

SUB-AMBIENT AND MEDIUM TEMPERATURE CALIBRATION

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With some attention to temperature calibration but no other special precautions the temperatures of both solid–solid and melting transitions can be determined to within a few tenths of a Kelvin of absolute values in a range of heat-flux and power-compensation DSC instruments. Materials showing several solid–solid transitions are potentially useful multiple calibrants but require some work to define appropriate thermal treatments that lead to reproducible behaviour.

Keywords: DSC, melting transitions, reproducible behaviour, solid–solid transitions, temperature calibration

Introduction

ICTAC temperature standards have long been available through the US National Institute of Standards and Technology (NIST, formerly NBS). Their selection and round-robin testing have been comprehensively documented [1, 2]. Standards were originally intended to facilitate the intercomparison of results rather than to define precise temperatures and the thermodynamic transition or melting temperatures (mainly the former, at the time of testing many instruments could not accept liquids) were not certified although literature values were given.

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By the nature of the procedures used (which gave a mean value from many different types of equipment), the certified values of 'onset' and 'peak' temperatures have large uncertainties, often several degrees, associated with them. ICTAC recognises that these are unacceptable for present-day applications of DSC and their Standardisation Committee is undertaking a review of all existing standards together with an investigation of potential additional or replacement materials.

The present paper reports preliminary work on some standards for lower temperatures (up to 350°C) and considers the viability for this purpose of compounds which show multiple transitions. Only temperatures are discussed at this stage but the final aim is to certify both temperature and enthalpy. Practical aspects have changed considerably since the original ICTAC work because DSC, not DTA, is now the method of choice for quantitative work. Commercial equipment is almost always used and the temperature sensor is never in direct contact with the sample as it often was in DTA instruments. Thermal lag is inevitable under normal (scanning) conditions and instruments must therefore be calibrated to allow for lag by using materials having known melting or transition temperatures.

An ideal calibrant should give reproducible results from run to run, from sample to sample, and from one instrument to another. This paper reports results on these aspects for a range of materials that have been investigated using several types of modern DSC instruments. This work is essential to ensure that resources are not wasted on the certification of materials that, for whatever reason, prove to be unsuitable for DSC purposes. At the same time the validity of DSC as a thermometer is considered—what reliance can be placed upon DSC-determined transition temperatures? Some emphasis is placed on the lower temperatures because there are some practical problems associated with the components of the current set: diphenyl ether and, especially, *o*-terphenyl show considerable supercooling; cyclohexane and 1,2-dichloroethane both have high vapour pressures at room temperature and, once the original ampoules have been opened, they are difficult to contain for any length of time.

Experimental

Materials

1,2-Dichloroethane and cyclohexane were from the NIST/ICTAC Low Temperatures Set GM-757. Participants were asked to use mercury, gallium and indium of better than 99.999% purity. Ammonium sulphate (99.999%) and rubidium nitrate (99.99%) were used as received from Aldrich Chemical Company.

Calorimetry

Measurements were made using the following instruments: Netzsch: DSC200, Perkin Elmer: DSC2, DSC7, Polymer Laboratories: PL-DSC, TA Instruments: DSC2910.

Procedure

Participants were asked to use their normal experimental and computational procedures (the latter generally referred to software supplied by the instrument manufacturers) to determine the extrapolated onset temperature (T_e , Fig. 1) at a heating rate (β) of $10 \text{ K}\cdot\text{min}^{-1}$. It was recommended that instruments were calibrated with mercury, gallium and indium (three metals, readily available in high purity, whose melting points are used for the practical realisation of the ITS90). However some participants were reluctant to use either mercury or gallium and other materials (Table 1) were used to define the temperature calibration. In some cases measurements were also made at sufficient other rates to allow extrapolation to $\beta = 0$ —there is evidence [3] that $dT_e / d\beta$ is a material-dependent quantity so that calibration at a single value of β may lead to errors. Repeat measurements were always made on a given sample and the whole procedure was generally duplicated on at least one fresh sample.

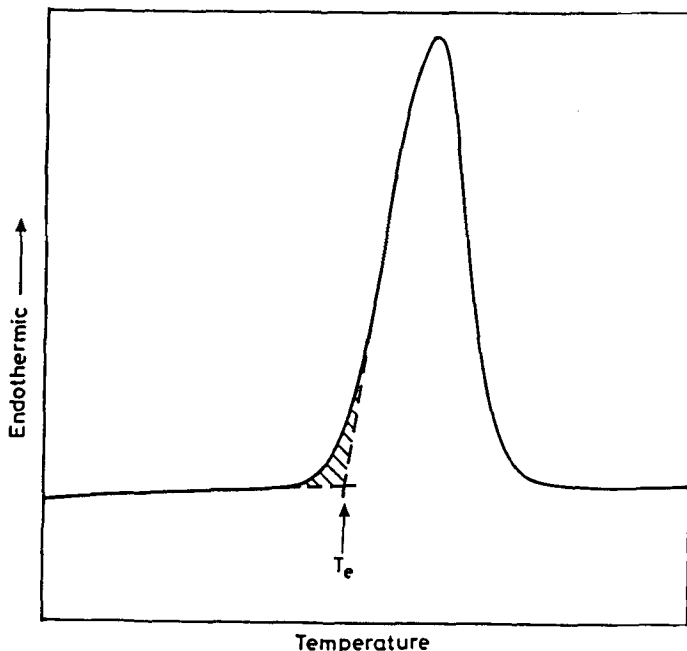


Fig. 1 Definition of the extrapolated onset temperature T_e . The shaded area represents premelting

Results and discussion

Results for the low-temperature materials are shown in Table 1. Data refer to observed (uncorrected) values of T_e (laboratory D excepted, see below); quantities in brackets are the temperature corrections $\delta T = T_t - T_e$, where T_t is the literature value of the transition or melting temperature given in the first line of Table 1. Most laboratories quoted T_e to hundredths of a degree but, although reproducibility of this order can be achieved in immediate reruns (B, Table 1), for fresh samples, or from day to day, differences of a few tenths of a degree are observed.

Table 1 Extrapolated onset temperature (T_e /K) at $\beta = 10 \text{ K}\cdot\text{min}^{-1}$. Uncorrected values (figures in brackets indicate deviation from literature values)

T_t	Ammonium	Mercury	1,2-	Gallium
	sulphate		Dichloroethane	
	223.4 ^a	234.32 ^b	237.5 ^c	302.91 ^b
Laboratory	$T_e(\delta T)$	$T_e(\delta T)$	$T_e(\delta T)$	$T_e(\delta T)$
A ⁺	225.4 (-2.0) 225.8 (-2.4)	235.1 (-0.8)	239.5 (-2.0) 239.1 (-1.6)	-
B	225.40/.37 (-2.0) 225.08/.08 (-1.7)	-	239.12/.10 (-1.6) 239.15/.15 (-1.7) 239.00/8.99 (-1.5)	304.19 (-1.3) 304.32 (-1.4) 304.35 (-1.5)
C	-	234.24 (+0.1)	237.21 (+0.3)	
D ^x	221.79 ^o 223.83 ^o	-	244.11 (-6.6) 244.37 (-6.9)	303.35 (-0.5)
E [*]	223.84 (-0.4) 223.98 (-0.6)	234.79 (-0.5) 234.99 (-0.7)	238.25 (-0.8) 238.27 (-0.8) 238.12 (-0.6)	-

⁺also 188.3, 188.2 (-2.0, -1.9) cyclohexane

^xalso 432.19 (-2.4) indium

^ocorrected value, see text

^{*}also 216.84 (-0.5), *n*-octane

^odenotes reruns on the same sample; data on successive lines refer to new samples

^aD. G. Thomas and L. A. K. Staveley, *J. Chem. Soc.*, (1951) 2572

^bR. L. Rusby, R. P. Hudson, M. Durieux, J. F. Schooley, P. P. M. Steur and C. A. Swenson, *Metrologia*, 28 (1991) 9

^cSelected Values of Chemical Thermodynamic Properties' Circular 500 National Bureau of Standards, Washington, D. C 1952

Although temperature calibration in modern DSCs is a semi-automatic operation involving software packages that call for two or more standards, the 'software effect' has been eliminated from the data of Table 1 except for the results for ammonium sulphate from laboratory *D*. For this particular case T_c and T_i data for three materials (1,2-dichloroethane, gallium and indium) were used to derive the algorithm that gave the corrected transition temperatures shown for ammonium sulphate. The example is a valuable demonstration of the need for at least three calibrants in any operation covering a wide range of temperature—even if only to confirm that a simple form (e.g. the two-point ASTM method E967) may be acceptable.

Data from the remaining laboratories of Table 1 showed that, for the restricted temperature range considered, δT was almost independent of temperature and it was justifiable to use either mercury or gallium as single-point calibrants for 1,2-dichloroethane or ammonium sulphate. This conclusion is, of course, based on literature values of T_i ; a prime object of the present work, however, is to investigate the consistency of DSC-determined values of T_i and a constant δT could only be assumed if T_i (calibrant) $\approx T_i$ (unknown) as, for example, with mercury and 1,2-dichloroethane for which $\Delta T_i \approx 3$ K. For temperature ranges of some tens of degrees (as in Table 1) at least one other calibrant must be used.

Rate effects: 1,2-dichloroethane

The effects of heating rate on T_c are shown in Table 2 which gives T_{c0} the "equilibrium" ($\beta=0$) onset temperature, and the slope $\alpha=dT_c/d\beta$ in the equation $T_c=T_{c0} + \alpha\beta$. In all cases α is of the order of 0.1 min and there is no obvious distinction in this respect between heat-flux and power-compensation calorimeters; values of α are similar to those reported earlier [3] for a Perkin-Elmer instrument. The data of Table 2 give the T_i results for 1,2-dichloroethane at $\beta = 0$ and 10 K·min⁻¹ that are shown in Table 3. When compared with the literature values (Table 1) of 237.5 K, the agreement is excellent. With no special precautions, except for ensuring that a relevant temperature calibration has been used, DSC has been shown to be capable of determining temperatures to within a few tenths of a degree. This level of resolution demands improved certification of existing ICTAC standards and implies that transition temperatures should be known (preferably by using independent methods) to only a few hundredths of a degree. Intuitively it would be thought that the 'equilibrium' data are the more accurate but there is little evidence in Table 3 of any rate effect. Perhaps fortuitously, calibrant(s) and unknown have similar values of α (see, especially, data from laboratory *E*) but it is possible that great differences should not be expected. The slope α is influenced by material properties and by interfacial effects between the temperature sensors and the sample. As β is increased the sample temperature progressively lags behind that of the sensor which at some stage detects (at T_c) the onset of bulk melting (the construction in Fig. 1 is an attempt to nullify the effects of premelting – the shaded area – that are frequently observed). T_c is the recorded

Table 2 T_{e0}/K , α/min for various materials

Laboratory	Ammonium sulphate	Mercury	1,2-Dichloroethane	Gallium
B	224.02, 0.122	–	238.11, 0.098	303.56, 0.074
C	–	233.51, 0.076	236.75, 0.047	–
D	222.15, 0.176	233.39, 0.148	236.77, 0.146	–

Table 3 T_i/K for 1,2-dichloroethane via T_c ; $\beta = 0$ or $10 \text{ K}\cdot\text{min}^{-1}$

Laboratory	$\beta = 0$	$\beta = 10$
A	–	238.50
B	237.46	237.61
C	237.56	237.29
E	237.70	237.65

temperature that corresponds to a true sample temperature of T_i at the interface that is in 'contact' with the sample pan. 'Contact' is emphasised because it can vary appreciably with the type of sample and the geometry of the pan: liquids generally give good thermal contact (although surface tension effects may lead to problems) but for solids the interfacial heat transfer is probably as much a function of sample preparation as it is of the material properties themselves. In any case both instrumental and sample effects contribute to α . The former are fixed in the sense that they are beyond the control of the experimenter (although they may be functions of temperature) and the latter are related only to heat transfer across the DSC/pan/sample interfaces – and only the last of these involves the sample. Of course once melting, for example, has started, material properties influence the shape of the melting curve very strongly but interest here is in T_c , the onset of melting (or transition).

Solid–solid transitions: ammonium sulphate

Although the work reported above clearly confirms the suitability of 1,2-dichloroethane as a temperature standard, the vapour pressure of about 10 kPa at room temperature leads to difficulties with storage of the bulk material; as a chlorinated hydrocarbon it may, in addition, face future legislative problems. For routine work it is convenient to have a more robust calibrant and the solid–solid transition in ammonium sulphate at 223 K was investigated with this in mind. The transition (between ferroelectric and paraelectric orthorhombic forms) is clearly revealed by DTA [4] and the present work confirmed this (Fig. 2). T_c was generally reproducible to within one or two tenths of a degree (Table 1) although wider variations were also reported. These are believed to be related to the thermal con-

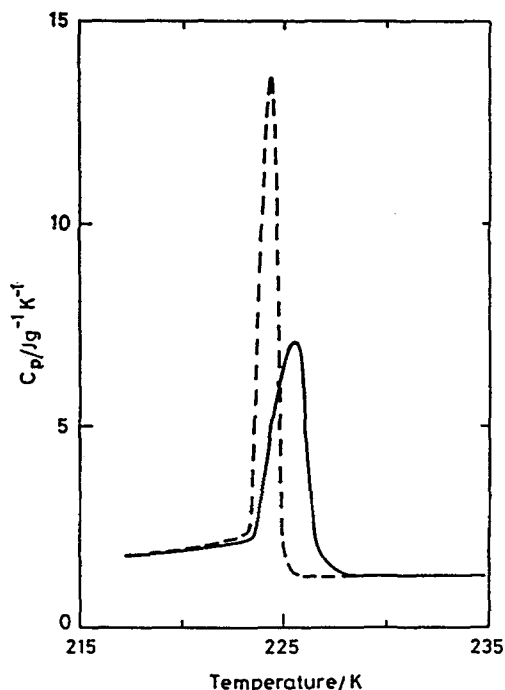


Fig. 2 Specific heat behaviour at the phase transition in ammonium sulphate (— 10 K·min⁻¹; --- 2.5 K·min⁻¹)

tact effects discussed above. They are a potential problem with any solid–solid transition and can be overcome by attention to experimental details. Subsequent work showed that consistent results were always obtained by compacting the polycrystalline sample in its pan using a metal tool under hand pressure (preparation of a thin disc in a die is also acceptable, however subsidiary experiments should always check that the applied pressure is not enough to give problems with stored energy effects which reveal themselves as exothermic events).

Corrected transition temperatures, via $\beta = 10 \text{ K}\cdot\text{min}^{-1}$ data, are: laboratory *A* 223.7, *B* 223.6 (223.4 via $\beta = 0$), *D* 222.8, *E* 223.4 K. Each of these is the mean of two independent determinations and, if the single point from laboratory *D* at 221.8 K is neglected, the remaining seven values can be accommodated within $223.6 \pm 0.2 \text{ K}$ – limits refer to the extremes of the measurements. This is excellent agreement and ammonium sulphate, which is cheap and readily available, is clearly suitable to use as a temperature calibrant.

Although not directly relevant to the present discussion, it could be argued that the accompanying enthalpy change is inappropriate as an energy standard because the large step in the specific heat curve on passing through T_i (about $-0.8 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ Fig. 2) makes it difficult to define a conventional baseline. This is

undeniable but it is also true of many real materials. Procedures must exist to deal with such cases, users must be familiar with them, and materials must be available to verify them. Ammonium sulphate has many advantages as such a material (note also the II/I transition in Fig.3).

Polymorphic transitions: rubidium nitrate

Many materials show polymorphic transitions (including a majority of the current ICTAC standards). They are attractive potential calibrants because a wide range of temperature may be covered using only one or two substances when these display multiple transitions. For example, among the inorganic nitrates the ammonium salt is reported [5] to have five transitions (including melting) ranging from 255 to 450 K, those for rubidium nitrate extend, in turn, from 430 to 580 K. In principle, therefore, these two materials cover 325 K – but careful work is needed to investigate all aspects of reproducibility (to ensure this, ICTAC potassium nitrate must be given a specific thermal treatment before use).

The present report considers the four phase changes in rubidium nitrate. Results (Table 4, phases are numbered I, II, III, IV; I is stable at the highest temperature) show that all laboratories found larger variations than were observed with other materials (Table 1) – including the comparable solid–solid transition in ammonium nitrate. The work summarised in Table 4 was designed to examine sample-to-sample differences (laboratory *A*, *B*), the effect of mass (*B*), repeated cycling (*D*), and thermal history (*E*). Only T_c is considered because conditions for the determination of T_i have not been defined at this stage. The poor reproducibility shown in Table 4 was not due to inadequate thermal contact: the material, though hard and difficult to compact, flowed readily on melting and

Table 4 Rubidium nitrate: observed transition temperatures; T_c/K , $\beta = 10 \text{ K}\cdot\text{min}^{-1}$

Laboratory	IV/III	III/II	II/I	I/Liquid
A	437.6/438.7	502.0/505.4	558.1/557.8	584.2/581.4
	438.8/438.7	506.2/502.1	558.0/557.7	583.9/582.8
B*	435.3/437.5	498.4/500.5	558.6/559.2	581.4/575.5
	434.5/437.4	498.8/506.3	558.4/558.5	581.4/578.9
	438.0/439.1	507.9/507.0	558.9/558.8	581.6/582.2
	436.5/437.0	498.9/506.0	557.6/557.6	582.2/578.7
	437.5/438.3	502.7/507.4	557.2/557.5	580.3/580.7
D	436.3/437.2/437.6	499.2/506.5/507.0	556.8/556.1/556.5	580.7/580.7/581.0
E	See Fig. 3; $\alpha(\text{IV} / \text{III}) \approx 0.1$			

*Sample mass 2–14 mg

Consecutive runs separated by "/"

there was little, if any, improvement for the reruns. Decomposition should not have been a problem because rubidium nitrate is reported [6] to be stable until about 870K – well above the present limit of 600 K.

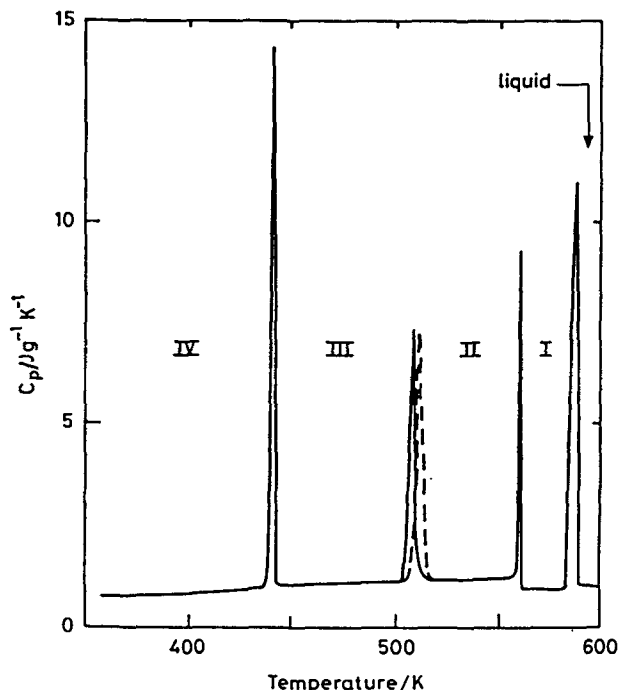


Fig. 3 Phase behaviour of rubidium nitrate, thermal history affects only the III/II transition (cooled at — 0.3125, --- 40 K·min⁻¹; β = 10 K·min⁻¹)

Thermal history (various cooling rates plus isothermal annealing) had no effect on three of the transitions but did influence the III/II event at 500 K. Here T_c appeared to shift downward for samples that had been formed at slower cooling rates – 0.3125 v 40 K·min⁻¹ – although the magnitude and shape (which was broader and less well-defined (Fig. 3) than any of the other transitions) were unchanged: the transition was also unusual in that the peak shape appeared to be unaffected by heating rate. Although these effects merit further study they do imply that the III/II transition is unsuitable for calibration purposes. The remaining transitions were insensitive to thermal history and to sample size (which often determines supercooling behaviour). They merit additional work to better define reproducibility. There are indications that the melting transition may be a closely spaced doublet (a test for resolution?) and work is under way to examine this possibility.

Concluding remarks

Both solid–solid transitions and conventional melting points can be measured by DSC to within a few tenths of a degree if care is used in the calibration of the instrument. Definition of temperature on this scale requires calibrants of high purity (with impure materials there is an uncertainty associated with the definition of T_c itself) which must be individually certificated.

Multiple polymorphic transitions may be used to rapidly characterise calibration behaviour over a wide range of temperature. The relevant materials require careful work to define conditions that lead to reproducible transitions – it is important to ensure that the small samples and relatively rapid changes of temperature in DSC work do not stabilise unusual structures. These comments refer only to heating experiments but associated work (not reported here) suggests that at least some of the solid–solid transitions show negligible supercooling and may be used to supplement the only other transitions with such a property—those in liquid crystals [7].

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Zusammenfassung — Unter Beachtung der Temperaturkalibrierung, jedoch ohne jegliche andere Vorkehrungen können in einer Reihe von Wärme- und Leistungskompensations- DSC-Geräten sowohl die Temperaturen von Feststoff-Feststoff-Umwandlungen als auch von Schmelzvorgängen innerhalb einiger Zehntel Kelvin (absolut) bestimmt werden. Substanzen mit mehreren Feststoff-Feststoff-Umwandlungen sind potentiell anwendbare Mehrfach-Kalibrierstoffe, bedürfen jedoch einiger Arbeit zur Festlegung entsprechender thermischer Behandlungen, um ein reproduzierbares Verhalten zu erreichen.