

TEMPERATURE CALIBRATION OF DIFFERENTIAL SCANNING CALORIMETERS

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Abstract

A procedure for calibrating the temperature scale of a DSC is described. A different calibration trend was obtained using the transition points of organic compounds compared to that found using the melting points of highly pure metals. The crystal-crystal transitions of three ammonium salts were studied by this method; ammonium dihydrogen phosphate and ammonium sulphate were found to be suitable reference materials in the region -150 to 0°C, but ammonium nitrate was found to be unsuitable due to poorly defined transition points and inconsistent thermal behaviour.

Keywords: ammonium salts, crystal-crystal transitions, DSC, melting transitions, reproducible behaviour, temperature calibration

Introduction

Differential scanning calorimetry (DSC) is probably the most popular thermoanalytical technique within materials science. It partly owes this position to its ability to determine useful material parameters (e.g. melting point, T_g etc.) rapidly, and with high precision. The accuracy of such measurements is dependant on calibration with substances which have well-defined transition temperatures. This is especially important where measurements may be carried out in various laboratories, on different instruments, perhaps over a long period of time. Suitable experimental procedures have been comprehensively described in the literature [1-3] although the choice of reference materials is still open to debate [4,5].

High purity metals exhibit sharp melting peaks by DSC which makes them popular for calibrating the instrumental response against accurate values determined by classical calorimetry. For many practical purposes, this may not be appropriate - when studying organic materials, such as high polymers, there is an argument for calibrating "like with like" since there are significant differences in thermal conductivity, heat capacity and transition enthalpy between metals and organic substances [6]. In addition, some metals are difficult to work with because of their toxicity (mercury) or ease of handling (gallium) and even commonly-used organic compounds, such as dichloroethane, present problems due to environmental issues [7] and volatility. Even so, it is likely that indium, tin, lead, etc. will remain as convenient temperature (and enthalpy) standards for DSC for the some time to come.

The use of DSC by the industrial chemist presents a need for "secondary" or "working" standards for DSC calibration. These would have the properties of having one (or more) transition points in the region of most common interest (ca. -100 to 400°C), being inexpensive, readily available in high purity, easy to handle and presenting little difficulty with toxicity and disposal. Some of these criteria can be met by existing materials e.g. lead has a melting point close to that of poly(tetrafluoroethylene) and makes a convenient single-point

temperature (and enthalpy) calibrant for studies on this substance [8] despite oxidising readily. Indium and tin are useful in the intermediate temperature range, however measurements in the region below 150°C are problematic since there is little published data on convenient reference materials which fit the above criteria.

The purposes of this study were therefore threefold; *i.* to calibrate a DSC instrument according to a recommended procedure [9] using high purity metal standards whose melting temperatures represent fixed points in the International Temperature Scale of 1990 [10,11] or its predecessors [12], *ii.* to explore the use of some low molecular weight organic materials as temperature calibrants, and *iii.* to investigate the suitability of the phase transitions of readily available inorganic ammonium salts for sub-ambient and medium temperature calibration [13].

Materials

Mercury, gallium, indium, tin, bismuth and lead (99.999%+ pure) were obtained from Johnson-Matthey. Cyclohexane, octane, decane and dodecane were 99.9%+ purity were obtained from the Aldrich Chemical Co. Benzoic acid (99.99%), ammonium dihydrogen phosphate, ammonium sulphate and ammonium nitrate (all 98%+ pure) were obtained from BDH. Freshly distilled water was used direct from the still.

Experimental

All measurements were made with a Mettler DSC-30 heat-flux differential scanning calorimeter and TC11 controller. Data storage and analysis was performed on a IBM personal computer running Mettler TA72.1 GraphWare which displayed transition temperatures to the nearest 0.1°C. Samples were weighed into aluminium crucibles which had been previously baked at 500°C for 30 minutes to establish an inert oxide coating on the container. Metallic samples were freshly cut and cleaned to remove any existing oxide layer. The crucible was then hermetically sealed to minimise interaction with the atmosphere and inhibit evaporation of the more volatile materials studied. The crucibles were weighed before and after each series of experiments to confirm that no change in mass had taken place.

Measurement of the sample's transition temperature was made by heating the DSC cell from 50°C below the onset of the transition (to ensure that the material was in the desired phase prior to heating) to 30°C above the end of the transition. Each crucible was subjected to seven heating programmes in the order 10, 10, 1, 2, 5, 20 and 10°C/min, quench-cooling the cell with liquid nitrogen in-between scans. Even at the highest heating rates employed, the starting temperature was sufficiently below the onset of the transition for the DSC cell to have reached steady-state heating conditions. The effect of cooling rate on the transitions of the ammonium salts was also examined in which case the samples were re-heated at 2°C/min. The DSC cell was purged with dry nitrogen (flow rate: 20 ml/min) and care was taken to seal the base of the instrument to prevent the ingress of air along the leads to the sensor.

Before starting this work the cell had been calibrated according to the manufacturer's instructions. For the purposes of this study, the response of the instrument was deliberately altered by removing the optional nickel liner that had protected the furnace wall against oxidation at high temperatures.

Results and discussion

Transition temperatures were taken as the extrapolated onset temperature (T_e) for the endothermic peak in the DSC response [3]. This was determined by constructing two straight lines on the DSC curve; the first being an extrapolation of the linear portion of the DSC curve 5-10°C below the start of the process, and the second line being drawn as a tangent the steepest part of the leading edge of the peak (Fig. 1). The intercept of these two lines defined T_e .

An example of one of the difficulties encountered during this work is shown in Fig. 2. A fresh sample of gallium was encapsulated in an aluminium crucible which had not been rendered sufficiently passive by baking at high temperature. Over a series of temperature cycles, a layer of gallium-aluminium alloy developed at the sample-crucible interface which produced a double melting peak [14]. It was for this reason that each set of experiments began and ended with heating scans at 10°C/min - any discrepancy between the initial and final values of T_e indicated a problem with the sample (e.g. interaction with the crucible, oxidation, loss of material etc.) and the results were discarded.

The effect of thermal lag was accounted for by plotting T_e as a function of heating rate (β) and determining the effective transition temperature as the heating rate tended to zero ($T_e(\beta \rightarrow 0)$) by a simple least-squares linear regression according to the expression:

$$T_e(\beta) = s.\beta + T_e(\beta \rightarrow 0)$$

where $T_e(\beta)$ is the experimental value of the extrapolated onset temperature at heating rate β (°C/min), β is the heating rate, s and $T_e(\beta \rightarrow 0)$ are the slope and intercept of the $T_e(\beta)$ vs. β plot respectively.

Experimental values for $T_e(\beta \rightarrow 0)$ and s for the metallic and organic materials are given in table 1 with the corresponding literature values for the transition temperature (T_t). Note that cyclohexane undergoes a crystal-crystal transition at -87.1°C [15] which was also measured. In all cases the temperatures have been rounded to the nearest 0.1°C since this was the degree of precision afforded by the computer software. The standard errors in the regression analysis used to determine $T_e(\beta \rightarrow 0)$ and s were less than 0.1°C and 0.02 min respectively.

The difference between the true transition temperature and the observed transition temperature ($?T_{\text{corr}}(\beta \rightarrow 0) = T_t - T_e(\beta \rightarrow 0)$) is plotted against $T_e(\beta \rightarrow 0)$ in Fig. 3. For clarity, transitions corresponding to the melting temperatures of the metallic and organic materials have been distinguished, as has the crystal transition of cyclohexane. A solid and a dashed straight line depicts the general trend observed for the two categories of samples. Although it should not be assumed that the relation between $?T_{\text{corr}}(\beta \rightarrow 0)$ and $T_e(\beta \rightarrow 0)$ is linear, the results lend support to the hypothesis that the temperature calibration resulting from the use of organic materials (water being included in this class) may be different than that obtained from metals. The main causes of thermal lag for small to moderately sized samples in a DSC cell are considered to be the interfaces between the crucible and the sensor and the sample and the crucible [18]. Given that the crucible/sensor interface is constant in all cases, this suggests that heat transfer (mainly though the base of the crucible) to a melting low thermal conductivity organic material may be less efficient than to a metal. This can be confirmed visually with a substance like paraffin wax - when placed on a hot plate, the solid floats on a sea of molten material as the wax melts. Differences in heat capacity and the high heat of

transition compared to metals, cannot be discounted as factors which lead to this discrepancy. Interestingly, the crystal transition of cyclohexane lies on the trend shown by metals which implies that the problems of heat transfer between the melt and solid is a significant factor since this is an example of a solid I - solid II transformation.

Table 1 Transition temperatures of metals and organic materials

material	$T_l/^\circ\text{C}$	mass/mg	$T_c(\beta \rightarrow 0)/^\circ\text{C}$	s/min
mercury [16]	-38.8	28.200	-38.3	0.14
			-38.2	0.19
gallium [10,14]	29.8	12.093	28.1	0.08
indium [10,14]	156.6	2.507	151.2	-0.05
		7.335	151.2	-0.05
		11.114	151.2	-0.05
		14.457	151.2	-0.05
tin [10,14]	231.9	14.974	224.0	-0.13
		26.869	224.0	-0.14
bismuth [16]	271.4	12.251	260.9	-0.16
		30.709	260.8	-0.14
lead [14,16]	327.5	11.369	314.9	-0.18
		25.868	315.6	-0.18
water [10]	0.0	6.408	-3.1	0.10
octane [17]	-56.8	18.000	-57.1	0.04
decane [17]	-29.6	16.547	-31.5	0.05
dodecane [17]	-9.6	16.512	-12.1	0.05
cyclohexane [15]	-87.1	7.000	-84.5	0.12
		6.7	2.8	0.09
benzoic acid [9]	122.3	6.755	115.4	0.04

Of great practical interest are materials which show transitions in the sub-ambient and medium temperature range [13]. Many ammonium salts exhibit transformations between crystal types due to the onset of rotational motion of both cation and anion causing changes in packing [19]. These materials are readily available in high purity and present little difficulties in terms of their toxicity and ease of handling. Preliminary work on the crystal-crystal

transition of ammonium sulphate has already been reported [13]. The present study found that the transition temperature on heating was unaffected by the cooling rate employed to bring the instrument to the starting temperature for the measurements. Although not pertinent to this discussion, the enthalpy change associated with the transition was also independent of thermal history indicating that this material could also be used as an enthalpy standard. The crystal structure transition of ammonium dihydrogen phosphate around -120°C also exhibited these qualities.

The values of $T_e(\beta \rightarrow 0)$ for ammonium sulphate and ammonium dihydrogen phosphate were found to be -121.4 and -48.8°C respectively within an error of $\pm 0.1^{\circ}\text{C}$. Literature values for these transitions are -125.6°C [20] and -49.8°C [21]. It should be noted that transition in ammonium sulphate is caused by the onset of rotation in the cation, whereas the transition in ammonium dihydrogen phosphate is due to rotation of the anion. Potassium dihydrogen phosphate exhibits the latter type of transition at -151.2°C [22] and the corresponding dihydrogen arsenates show transition temperatures of -177.6 and -57.1°C for KH_2AsO_4 and $\text{NH}_4\text{H}_2\text{AsO}_4$ respectively [23,24]. Deuteration raises the transition temperature.

Also noted, was the difference between $T_e(\beta \rightarrow 0)$ obtained on cooling from the corresponding value obtained on heating which amounted to 2.9°C in the case of $\text{NH}_4\text{H}_2\text{PO}_4$ and 3.3°C for $(\text{NH}_4)_2\text{SO}_4$. This hysteresis effect has been reported in the literature [20,25]. By employing a coarse mixture of both salts a simple two point temperature calibration could be obtained (Fig. 4). No changes in the transition temperatures of this mixture were observed over repeated thermal cycling in the range -150 to 30°C .

The advantages of samples with multiple transitions (e.g. a mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, or a substance with more than one transition such as cyclohexane) is most clearly given by examining the thermal behaviour of another ammonium salt - ammonium nitrate. Although its thermal instability is well-known, when pure, the compound may be heated above its melting point (170°C) to around 200°C without decomposition [26]. According to the literature [27], ammonium nitrate exhibits five transitions in the region -20°C to 150°C . These comprise the crystal-melt phase change and four crystal-crystal transformations:



$I = \text{cubic}$, II and $V = \text{tetragonal}$, III and $IV = \text{orthorhombic}$

A metastable transition, orthorhombic (IV) - tetragonal (II) at 45 - 50°C has been reported by many workers; this is often dependant on the amount of moisture in the sample [28-32]. The influence of impurities or deliberate admixture with other salts has also been studied.

The effect of thermal history on the DSC response of NH_4NO_3 is shown in Fig. 5. By rapidly cooling the sample from the melt and re-heating it at a moderately fast rate, five exothermic transitions are observed as expected. Slowly cooling and reheating the material only records four transitions; the $III \rightarrow II$ change being absent. The intermediate stage of rapidly-cooling the sample and slowly re-heating it is also depicted - the reverse process of slow-cooling followed by moderately fast heating also generates the same response. The nature of these effects is outside the scope of this paper but has serious implications if one wishes to use this material for temperature calibration. The transition temperatures corrected for thermal lag, $T_e(\beta \rightarrow 0)$, for the phase changes in this material are given in table 2 along with their corresponding literature values. The results support those of Sowell et al. who found

that the $II \rightarrow I$ and $I \rightarrow$ melt transitions were unambiguous but that the $III \rightarrow II$ phase change occurred at a consistently higher temperature than previously reported [33]. Stephenson et al. found difficulty in determining the $V \rightarrow IV$ transition due to the slow rate by which it proceeds [34]; this work encountered the same difficulties which probably account for the difficulty in obtaining a consistent result. The $IV \rightarrow III$ transition at 50.6°C, although well-defined, does not match the literature value [35]. This feature is ascribed to the occurrence of a $IV \rightarrow II$ metastable transition which is known to take place in dry samples [32]. These findings imply that both the $II \rightarrow I$ and $I \rightarrow$ melt transitions are suitable for temperature calibration, the remainder are either subject to thermal effects or consequences of sample preparation: factors which preclude them from general use.

Table 2. Transition temperatures of ammonium nitrate

Transition	$T_t/^\circ\text{C}^*$	$T_c(\beta \rightarrow 0)$	comments
$V \rightarrow IV$	-17	-8 ± 1	large error in determinations, T_c difficult to define, decreases with increasing cooling rate.
$IV \rightarrow III$	32.1	50.6 ± 0.1	satisfactory result, not affected by cooling rate.
$III \rightarrow II$	84.2	85-90	often absent depending on conditions.
$II \rightarrow I$	125.2	124.8 ± 0.1	satisfactory result, not affected by cooling rate.
$I \rightarrow$ melt	169.6	167.3 ± 0.1	satisfactory result, not affected by cooling rate.

* T_t taken from references 34 and 35

The correction to the temperature scale, $? T_{\text{corr}}(\beta \rightarrow 0)$, obtained from measurements on the inorganic ammonium salts are shown in Fig. 6., overlaid on the trends found for metallic and organic reference materials. The results for $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ fit the pattern for metals exactly whereas the two transitions for ammonium nitrate that were considered suitable reference points show considerable deviation from the expected trend. This may be due to impurities in the material or a genuine feature of its behaviour. Such findings illustrate that it is important to check that different reference materials behave in the same way.

Conclusions

Studies based on a recognised calibration procedure show that different results can be obtained using different classes of reference materials. This is ascribed to differences in thermal properties. The crystal-crystal transitions of ammonium dihydrogen phosphate are considered to be suitable reference points for sub-ambient work and can effectively replace mercury and dichloroethane as standards. Although three of the transitions in ammonium nitrate were found to be unambiguous, one was discarded due to doubts about the nature of the transition (metastable) and the remainder showed behaviour which deviated from the expected trend of correction factors. Further work is desirable to establish suitable materials for temperature calibration in the medium temperature range, especially between 0°C and 100°C. Although not addressed in this study, a similar approach could be employed to screen

materials for suitability as enthalpy calibrants for DSC.

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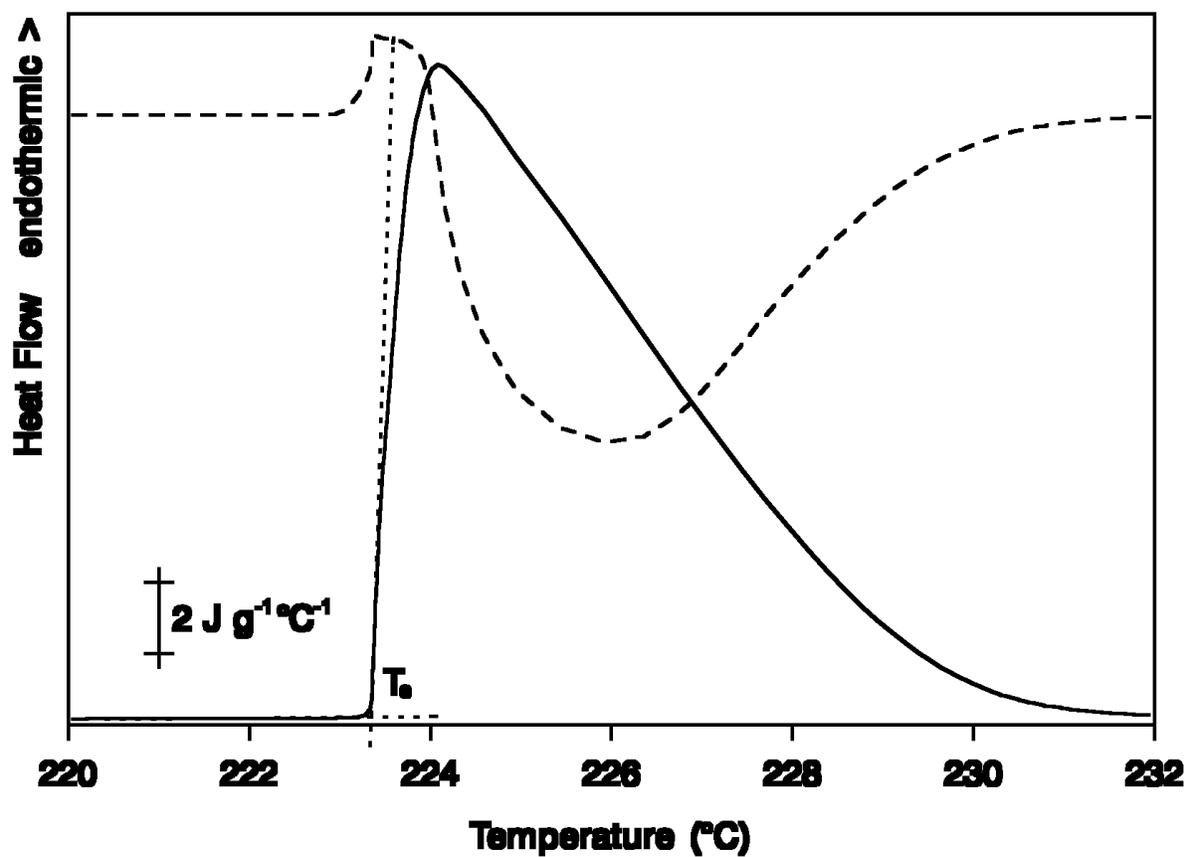


Fig. 1. DSC plot of differential heat flow (solid line) and derivative differential heat flow (dashed line) vs. temperature for tin heated at $5^{\circ}\text{C}/\text{min}$ showing the construction of tangents used to determine T_e .

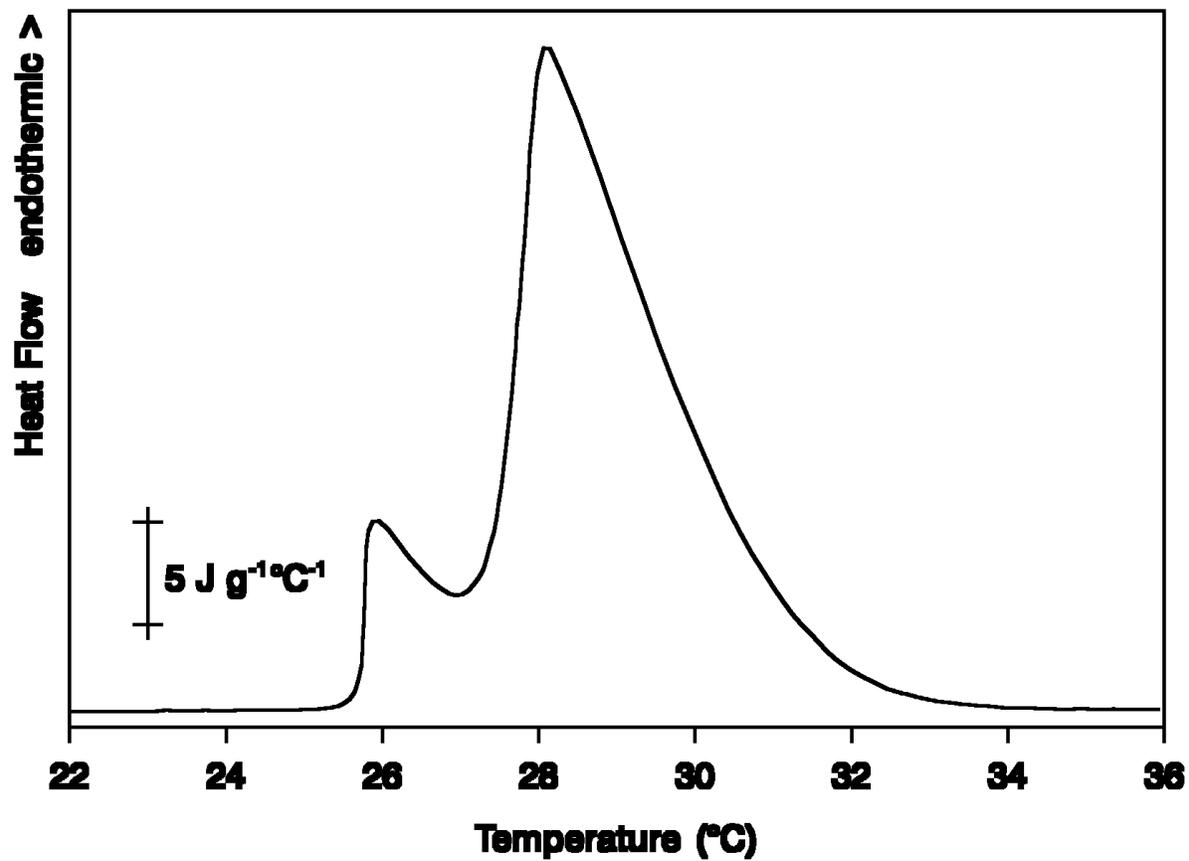


Fig. 2. DSC plot of a gallium sample that had reacted with the aluminium crucible showing double melting peak due to the formation of some Ga/Al alloy.

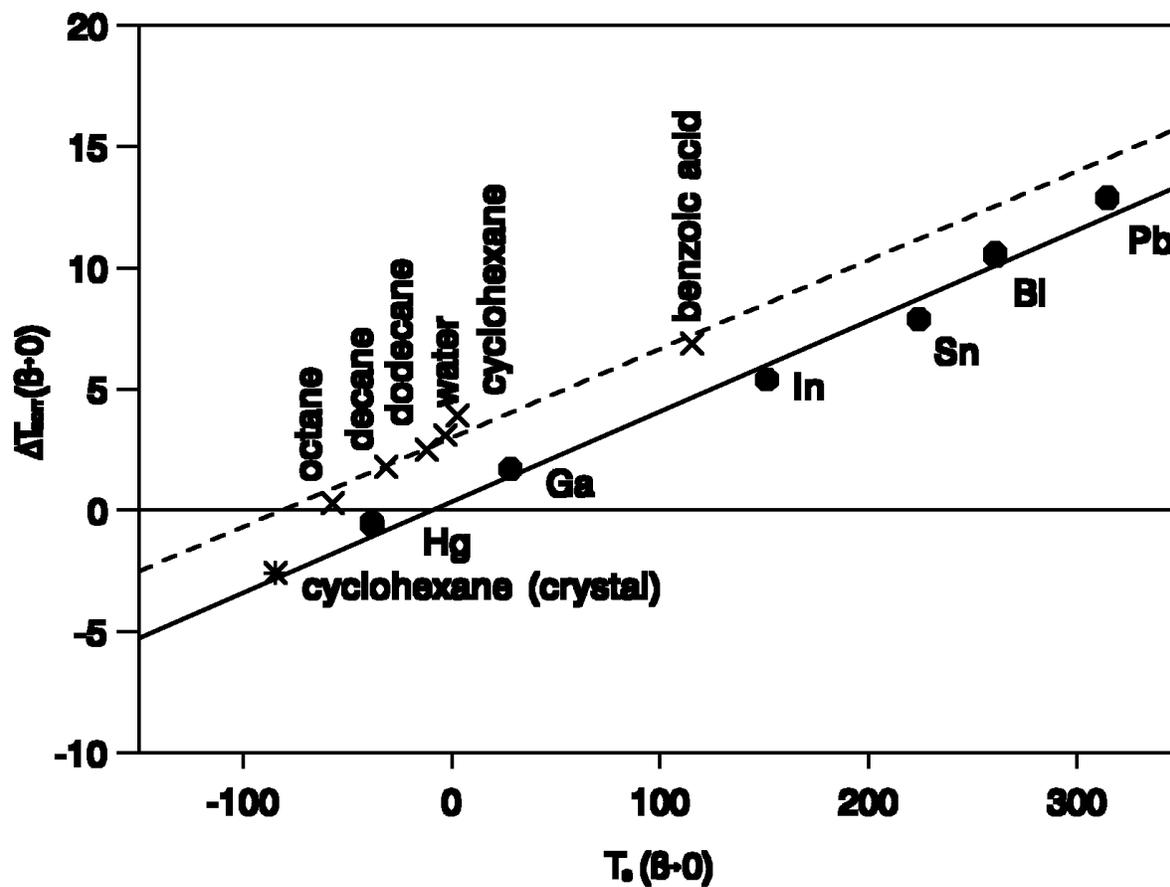


Fig. 3. Temperature correction factors, $\Delta T_{\text{corr}}(\beta \rightarrow 0)$, as a function of measurement temperature, $T_e(\beta \rightarrow 0)$, for metals (solid circles) and organic samples (crosses). The general trends are shown as solid and dashed lines respectively. The crystal-crystal transition of cyclohexane is plotted as a separate point.

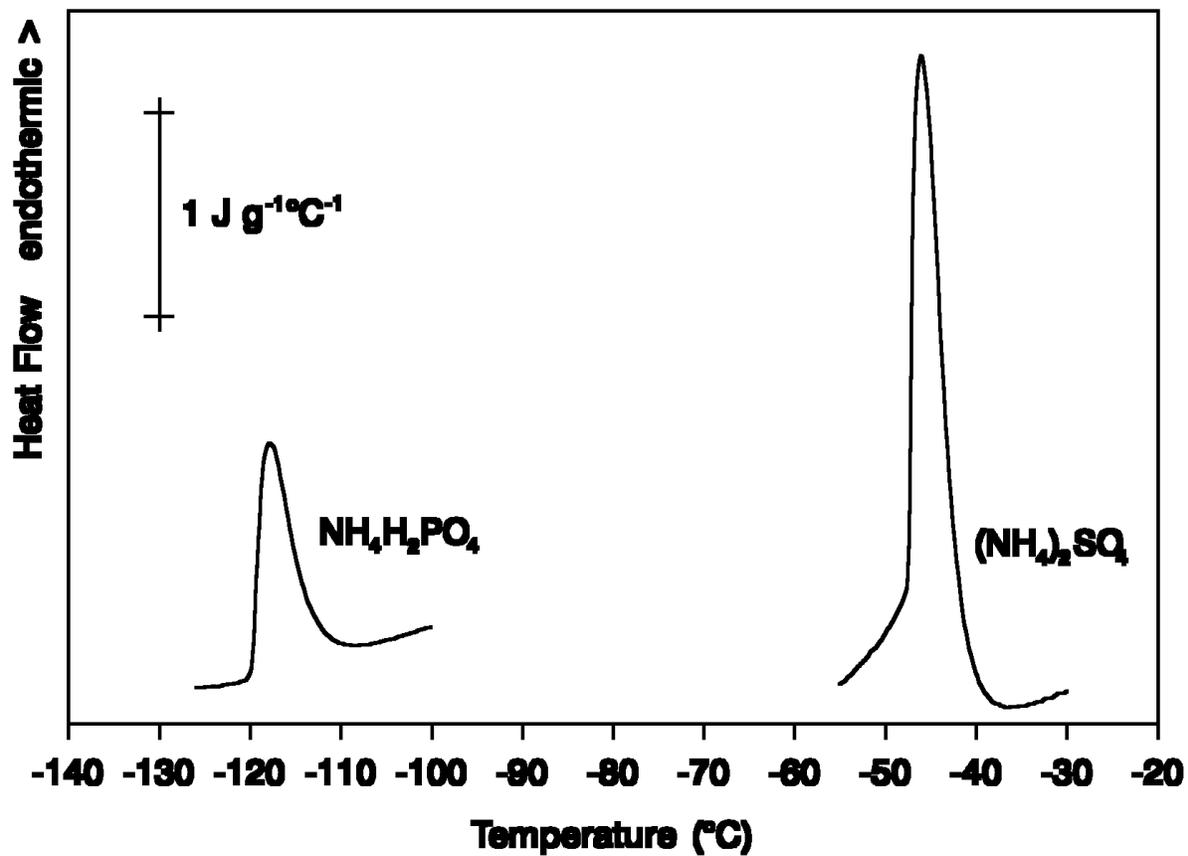


Fig. 4. DSC plot of differential heat flow vs. temperature for a coarse mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$. The individual transitions have been corrected for the mass of each component present.

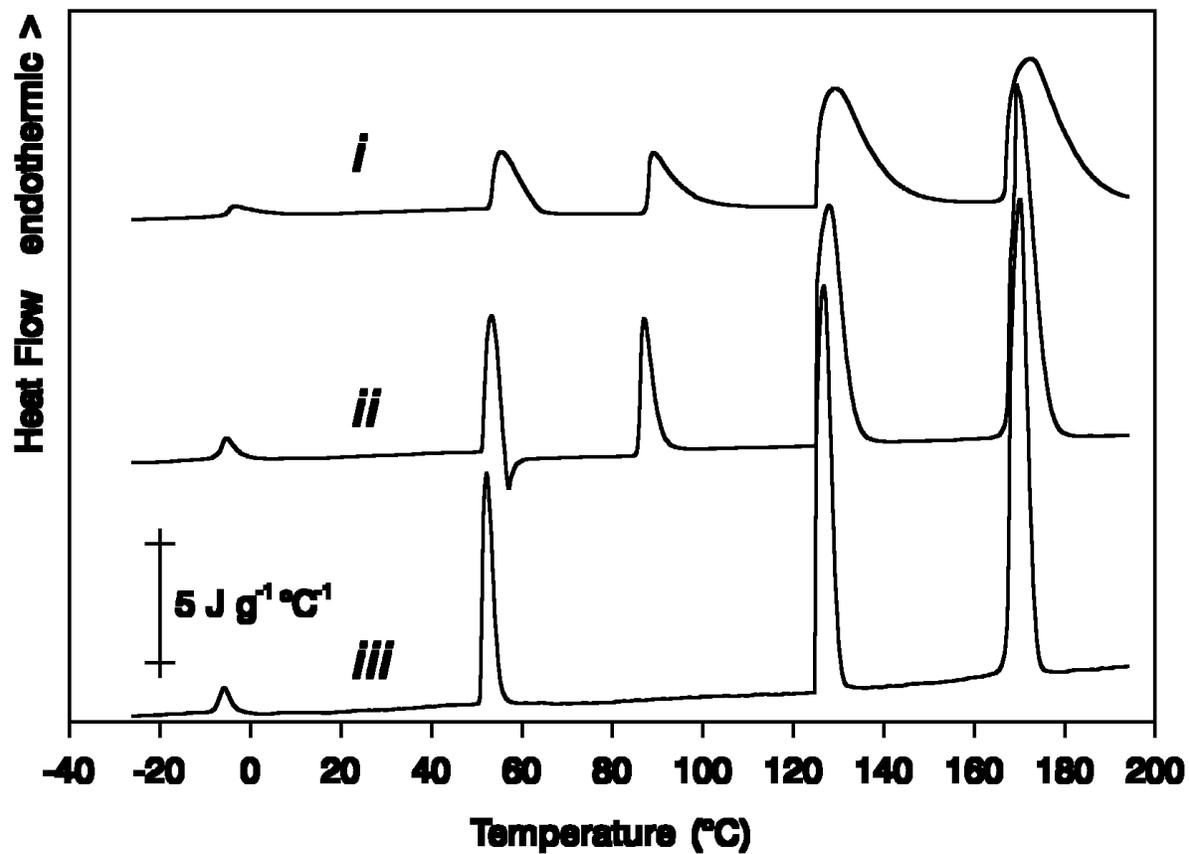


Fig. 5. Composite plots of the DSC response of ammonium nitrate; *i*, cooled at 80°C/min, heated at 20°C/min, *ii*, cooled at 80°C/min, heated at 2°C/min and *iii*, cooled at 2°C/min, heated at 2°C/min.

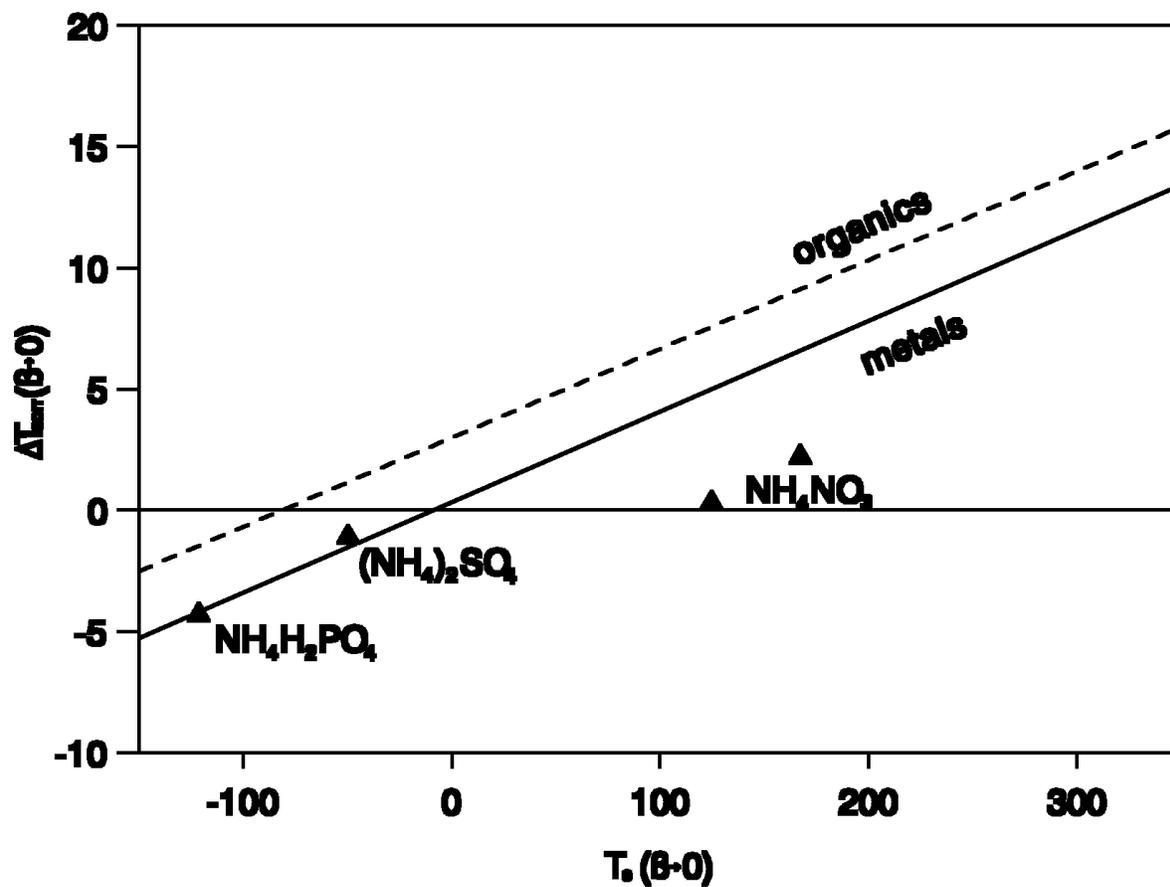


Fig. 6. Temperature correction factors, $\Delta T_{corr}(\beta \rightarrow 0)$, as a function of measurement temperature, $T_e(\beta \rightarrow 0)$, for ammonium salts. The general trends for metals and organic materials are overlaid as in Fig. 3.