalpy that can be used at high temperatures. The development of such reference materials by DTA will offer the same advantages that the development of lower temperature materials by DSC has offered: the certification of materials at reasonable cost with an accuracy and within a time frame that will meet the needs of industry. The interest in using a DTA for such certification stems from the higher temperature range of the materials to be certified. In general, DTAs are capable of operation at higher temperatures than those normally accessible to a DSC. However, the DTA must be operated in such a way that enthalpies, as well as temperatures, of transitions are determined. In this communication, such operation will be referred to as DSC mode; the DTA operated so as to indicate temperatures only will be referred to as DTA mode.

This study was undertaken to evaluate the performance of a high-temperature differential thermal analyzer in both DSC and DTA modes. The objective was to determine whether reference materials for high-temperature measurements can be certified with the DTA, in much the same way that the DSC has been used in the past. The study included an evaluation of the precision and accuracy of measurements of temperature and enthalpy. Aluminium, silver, and gold were the test materials. American Society for Testing and Materials (ASTM) procedures (E967) were used for temperature [4]. The modification of ASTM procedures used in our laboratory for enthalpy calibration has been applied to the measurements of enthalpy of fusion [2, 5].

Experimental method

Materials and instrumentation

Gold foil with a nominal purity of 99.99% was obtained from a commercial supplier. Aluminum specimens consisted of shavings from SRM 44f aluminum, which was obtained from the Office of Standard Reference Materials (OSRM) [6]. The silver specimen was taken from a high purity single crystal ingot available in the Boulder Laboratory. Powdered alumina distributed by the instrument manufacturer was used to improve the heat-transfer properties of the system.

Measurements were made on a commercial DTA in an atmosphere of flowing nitrogen (35 ml/min). The instrument-calibration procedures recommended by the manufacturer were applied. The system was cooled at the end of each measurement by means of compressed air; this air did not come in contact with the specimens. Masses were determined on a microbalance accurate to ±2 μg.

Data analysis

The data were analyzed initially with the software supplied by the manufacturer. In addition, all curves were plotted, and the fusion temperature determined graphically. Temperatures reported here were obtained by the graphical extrapolation of the onset curve until it met the extrapolated baseline. This procedure has been demonstrated to give transition temperatures closes to thermodynamic transition temperatures of materials when an instrument is properly calibrated. Peak temperatures were also recorded in order to evaluate the precision of their measurement.

Enthalpies were determined from the integrated area under the fusion curve and the mass of the material.

Procedures

The alumina was heated to 1450 K for an hour at the beginning of the study and stored in a desiccator. Measurements were made with dried alumina in both sample and reference cups of the instrument; use of alumina in this way improves the thermal contact between the thermocouple, which is located at the base of the sample cup, and the metallic specimen. Alumina sample cups of 60 mm^3 were used, without lids, in this study.

Instrument repeatability was assessed, before the calibration measurements were begun, by multiple determinations of the fusion temperature (DTA mode) or the fusion temperature and enthalpy (DSC mode) without disturbing the specimen or system in any way. Five measurements were made on the same specimen for both gold (DTA mode) and aluminum (DSC mode).

The specimens for the calibration measurements were run in the sequence prescribed by ASTM method E967 for calibration of a DTA: lower temperature reference material, test material, higher temperature reference material [4]. The furnace was heated at 100 deg·min^{-1} from room temperature to a temperature 100–150 K below that at which measurements were to begin and held at that temperature for ten minutes before measurements were begun. Data were acquired at a heating rate of 10 deg·min^{-1} from about 100–150 K below the fusion temperature until the scan had returned to the baseline for 20–30 K.

Specimen masses in the calibration measurements were chosen to give curves of roughly comparable size. Specimens were weighed after each use and masses for the calculations adjusted if necessary. Mass changes that did occur will be discussed in later sections of this paper. The amount of alumina used varied from one material to another because of differences in the volume of the specimens.

Because previous work, in the Boulder laboratory and by statisticians associated with our work, has dealt satisfactorily with the question of material inhomogeneity, no testing for material homogeneity was included here.

Results

Instrument repeatability was assessed, before the calibration measurements were begun, by five repeated measurements on gold (DTA mode) and on aluminum (DSC mode). The uncorrected fusion temperature for gold was (1328.47±1.08)K. The uncorrected fusion temperature and enthalpy for aluminum were (927.13±0.28)K and (309.2±2.0)J·g^{-1}. All variabilities in this communication are expressed as one standard deviation.

Literature values for temperature are the defined values for the IPTS-68 temperature scale (gold, silver) or secondary reference temperature for the same scale (aluminum). Values used and the appropriate references are given in Table 1.

Table 1 Literature values for temperature and enthalpy of fusion

Substance	$T_{(fus)}$/K[8]	$\Delta H_{(fus)}$ / J·g^{-1}
Aluminum	933.61	369.989[9]
Silver	1235.08	110.75 [10]
Gold	1337.58	62.765[10]

The average temperatures and enthalpies obtained in this work, the number of measurements N on which each average is based, and the standard deviation of the measurements are presented in Table 2. The percent deviation associated with each of these measurements is given in this table in parentheses. The two values cited for the enthalpy measurements of silver are discussed below. Instrument values for the peak temperature and their experimental variability are shown also in Table 2.

Table 2 Temperature and enthalpy of fusion

Substance	N	$T_{\rm (fus)}$/K	%	$\Delta H_{\rm (fus)}$ / J·g^{-1}	%	$T_{\rm (peak)}$/K
Aluminum	11	925.5 ± 1.2	(± 0.1)	317.60 ± 6.3	(± 2.0)	934.5 ± 0.7
Silver	10	1224.0 ± 1.0	(± 0.11)	92.10 ± 4.2	(± 2.2)	1223.2 ± 1.1
	9			93.30 ± 2.1	(± 4.6)	
Gold	11	1327.1 ± 0.8	(± 0.8)	58.16 ± 2.3	(± 3.6)	1335.7 ± 0.6

Corrected values

Substance	N	$T_{\rm (fus)}$/K	$\Delta H_{\rm (fus)}$ / J·g^{-1}
Silver	10	1234.4 ± 1.0	108.4 ± 3.3
	9		106.7 ± 6.7

The range of the measured values is given in Table 3, both for the hand-drawn curves and those generated by instrument software. In Fig. 1 the observed values of the fusion temperatures are plotted as a function of the literature values. Figure 2 shows the same information for the enthalpies of fusion. Corrected values for silver, using aluminum and gold as bracketing reference materials, are shown also in these figures. The solid line connects experimental values; the dashed line, the literature values.

Table 3 Range of measured values for temperature and enthalpy of fusion

Substance	$T_{\rm (fus)}$/K	$\Delta H_{\rm (fus)}$ / J·g^{-1}
Aluminum	[a] 923.2–926.6	312.4–326.3
	[b] 927.2–929.4	
Silver	[a] 1222.8–1225.2	[c] 81.3–96.2 (10)
	[b] 1223.4–1226.4	[d] 90.0–96.2 (9)
Gold	[a] 1325.4–1328.2	54.3–60.7
	[b] 1328.2–1330.4	

[a] Intercept drawn by hand; baseline, by software, [b] Intercept and baseline drawn by software, [c] Based on all measured enthalpies, [d] Based on all measured enthalpies; very low first value excluded

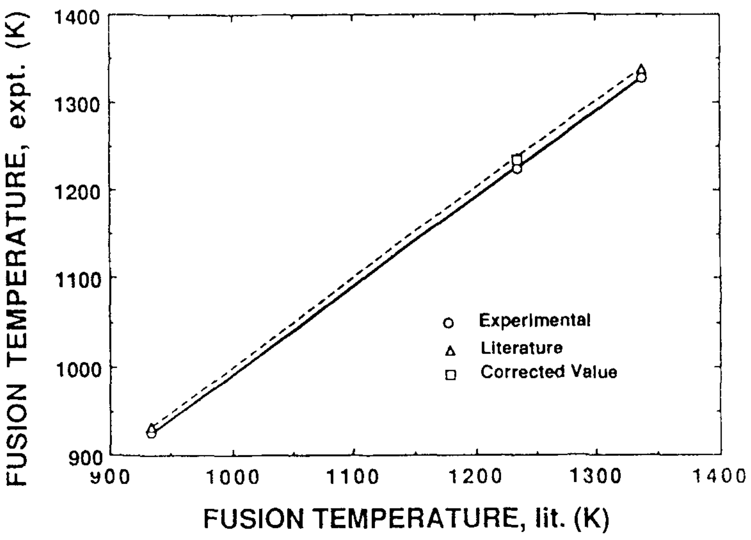

Fig. 1 Average experimental temperature *vs.* literature temperature

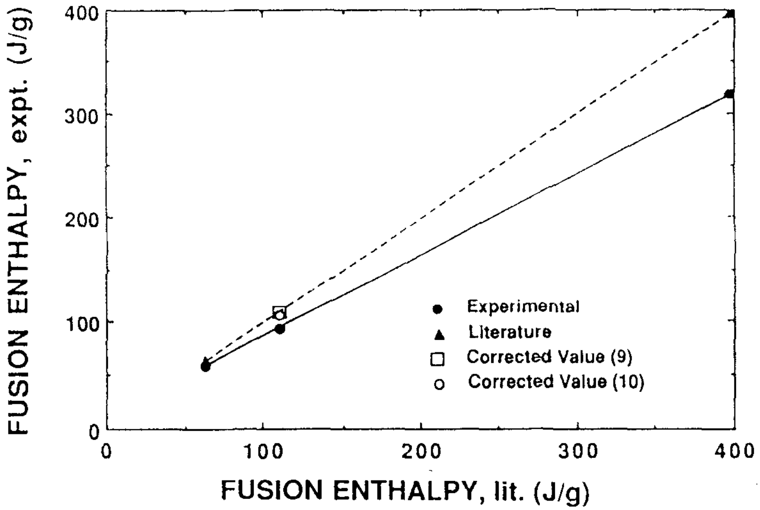

Fig. 2 Average experimental enthalpy of fusion *vs.* literature enthalpy of fusion

The calibration procedures cited above were applied to each individual series of three measurements to obtain corrected values for silver. The average of the corrected temperatures is (1233.9±1.0)K. For enthalpy, the average based on nine measurements is (108.4±3.3) J·g^{-1}; that based on ten measurements is (106.7± 6.7)J·g^{-1}.

No variability in results was observed as a result of different specimen masses (16.01 to 41.7 mg).

Discussion

All curves for these materials were well-behaved (Fig. 3). The shapes of the curves did not deteriorate with reuse of the specimens. The precision of the measurements is satisfactory, particularly in view of the high temperatures.

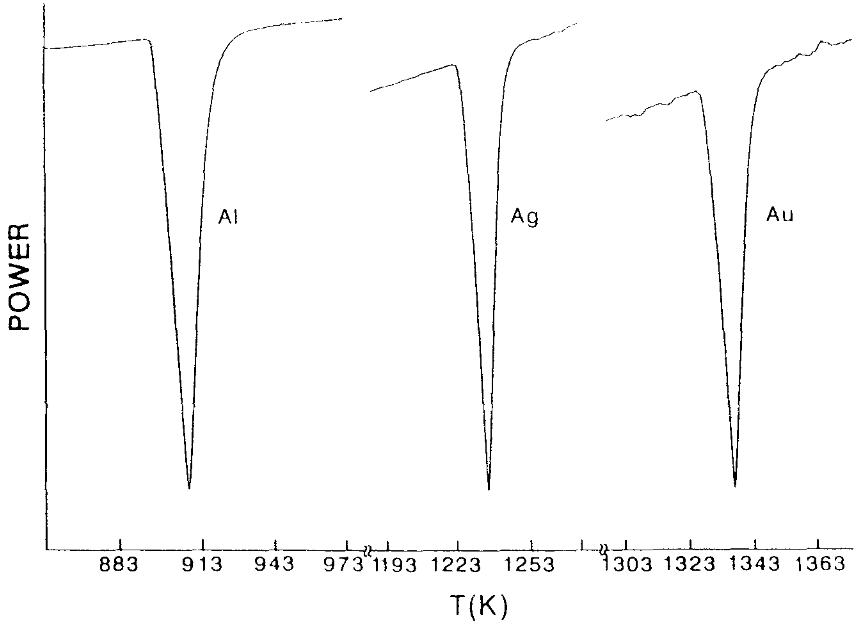

Fig. 3 Typical curves for the test materials

Calibration procedures recommended by manufacturers for the DTA allow for adjustments to and matching of thermocouple readings. The instrument has no provision for calibration with materials by adjustment of resistances as do some DSCs. The operation of a DTA is different from that of a DSC in that adjustments are made only in the software or data treatment, not in the instrument itself. In a frequently used procedure, the difference between the observed transition temperature and the accepted value for it is determined for one material; the same correction is then applied to other materials at different temperatures. For enthalpy, a correction factor is derived for one material and applied for all measured enthalpies at all temperatures. Application of these procedures to the results obtained in this study showed that this procedure does not give results as reliable as the methods used in our laboratory [3]. The corrections determined from gold and applied to aluminum and silver are shown in Table 4, along with the appropriate reference values. These results are not surprising in light of the slopes shown in Figs 1 and 2.

The linearity of our results is encouraging and lends credibility to the correction procedures used. The difference between the corrected fusion temperature for silver and the literature value is insignificant. The difference between the corrected and the selected literature values for the enthalpy lies between 2.1 and 3.8%.

Table 4 Results of application of one-point corrections

For aluminum corrected with gold values			
Temperature/K		Enthalpy/J·g^{-1}	
Corrected	Literature	Corrected	Literature
933.3	933.61	343.0	397.0
For silver corrected with gold values			
Temperature/K		Enthalpy/J·g^{-1}	
Corrected	Literature	Corrected	Literature
1234.2	1235.08	100.8	110.8

The major experimental difficulty during the course of this work involved the silver specimen. It lost very small amounts of mass from one measurement to another. After a series of minor losses, the mass stabilized. Neither gold nor aluminum showed this tendency. As there was no way of telling when, during a particular heating cycle, mass was lost, the mass at the completion of each heating cycle was used as the adjusted mass in determining the enthalpy of fusion for silver for that cycle. The maximum loss between measurements occurred in the initial heating, 0.14 mg (0.33%). After the first heating, the losses varied between 7 and 32 μg (0.02–0.08)%. The total mass loss over the series of measurements amounted to 0.6%.

The difficulty with the mass loss of silver resulted in variations in the enthalpy of silver determined in each run. For the first two melts, the enthalpy of fusion for silver was about 81.59 J·g^{-1}. For all further melts, the enthalpy was in the 90–96 J·g^{-1} range. Both gold and aluminum had been melted five times each before the calibration study was begun. No unusual differences between values on first melts and subsequent melts was observed. The first melt of silver was not used in the calibration calculations because it was meant only to premelt the specimen. The second melt was included and is markedly different from other values obtained for silver in these measurements. Statistical tests permit the rejection of this datum, but normally we do not exclude any experimental measurement unless there is clear instrumental or manipulative failure. However, in previous cases, values fluctuated; in this instance, after the first two melts, the fusion enthalpy never returned to the unusually low value. For that reason, two values are given in Table 3. One, based on ten measurements, includes all measured values. The other, based on nine measurements, eliminates the value that is suspect.

The materials problems with the silver are puzzling. The silver specimen was prepared by removing a piece from an ingot with a small laboratory saw. It is possible that a material that volatilized at the high temperatures used in this study had adhered to the blade and been transferred to the silver specimen. It is unlikely, however, that such contamination would have persisted through eight heating cycles. Though the vapour pressure of silver is higher than that of either gold or aluminum, the silver is not presumed to have vaporized to a measurable extent. Indeed, the fact that the mass had stabilized after nine heating cycles seems to eliminate that suspicion.

It was suggested to us that the mass loss observed may have resulted from loss of oxygen from the silver, as silver is known to dissolve oxygen. It would have been desirable to make thermogravimetric measurements on the specimen used and the sample from which it was obtained, but neither was available.

The use of the masses adjusted for loss resulted in enthalpy values for the series of measurements that varied in a manner similar to those of other materials studied in this laboratory. The specimens were placed in the DTA at room temperature and then subjected to a reproducible heating program. However, there is uncertainty about the period in the measurement cycle during which the mass loss occurred. This uncertainty may have contributed to the variation in enthalpies observed, but does not account for the large difference between the second and third heating. The adjustment of the initial enthalpy value for the total mass loss in the whole series of measurements, which had not taken place by then, results in an enthalpy increase of less than two joules. For certification measurements, material problems of this sort would need to be addressed individually and solved before the material could be considered for certification.

Because this is a pilot study, not intended for certification, the reference values for enthalpy were taken from a reliable source, without exhaustive searching of the literature.

Conclusion

The results of the brief series of measurements reported here and those obtained earlier by DSC [3] show that it is feasible to undertake the certification of high-temperature reference materials by DTA. A number of materials, both metals and salts, with certified values for temperature are available [7]; however, the variability limits for these are often unacceptably wide (±6–7 K). Until absolute enthalpy measurements are available for these materials, the choice of the reference values for enthalpy must be determined through the careful evaluation of literature values found through an exhaustive literature survey. If, in the future, narrower temperature limits and absolute enthalpies are determined for some bracketing materials, certificates can readily be reissued on the basis of the new information.

* * *

The author is grateful to Prof. P. K. Gallagher and to C. J. Williams for helpful discussion about this work and to the Office of Standard Reference Materials of NIST and the Royal Military College of Canada for partial financial support.

References

1 S. L. Randzio, J. Calorim. Anal. Therm., 11 (1980) 2–12–1.
2 J. E. Callanan and S. A. Sullivan, Rev. Sci. Instrum., 57 (1986) 2592.
3 J. E. Callanan, S. A. Sullivan and D. F. Vecchia, U. S. National Bureau of Standards Special Publication No. 260–99 (U. S. Government Printing Office, Washington, D. C., 1985, 43 p.
4 ASTM standard practice for temperature calibration of differential scanning calorimeters and differential thermal analyzers E 967–83. Annual Book of Standards 14.02, 1991, p. 658.
5 ASTM standard practice for heat flow calibration of differential scanning calorimeters E 968–83. Annual Book of Standards 14.02, 1991, p. 662.
6 Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA.
7 J. Boerio-Goates and J. E. Callanan, 'Differential Thermal Methods' in Physical Methods of Chemistry, Second Edition Volume Six, B. W. Rossiter and R. C. Baetzold, eds. J. Wiley and Sons, New York 1992, p. 621–717.
8 The International Practical Temperature Scale of 1968. Amended Edition of 1975. Metrologia, 12 (1976) 7.
9 M. W. Chase, Jr., C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. J. Syverud, JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. Ref. Data, 14 (1985) 1319. Supplement 1.
10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, Selected values of the thermodynamic properties of the elements. Metals Park, Ohio: American Society for Metals, 1973.

Zusammenfassung — In einem DTA-Gerät wurden unter Einsatz der Referenzsubstanzen Gold und Aluminium die Schmelztemperatur und Schmelzenthalpie von Silber bestimmt. Dabei wurde das in unserem Labor für DSC erfolgreich eingesetzte Meßverfahren und Datenkalibrier- (oder Korrektions-)verfahren verwendet. Die experimentelle Schmelztemperatur (1233.91.0)K und Enthalpie (108.43.3) $J \cdot g^{-1}$ wurden mit dem zugeordneten Temperaturwert für die IPTS-68 Skala, 1235.08 K und mit dem Wert für die Enthalpie 110.75 $J \cdot g^{-1}$ verglichen.