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Thermal time constants in differential scanning calorimetry

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Abstract

We have examined thermal gradients in a differential scanning calorimeter. We quantified, as a function of sample heat capacity, the thermal lag, ΔT between sample and calorimeter. We found that $\Delta T = \beta(\tau_x + R_0 C_s) + \Delta T_c$; where β is the heating rate, ΔT_c is a constant, C_s is the total heat capacity of the sample and pan, R_0 is the thermal resistance between sample and calorimeter, and τ_x is an instrumental time constant. We observed that the value of ΔT_c depended on both the sample size and the thermal resistance between sample and calorimeter. Analysis of changes in ΔT_c with changes in R_0 led to an order of magnitude estimate of 3 mcal s^{-1} for the rate of heat flow between calorimeter and sample when the calorimeter is held at a constant temperature near 500 K. We discuss the effect of this heat flux on the accuracy of the temperature scale.

INTRODUCTION

Differential scanning calorimetry (DSC) is a sensitive and accurate means to measure small enthalpy changes associated with structural transitions in materials, and to measure the heat capacity of materials [1–19]. The temperature scale of a differential scanning calorimeter must be calibrated as a function of heating rate if the potential accuracy (±0.1 K) of its platinum thermometry is to be attained. All measurements must be made under operating conditions similar to those of the calibration measurements. Such a calibration is necessary because of the thermal resistance R_0 between the sample and the thermometer. In normal operation, heat always flows between sample and thermometer; thus there is a temperature difference between sample and thermometer which is proportional to R_0. During typical operation, this thermal lag is of magnitude 2 K,

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but it can be much greater. Essentially it is this thermal lag which a temperature calibration quantifies.

Thermal gradients have been examined previously in differential scanning calorimeters, including the investigations by Richardson and coworkers of thermal lag in a Perkin–Elmer [11] model DSC-1B [4] and in a model DSC-2 [3]. Richardson and co-workers [3,4] operated the calorimeter in the "specific heat mode" [6]. They analyzed the response of a loaded calorimeter to a thermal program of stepwise linear heating between two temperatures. In the present work we have utilized a Perkin–Elmer DSC-4, which has a calorimeter head similar to the DSC-7 and to the DSC-2.

The purpose of this paper is to characterize the errors in the temperature scale of a DSC which are due to thermal lag. We have analyzed the thermal lag under constant heating rate conditions by measuring the apparent melting temperatures of pure elements according to a standard calibration procedure [1,19]. The dependence of thermal lag on both sample mass and sample shape has been investigated. This thermal lag has been compared to the thermal lag observed upon stepwise heating over 0.1 K temperature intervals.

EXPERIMENTAL

The melting of indium or tin of at least 99.999% purity was examined in a number of samples of various mass. The In or Sn standards were hermetically sealed in commercially produced aluminum pans [20]. Different amounts of material were encapsulated with the standards to vary the heat capacity of the samples [19]. The heat capacity of In samples was varied by adding either Al_2O_3 disks, Al disks or In to the sample pan; whereas in the case of Sn, only Al disks were utilized to increase the heat capacity of the sample. In this paper the "sample" refers to the entire configuration of the pure metal temperature standard, the added Al or Al_2O_3, and the Al pan.

The mass of the samples varied from 30 to 130 mg. A typical pan mass was 24 mg. In most cases, the empty volume of the sample was minimized by pressing the temperature standard tightly against the pan bottom. Care was taken to ensure that all of the pan bottoms remained flat. Thus, as the sample volume increased, the tops varied from a shape which could be described as concave up (Fig. 1(a)) to one which was concave down (Fig. 1(b)).

Measurements of the melting temperatures of the pure elements were performed in both stepwise heating mode and in scanning mode with a Perkin–Elmer DSC-4 which was interfaced to a microcomputer for data acquisition and analysis. The stepwise method consisted of 0.1 K incremental temperature steps. The calorimeter was held at each temperature until the heat flow rate became constant. The midpoint of the temperature

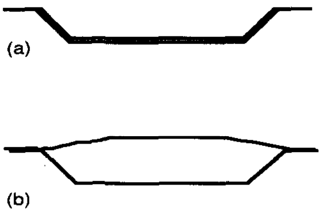

Fig. 1. Sketch of the cross section of a sample for (a) small volume samples and (b) large volume samples.

interval in which the metal was observed to melt was identified as the stepwise melting temperature [6].

The DSC-4 calorimeter head was cooled with an ice bath at a constant level. The ice bath and calorimeter were allowed to equilibrate for 5 h before data acquisition. A ±10 V signal was acquired at a point in the DSC circuitry so as to bypass the output electrical filtering circuits ($\tau = 0.8$ s) of the instrument. This is the standard operating mode for our instrument. Unless otherwise noted, the calorimeter was fitted with standard vented sample holder covers [21]. An Ar gas flow rate of 20 ml/min^{-1} was maintained. Samples were generally placed directly in the middle of the calorimeter sample holders, though in a limited number of cases a thin disk of aluminum was first placed directly on the calorimeter in order to vary the thermal resistance between the sample and calorimeter. Care was taken to ensure that constant operating conditions were maintained during the experiment. Gross changes in operating conditions affect the temperature scale. For instance, changes in bath temperature or level have been observed to result in changes of the order of 0.2 K in the temperature scale.

In this paper we have concentrated on differences in the apparent melting temperatures of a given metal temperature standard. For metals with masses close to 8 mg, encapsulated in an Al pan without added material, the difference between the melting temperatures of Sn and In was observed to be 75.2 ± 0.1 K, in accordance with literature values. Thus, these small samples were used as a primary reference for the temperature scale.

RESULTS

DSC scans at various constant heating rates were conducted for all the samples. Melting temperatures were determined from the intersection of a linear fit to the leading edge of the steady state (constant slope) endothermic melting signal and the baseline [13]. Values of the thermal resistance R_0 between sample and calorimeter thermometer were determined for each sample from these linear fits of melting signals (R_0 is given by the

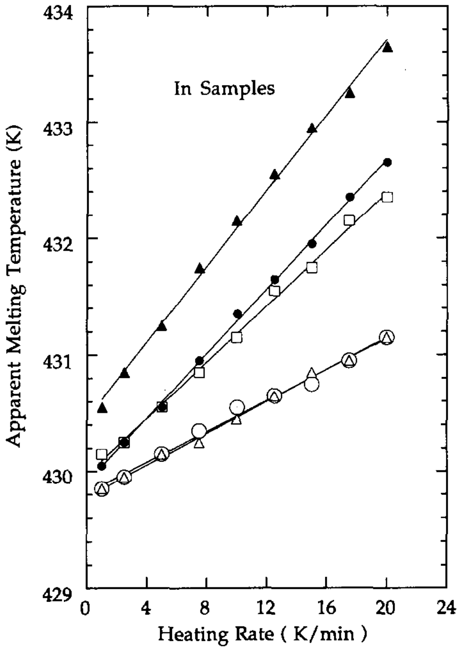

Fig. 2. The melting temperature of various In samples encapsulated in Al pans as measured by means of differential scanning calorimetry plotted as a function of the programmed heating rate of the differential scanning calorimeter. Data for particular samples are denoted by individual symbols: ▲, 23.4 mg of In encapsulated along with 45.5 mg of Al_2O_3 and 63.6 mg Al, including Al pan mass; ●, 49.3 mg of In encapsulated along with 45.1 mg of Al_2O_3 in a 25.5 mg Al pan; □, 40.3 mg of In encapsulated along with 29.8 mg of Al_2O_3 in a 25.5 mg Al pan; ○, 22.4 mg of In encapsulated in a 25.9 mg Al pan; △, 5.1 mg of In encapsulated in a 26.0 mg Al pan. Linear fits to the data for each sample are shown in the figure.

inverse of this constant slope, according to Newton's law of cooling) [1–18]. Averaging values of R_0 for all samples encapsulated in volatile sample pans and placed directly in the calorimeter, we found $R_0 = 280 \pm 30$ K s cal^{-1}.

The observed melting temperature as a function of heating rate for In samples is presented in Fig. 2 and for Sn samples in Fig. 3. For a particular sample, a linear fit [1–10] to the data for the apparent melting temperature as a function of heating rate yielded a value for the slope (for time constant τ) and a value for the y intercept (or apparent melting temperature for zero heating rate). These linear fits are presented along with the data in Figs. 2 and 3.

For both In and Sn samples, the observed values [1,13] of τ varied linearly with the heat capacity of the samples, see Fig. 4. The data of Fig. 4 are for all the samples including both In and Sn, where the sample was placed directly on the calorimeter. These data have been fit with a linear

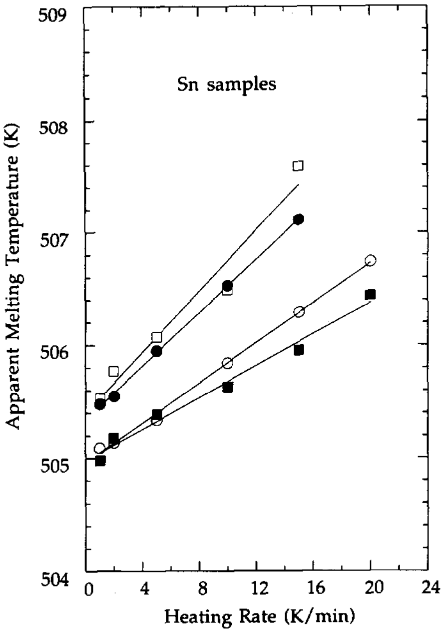

Fig. 3. The melting temperature of various Sn samples encapsulated in Al pans as measured by means of differential scanning calorimetry plotted as a function of the programmed heating rate of the differential scanning calorimeter. Data for particular samples are denoted by individual symbols: □, 8.1 mg of Sn encapsulated along with 81.8 mg of Al, including Al pan mass; ●, 7.8 mg of Sn encapsulated along with 63.3 mg of Al, including Al pan mass; ○, 8.0 mg of Sn encapsulated along with 36.6 mg of Al, including Al pan mass; ■, 8.5 mg of Sn encapsulated in a 25.1 mg Al pan. Linear fits to the data for each sample are shown in the figure.

relation which yields a slope of 290 ± 20 K s cal^{-1} and a y intercept of 2.4 ± 0.4 s.

The apparent melting temperatures for zero heating rate varied from sample to sample. A maximum variation of approximately 0.7 K was observed between the largest and smallest samples. Measurements of melting temperatures of the same samples performed by means of the stepwise heating method [1,3–5] revealed the same, reproducible variations in the apparent melting temperatures of these samples. (This would be expected, in that stepwise heating is associated with zero heating rate. The variation of the stepwise melting temperature with sample size is more surprising.)

Measurements of the melting temperatures were repeated with the standard vented sample holder covers being replaced with sample holder covers with no holes for a number of samples. It was observed that measurements of melting temperatures did not change significantly with the change in sample holder covers, regardless of whether the stepwise or the constant scan rate method was employed.

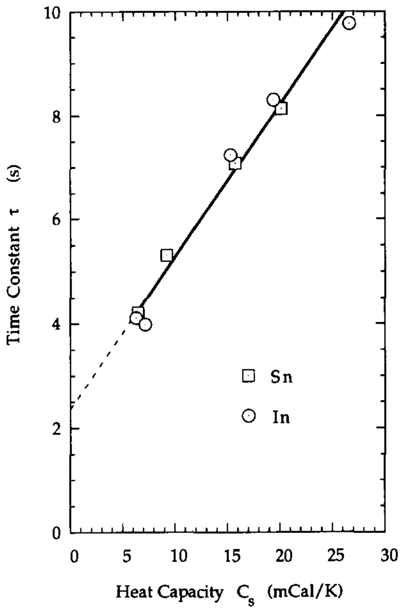

Fig. 4. The time constant τ (defined as the slope determined from the linear fit to the data for a particular sample in Fig. 2 or in Fig. 3) plotted versus the sample heat capacity C_s. Values of C_s were calculated from measured values of mass. The data for Sn samples are denoted by □; the data for In samples are denoted by ○. A linear fit to all the data is plotted with a solid line and the extrapolation of this fit to zero heat capacity is shown with a dotted line.

For one sample, R_0 increased to 700 K s cal^{-1} when an additional thin Al disk was placed between the sample and the calorimeter. It was observed that the stepwise melting temperature increased by 1.1 K with this change in thermal resistance.

DISCUSSION

It has been stated numerous times that operational conditions should closely mimic calibration conditions in order to avoid significant errors in the temperature calibration of a differential scanning calorimeter. This assertion is strongly supported by the data of Figs. 2–4, where variations in melting temperatures of several K are observed for relatively slow heating rates. Further support for this point is found with the surprising observation of variations up to 1 K in stepwise melting temperatures with changes in pan shape, total sample/pan heat capacity and values of R_0.

The behavior of the data of Fig. 4 is consistent with a description of DSC which includes both thermal responses (time constants) of the calorimeter and electrical responses of the calorimetry circuitry [13,15,19]. A development [13] based on Newton's law of cooling indicates that the dependence of thermal lag, ΔT on the heating rate is given by

$$\Delta T = T_0 - T_\mathrm{m} = \beta\tau + \Delta T_\mathrm{c} = \beta(\tau_x + \tau_\mathrm{s}) + \Delta T_c \tag{1}$$

where T_0 is the observed onset of the melting transition, T_m is the actual melting temperature of the pure metal, β is the heating rate, τ_s is the sample time constant, ΔT_c is a temperature scale offset independent of heating rate and τ_x is the instrumental time constant, independent of sample. It is assumed that the sample time constant τ_s is proportional to both the sample heat capacity C_s and to R_0, such that $\tau_\mathrm{s} = R_0 C_\mathrm{s}$ [13]. This development includes the assumption that R_0 is determined by the thermal resistance between the pan bottom and the calorimeter and not by interfaces inside the pan [13,14,19]. Such an assumption has been supported by previous investigation [13,14,19] and is further supported by the observation in the present study that measured values of R_0 do not vary appreciably from sample to sample. Thus τ can be rewritten as

$$\tau = \tau_x + R_0 C_\mathrm{s} \tag{2}$$

For different samples of varying C_s but a constant value of R_0, eqn. (2) predicts a linear dependence of τ on C_s. Our observations (Figs. 2 and 3) of the variations in the apparent melting temperatures of In and Sn as a function of heating rate and C_s are plotted in Fig. 4, in accordance with eqn. (2). A linear fit to the data yields a slope of 290 ± 20 K s cal^{-1}, in good agreement with the observed mean value of R_0 for individual samples ($R_0 = 280 \pm 30$ K s cal^{-1}). * The time constant for a "sample" of zero heat capacity, determined from the y intercept of the linear fit to the data, yields a value for the instrumental time constant of $\tau_x = 2.4 \pm 0.4$ s. Similar values of τ_x are found for each sample using eqn. (2) to calculate τ_x, by subtracting from measured values of τ the value of τ_s based upon a measurement of R_0 and the value of C_s calculated from literature values for the heat capacities of Sn, In, Al_2O_3 and Al. Thus for our calorimeter and samples encapsulated in standard Al pans, eqn. (1) can be rewritten as

$$\Delta T = \beta(2.4 + 290 C_\mathrm{s}) + \Delta T_\mathrm{c} \tag{3}$$

Values of ΔT_c were observed to depend upon sample size. The lowest observed time constant for small samples encapsulated in a standard aluminum pan was approximately 4 s. If standard aluminum pans are utilized and placed directly into the calorimeter, this may be considered the minimum attainable time constant. Thus inclusion of the output electrical filtering ($\tau = 0.8$ s) would increase the total time constant only slightly from 4 s and would not significantly affect most measurements.

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* The thermal resistance R_0 can be reduced from 300 to 125 K s cal^{-1} with the placement of a drop of silicone oil between the pan and calorimeter [22].

In a previous study [3], the response of a calorimeter to a step function from zero heating rate to a constant linear heating rate (as utilized in heat capacity measurements) was determined. The results of such a study are important to an understanding of the possible errors in the measurement of the heat capacity of materials. Flynn has stated [13] that in some instruments such a measurement may include transient signals no longer present in a measurement of melting at constant scan rate. Richardson's data for the thermal lag have been interpreted [3,5] in terms of time constants to yield $\tau_x = 3.6$ s in the absence of Al pans and 7.7 s with Al pans. In a separate study [13,19], Flynn utilized infrared light pulses to measure τ_x for a DSC-1B and found a value of $\tau_x = 1.7$ s. Considering variations in electrical time constants in the DSC electronic circuitry [23] and the error in our measurement, our observed value of $\tau_x = 2.4 \pm 0.4$ s would appear to be reasonably consistent with Flynn's measurement of $\tau_x = 1.7$ s for a DSC-1B.

The variation in the stepwise melting temperatures of pure elements with pan shape, and of the stepwise melting temperature of pure Sn with R_0, may be interpreted to be a result of the fact that some heat flows from the sample to the thermal bath along a path which does not include the calorimeter thermometer. In our discussion of this problem we concentrate on our data for the Sn sample. We assume that the calorimeter thermometer and heater are at the same, programmed temperature [1–7]. This heater/thermometer, HT is at a temperature, T_{HT}, while the thermal bath B is at a temperature $T_{\mathrm{B}} = 273.15$ K; on melting the Sn sample is at the actual melting temperature of Sn, $T_{\mathrm{s}} = 505.0$ K. The temperatures T_{B} and T_{s} are important reference points in this discussion (Fig. 5).

Heat must flow continually in order to maintain the temperature difference, $\Delta T_{\mathrm{b}} = T_{\mathrm{HT}} - T_{\mathrm{B}}$, between the calorimeter heater/thermometer and

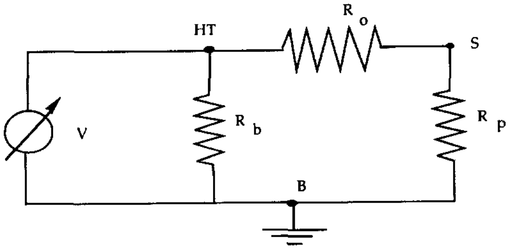

Fig. 5. A sketch of a portion of the DSC thermal circuit including the thermal bath, B, at a temperature T_{B}; the heater and thermometer HT are assumed to be at the same temperature T_{HT}, and the sample S at a temperature T_{s}. The thermal resistance between sample and heater/thermometer is R_0, the thermal resistance between the sample and temperature bath is R_{p}, and the thermal resistance between heater/thermometer and temperature bath is R_{b}. The temperature difference between HT and B is represented by V. With an ice bath, the observation of Sn melting implies that $T_{\mathrm{s}} = 505.0$ K, $T_{\mathrm{B}} = 273.15$ K, and that $T_{\mathrm{HT}} > T_{\mathrm{s}}$.

the thermal bath. A small fraction $\mathrm{d}Q/\mathrm{d}t_s$ of this heat flow to the bath is through the sample. The magnitude of $\mathrm{d}Q/\mathrm{d}t_s$ will depend on the value of the thermal resistance between the thermometer and sample (previously defined as R_0), and on the magnitude of the thermal resistance R_p between the sample and the thermal bath along paths which do not include R_0. The heat flow $\mathrm{d}Q/\mathrm{d}t_b$ to the thermal bath along paths which do not include the sample (these pathways are defined to constitute a thermal resistance R_b) is assumed to be a very large fraction of the total heat flow from heater to thermal bath. From Newton's Law of cooling we have

$$\Delta T_b = \frac{\mathrm{d}Q}{\mathrm{d}t_s}(R_p + R_0) = \frac{\mathrm{d}Q}{\mathrm{d}t_b}R_b \tag{4}$$

Some sources of the thermal conductance between sample and bath include the purge gas and also direct radiation [1,2]. Apparently the magnitude of this thermal link (independent of R_b) depends upon pan shape or sample heat capacity [2–5]. A finite value of both R_0 and $\mathrm{d}Q/\mathrm{d}t_s$ means that even when the DSC is programmed to hold at constant temperature, a temperature difference (a thermal lag) will exist between the calorimeter thermometer T_{HT} and the sample T_s

$$\Delta T_c = T_{\mathrm{HT}} - T_s = \frac{\mathrm{d}Q}{\mathrm{d}t_s}R_0 \tag{5}$$

A crude estimate of the magnitude of R_p, ΔT_c, and $\mathrm{d}Q/\mathrm{d}t_s$ can be made if we assume that $R_p \gg R_b$ and that $R_p \gg R_0$ (such that doubling R_0 does not significantly affect the value of $\mathrm{d}Q/\mathrm{d}t_s$), that adding a piece of aluminum between sample and calorimeter affects R_0, but does not significantly alter R_p or R_b, and that the temperatures of the sample thermometer and heater are the same. Because Sn always melts at the same temperature, a constant value of $T_s = 505.0$ K, and a constant value of $\mathrm{d}Q/\mathrm{d}t_s$ in eqn. (5) implies that an increase in R_0 results in an increase in ΔT_c. By varying the value of R_0 from 300 K s cal^{-1} to 700 K s cal^{-1}, we observed ΔT_c to increase by 1.1 K. Therefore eqn. (5) provides the estimated values: $\mathrm{d}Q/\mathrm{d}t_s \approx 3$ mcal s^{-1} and $\Delta T_c \approx 0.8$ K for $R_0 = 300$ K s cal^{-1}. With an ice bath and a tin temperature standard, ΔT_b is approximately 232 K. With our values for ΔT_b, $\mathrm{d}Q/\mathrm{d}t_s$, and R_0, we can estimate R_p from eqn. (4) as $R_p \approx 10^5$ K s cal^{-1}.

Our preliminary measurements of the total power supplied to the calorimeter as a function of temperature show values of 2 cal s^{-1} at 1000 K, with a value of the order of 0.5 cal s^{-1} at 500 K. Thus when the calorimeter is programmed to remain at constant temperature near 500 K, approximately 0.6% of the heat flow from heater to thermal bath is through the sample.

In the context of Newton's law of cooling, the estimated 3 mcal s^{-1} heat flow from the calorimeter heater/thermometer to the sample during isothermal operation at temperatures near 500 K provides some insight on the stability of the instrument. Assuming a sensitivity of 1 μW, it is indicated that variations of one part in one thousand in R_p in one of the calorimeters would significantly affect the observed differential power signal. It is thus understandable how changes in pan shape upon heating or changes in purge gas flow rate with time can significantly affect a baseline signal.

Assuming that the thermal lag ΔT is accurately described by eqn. (1), then the error in our estimate of ΔT depends upon our estimates of τ and of ΔT_c (the error in β is easily minimized so as to be negligible). For material encapsulated in standard Al pans, a value of τ for a particular sample in our calorimeter may be estimated by means of eqn. (2) with a value of $\tau_x = 2.4$ s, a value of $R_0 = 290$ K s cal^{-1}, and a calculated value of C_s. However, for our data we found variations of the order of 0.3 s between measured values of τ and predicted values. For a heating rate of 20 K min^{-1}, eqn. (3) implies that an error in τ of 0.3 s would result in a contribution to the error in the temperature scale of 0.1 K. (It is emphasized that these errors would increase if thermal resistances in the pan became significant in comparison to the thermal resistance between pan and calorimeter, which we have found to be about 290 K s cal^{-1}).

Errors in estimating ΔT_c also contribute to the total error in the temperature scale. For instance, differentiating eqn. (5) with respect to R_0 provides an estimate of the sensitivity of ΔT_c to changes in R_0

$$\frac{\mathrm{d}\Delta T_c}{\mathrm{d}R_0} = \frac{\mathrm{d}Q}{\mathrm{d}t_s} \approx 3 \text{ mcal s}^{-1} \tag{6}$$

Thus a change in R_0 of the order of 40 K s cal^{-1} will result in a change in ΔT_c of the order of 0.1 K. Considering only small samples encapsulated in volatile sample pans, we generally observe variations in R_0 of magnitude 20 K s cal^{-1}, which would indicate variations in ΔT_c of order of 0.06 K. Although for the smallest samples ΔT_c was observed to be the same within 0.1 K for both In and Sn standards, larger variations in ΔT_c were observed with increased sample size. Apparently these variations in ΔT_c with sample size are due to variations in the magnitude of R_p. We would estimate an error in ΔT_c of 0.1 K for small samples (Fig. 1(a)) and 0.2 K for larger samples (Fig. 1(b)).

Only by assuming that no other factors cause temperature errors, and that the identified errors contribute randomly, can the total error in the temperature scale at a heating rate of 20 K min^{-1} be identified as 0.14 K for small samples and 0.22 K for large samples. Other sources of error in the temperature scale exist; in particular variations in bath temperature will directly affect the temperature scale. In a previous study [24], Callanan et al. found that repeated measurements of the melting temperature of the same In foil sample revealed a standard deviation of 0.14 K. Randomly combining this error with our estimate of sample-dependent error, results in a total error in the temperature scale of 0.2 K for a small sample and the calorimeter in the Callanan study [24]. This estimate is consistent with the observed standard deviation of about 0.2 K for a large variety of small samples in Callanan's study [24].

CONCLUSION

Our data enforce the previous assertion that differential scanning calorimetry operational conditions should closely mimic calibration conditions, otherwise errors of the order of 10 K in temperature calibration can occur. It should be emphasized that calibration standards should not only be of similar heat capacity as samples, but they should have similar thermal conductances. We find for temperatures near 500 K that only with small samples, slow heating rates, excellent bath stability and diligent care can the potential accuracy, ±0.1 K, of the platinum thermometry be attained with DSC. We also find that with diligent care an accuracy of ±0.2 K in the DSC temperature scale can be attained with a reasonably wide latitude of pan shapes and sizes, heating rates and operating conditions.

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