Quantitative aspects of differential scanning calorimetry

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Abstract

The quantitative performance of differential scanning calorimeters is reviewed. Temperature calibration is discussed in terms of an isothermal correction plus a contribution from thermal lag, this can be derived from individual curves and is valid in both, heating and cooling. It is emphasised that baselines that are drawn to thermal events, such as melting and transition phenomena, must have thermodynamic significance and a general procedure is suggested. When this is used, a power compensation calorimeter calibrated for heat-capacity work can reproduce heats of fusion and transition for a diverse range of materials to better than 1%. © 1997 Elsevier Science B.V.

1. Introduction

Although differential scanning calorimeters have been in use for more than thirty years, many, perhaps even the majority, of applications remain qualitative or, at best, semi-quantitative in the sense that the temperature axis alone is calibrated – the calorimeter is only being used as a thermometer. Such applications may be quality control checks that focus on changes in the location and/or magnitude of an 'event' – or even something as basic as its presence or absence. These are, of course, perfectly valid uses and may give results that are otherwise difficult to obtain: a good example is the detection of small amounts of polyethylene in polypropylene. It is, however, strange that calorimetry, normally associated with thermodynamics, that most precise of sciences, should be so used. Some would argue that DSC is incorrectly

named and is really only suitable for order-of-magnitude measurements. Indeed, it was only a few years ago that papers using the technique were totally banned from the pages of one journal. Although the ban has now been lifted, some readers still feel that this was a retrograde step. My own first contact with DSC was certainly biased towards this view: it was merely used as a subsidiary technique, prior to adiabatic calorimetry [1], to define the thermal history needed to produce a stable, structurally homogeneous material. Subsequent attempts to reproduce the adiabatic results by DSC, using the 'chart recorder' techniques then available, were unsuccessful and simply confirmed my original prejudice. However, change to a crude (relative to modern equipment) data recording *and processing* system transformed the situation [2], and for more than 25 years, most of our DSC results have been produced as specific heat (c_p) vs. temperature (T) curves with overall errors of $\pm 1\%$ as judged by comparison with results on materials of known c_p.

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This paper is a personal account of some of the problems, and their solutions, of quantitative DSC. It explores some of the reasons (often very valid) for the widespread distrust of DSC among 'true' calorimetrists but, hopefully, will indicate how calorimetric data *can* be obtained when simple experimental and computational precautions are observed. The paper does not consider temperature-modulated DSC [3] which is currently undergoing very rapid development: interpretation is complex relative to conventional DSC, but real problems still remain for the latter and it is these that are addressed here. Most of the examples that will be given have been obtained using power compensation (Perkin–Elmer) DSC but, if sales literature is to be believed, comparable performances are also available from heat-flux instruments.

2. General comments on calorimetry

To obtain entropy changes, calorimetric measurements should be made under the conditions of thermodynamic reversibility that are approached in conventional adiabatic calorimetry [4]. Here heating rates must be low, a few degrees per hour, to maintain temperature uniformity in the large (grams/tens of grams) samples that are used. Adiabatic measurements on any material represent a major investment of time in addition to the considerable cost of developing the (generally) home-made equipment. However, all relevant parameters can be directly related to fundamental electrical quantities and the technique leads to primary thermodynamic standards, in particular, specific heat capacities and enthalpies of fusion, transition, etc.

DSC conditions for normal heating (or cooling) rates (β, say, 5–20 K min^{-1}) are far from reversible. Lower rates are, of course, possible (although penalised by noisier signals) but it is really these values of β that appeal to the majority of users. Here, in a properly calibrated instrument, the 'steady-state' conditions that are established in 'simple' c_p regions (where the only energetic processes involve c_p) effectively simulate the equilibrium state and meaningful entropy changes can be calculated from the measured c_p values. Once steady-state conditions have been perturbed by a physical or chemical 'event', reversi-

bility is lost and direct entropy calculations become meaningless.

Problems of this type are not unique to DSC. Much of our knowledge of high-temperature thermodynamic properties is based on drop calorimetry [5] which measures enthalpy changes over, typically, temperature intervals of hundreds of degrees. Specific heats (and also the presence of phase changes at intermediate temperatures) must be derived or inferred from a lengthy set of subsidiary experiments. Even then, further tests (DSC is very useful here!) are needed to check on the structure that has been quenched in by the 'drop' – is it really stable at room temperature or some atypical metastable form? Although real problems can arise, no experienced worker would use these as reasons for rejecting the whole technique of drop calorimetry. Even adiabatic calorimetry has its difficulties: in addition to the time factor and the requirement for large samples already mentioned, it is not generally possible to work in cooling. Interesting metastable states with lifetimes of the order of minutes may therefore be inaccessible to this technique although perfectly satisfactory for analysis by DSC.

The several forms of calorimetry clearly complement each other very well – if it can be demonstrated that DSC is indeed a calorimetric technique. It is important to emphasise that DSC is a relative, not an absolute, method. Instruments *must* be calibrated with substances that have well-defined properties. Derived data are critically dependent on the calibration procedures used. Of course, the total experimental package contributes to successful measurements and care is needed at all stages. The prime requirement is to ensure that the complex heat-flux conditions that exist in any DSC are reproduced as closely as possible between one set of measurements and another – in particular when going from the calibrant to an unknown substance. A simple example will illustrate this. Heat losses (especially at high temperatures) from unlidded pans containing graphite, titanium dioxide and synthetic sapphire will differ among themselves and useful c_p data cannot be derived under these conditions: the use of a lid gives a constant-emissivity package, independent of the pan contents, and meaningful heat capacities are readily obtained. When heat-flux conditions are correctly established, DSC is an extremely simple technique to use (one

reason for suspicion on the part of those used to more complex procedures!) and one that can give results that may not be achievable in any other way. The experiment is basically a comparison of two signals, one of which is calibrated against some known property – temperature, enthalpy or specific heat. The problems that must be resolved, both experimental and computational, are discussed below in this same order.

3. Temperatures

3.1. Onset temperatures

Differential scanning calorimeters still find far more 'quantitative' uses as thermometers rather than as calorimeters. Although a very expensive form of thermometry, DSC is especially useful when only a small amount of sample is available. Unfortunately, great care is needed before DSC-derived temperatures have thermodynamic validity [6]. The 'extrapolated onset' (T_e, Fig. 1) is taken to represent the melting or transition temperature (T_m, T_t) of a material but, as will be seen below, certain conditions must be fulfilled before T_e can be unambiguously defined. A calibration curve is then set up using standards with known T_m. The number of calibration points that are needed
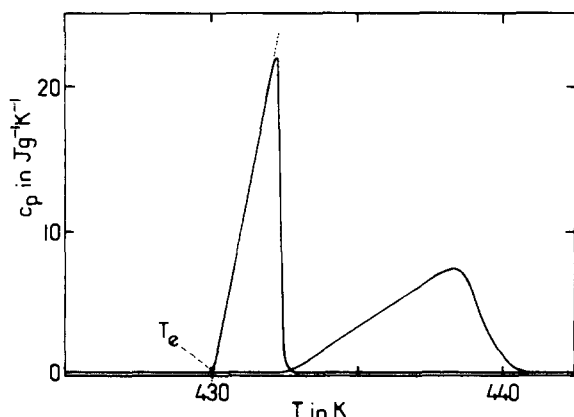

Fig. 1. The melting of 62.30 mg of indium at 2.5 and 20 K min^{-1}. Temperature scale corrected for isothermal conditions (T_m = 429.74 K). The construction defining T_e is shown. $\Delta_{fus}h$ 28.68 (2.5) and 28.59 (20 K min^{-1}) J g^{-1} (based on alumina calibrant).

clearly depends on the curvature. The widely used ASTM method [7] uses only two but a minimum of three would seem sensible even if they either only confirm the implied linearity or indicate appreciable curvature – in which case further points must obviously be added. 'Unknown' temperatures can then be read from the calibration curve. Any first-order transition temperature (T_t) can be used in place of T_m – the ICTAC standards[8] actually contain a majority of solid/solid transitions because many instruments could not accept liquids when the standards were first developed.

This is not a problem nowadays when instruments are increasingly 'user friendly' – perhaps too friendly? It is possible for a newcomer, on a first attempt, to produce a very elegant curve containing information that appears to have real value. For many, this is their sole exposure to DSC, no rerun is attempted, the curve is analysed (using equally amiable software) to give a T_m with what appears to be remarkable accuracy. It would certainly be very gratifying if temperatures could be obtained to the three decimal places that are often quoted in the literature. However, a rerun or a repeat using a fresh sample should soon dispel this illusion and the similar implied precision for the associated heat of fusion ($\Delta_{fus}h$). Additional reruns, without touching the sample and using identical conditions, may then give remarkably constant figures that are a genuine demonstration of instrumental stability and reproducibility.

The apparent decrease in the melting point of a sample that is often observed after the first DSC run often reflects no more than the improved sample/pan contact that follows when a poorly packed sample melts. Progressive decreases in T_m may be due to slow degradation or to the very gradual flow of a polymer of high molar mass (and therefore high viscosity) to, again, improve thermal contact. Unless this type of behaviour is suspected, it is not necessary to progress beyond one rerun especially if there is specific interest is in the 'as received' state. In this case, great care must be taken to ensure optimum packing and it is always helpful to check this with a rerun so that the initial result has an internal reference state against which it may be compared. Ideally, both 'as received' and 'rerun' T_m values should have similar reproducibilities – undue scatter in the former relative to the latter suggests problems in packing.
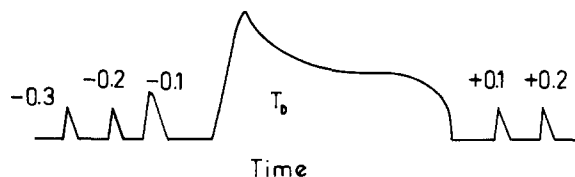
Fig. 2. Isothermal (stepwise) melting procedure showing 0.1 K increments (schematic). T_D is the observed DSC melting temperature, the isothermal correction is $T_m - T_D$. Some premelting is shown at $T_D - 0.1$ K.

It is clear from the foregoing that the melting of even a stable structure may not reproduce between the first and subsequent runs. The second run generally gives a sharper peak although two such rerun curves for different masses (and after normalisation to unit mass) may still have different shapes – the analysis of curve shapes is only valid at very slow heating rates when conditions approach thermodynamic reversibility. These effects are due to the finite times needed to transfer massive heats of fusion (relative to specific heat) to the sample. Pure indium, probably the most popular calibration material, is typical: melting of a 99.999% (5N) sample appears to extend over several degrees (Fig. 1) but slow, stepwise heating (Fig. 2) readily shows that this is an artefact and, as would be expected for a pure substance, melting is actually complete in less than 0.1 K. This behaviour is hinted at in Fig. 1, where the peak width decreases with decrease in heating rate. (Note that, for ease of comparison, the data are shown as specific-heat curves – they are normalised with respect to the sapphire calibrant – so that the melting peaks are better defined at low β.) Extrapolation to zero heating rate therefore becomes a potential approach to thermodynamic temperatures [6]. For reasons of productivity, however, most users are more attracted by high heating rates and must be prepared to accept that the values so obtained are only approximate relative to equilibrium conditions. 'Approximate' is emphasised because for any real sample at heating rates of, say, 20 K min^{-1}, there must be a temperature gradient between the hot base and relatively cool upper surface. Traditional adiabatic calorimetry uses very slow heating rates and so approaches conditions of thermodynamic reversibility. DSC conditions are far from reversible and it is fair to ask to what temperature does a DSC value refer?

The answer depends very much on how the instrument is being used – as a thermometer or as a calorimeter. The conventional 'onset' calibration defines the temperature when the calibrant starts to melt: this is at the area of contact with the pan (through which heat is transferred) and the upper face may still lag behind by some degrees. The reverse procedure, the start of melting of an 'unknown', is assumed to represent the desired T_m. Implicit in all this is the assumption that T_e is identical with the melting point. There is a paradox here in that one common application of DSC involves the determination of purity, essentially using the width of the melting range. In fact, the equilibrium melting temperature is defined by the end, rather than the start, of melting: it is that temperature when the most perfect crystals finally vanish. (This is not the end of melting as observed in a DSC which is a complex combination of instrumental and material effects.) There is no ambiguity in equating T_e and T_m for the ca. 5 N purity metals that are widely used as calibrants. Not all temperature ranges can be covered by these ideal materials, however. Less pure calibrants must be used – and the significance of the 'onset' temperature becomes increasingly ambiguous as purity decreases (it should be emphasised that even 3N purity is exceptional for many organic materials). Another problem emerges here: many abstracted 'literature' T_m refer to data that were corrected, as part of the original paper, to 100% purity, the measured T_m are therefore slightly lower. The correction is trivial (on a DSC scale) for typical metallic calibrants but may be some tenths of a degree for organics.

A simple stepwise DSC procedure [2,9] will give the true final melting temperature of a material: the T_m region is passed through in small (perhaps 0.1 K) temperature increments (Fig. 2) allowing sufficient time between increments for the signal to return to a constant value. Melting is obvious, the signal increases and a lengthy period is needed before it returns to the steady-state baseline. The time factor is particularly important when close to T_m because there is little thermodynamic driving force for the rapid transfer of the necessary heat of fusion, many minutes may be needed before melting is complete. The stepwise procedure gives highly reproducible results, not only for T_m but also for first-order solid/solid and liquid crystal transitions. Only small samples should

be used because, as the technique shows when a phase vanishes, any thermal gradient in a sample will appear to give an anomalously high melting or, especially, transition temperature (for which thermal contact cannot be optimised by melting). The procedure gives an isothermal calibration curve – the correction needed to convert the indicated (steady) temperature to the true sample temperature. The calibration is independent of the nature of the material – metals, organics, and inorganics all fall on the same curve and an 'unknown' can be determined to ±0.1 K with some confidence. An isothermal calibration is needed, even if the sensors are behaving ideally, since they are located away from the sample and there may be a thermal gradient between the two. Because of this, a

fresh calibration may be necessary if the type of sample holder is changed – this should always be assumed unless experience proves the contrary.

The alternative isothermal calibration procedure, extrapolation of T_e as a function of heating rate to $\beta = 0$ [6], gives a curve that agrees well (Fig. 3) with that obtained using the stepwise procedure. However, the rate measurements clearly illustrate the problems faced when deriving temperatures at specific values of β because the slope $dT_e/d\beta$ differs for different materials [6,10]. Ideally, material properties should only influence the *subsequent* shape of a melting curve, heat transfer to the sample face being part of the 'instrument constant'. Deviations from a common slope probably reflect, not only problems in reprodu-
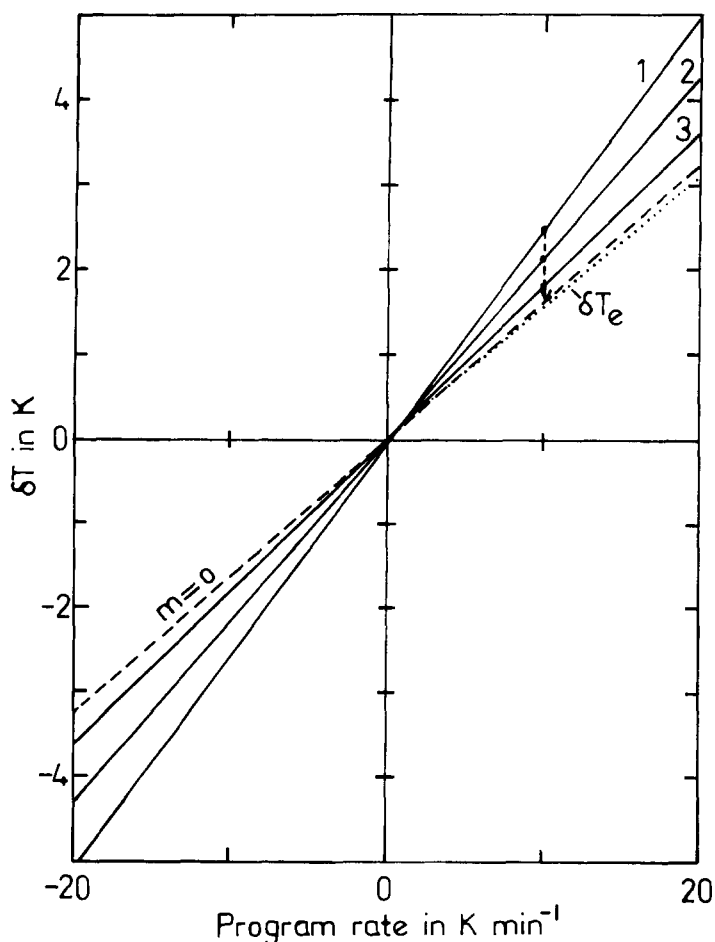

Fig. 3. Thermal lag (δT) in 6.3 mm diameter sapphire discs: (1) 129.60; (2) 74.82; and (3) 25.94 mg. Extrapolation to m = 0 (broken line) is shown; dotted line (δT_e) shows how the extrapolated onset changes with rate.

cing identical sample/pan contact between, say, a metal and an organic compound, but also the uncertain equivalence of T_e and T_m for the latter. Whatever the reasons, a curve that is material-independent at $\beta = 0$ loses this independence for finite heating rates. The subsequent calibration curve at rate β therefore becomes material-dependent. As a result, the accuracy of T_m or T_t determinations decreases from ± 0.1 K in the isothermal mode to only ± 1 K at the more popular rates of 10–20 K min^{-1}.

3.2. Thermal lag

The foregoing discussion has concentrated on the start of melting (or of a transition) but a heat capacity experiment really needs an average sample temperature and this will lag behind any value obtained from an 'onset' curve. The practical consequences of the resultant temperature error are often small because c_p is generally only a mild function of temperature. There may, however, be occasions (e.g. broad transitions with regions of large dc_p/dT) when thermal lag is important and instrumental potential is not fully realised. In any case, there is no justification for using an erroneous temperature when the correction is easily made.

In principle, the temperature distribution within a DSC cell can be described using computer simulation and assuming various idealised configurations [11,12]. Unfortunately, these are rarely achieved in practice and it is necessary to have some practical measure of real behaviour. A simple and useful approach is via the 'enthalpy lag' (δH) at the end of a run [13,14]. Any sample needs a finite time to come to isothermal equilibrium after heating or cooling. The area (δA, Fig. 4) enclosed by the DSC curve during this time is equivalent to δH and this may be transformed to a
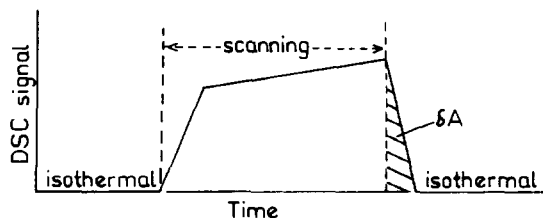

Fig. 4. The area (δA) used to calculate thermal lag (schematic).

thermal lag (δT) through $\delta H = m_x c_{px} \delta T$ where m is mass (subscript x may refer to sample(s) or calibrant(c)). By using samples of similar geometry but different thickness, it is possible to distinguish between material and instrumental effects. Extrapolation to zero thickness (mass) gives thermal lag at the sample/pan interface [13] (Fig. 3) and the resultant curve is very similar to that found using the $T_e(\beta)$ vs. β procedure: in Fig. 3, for example, the two differ by 0.2 K at 20 K min^{-1}. Any point above the $m = 0$ line of Fig. 3 is not accounted for by the $T_e(\beta)$ calibration and errors of 2–3 K at 20 K min^{-1} are common – the sapphire examples of Fig. 3 approach the minimum values possible because of their near-ideal geometries.

The two temperature-calibration procedures can be demonstrated for the indium ($T_m = 429.74$ K) shown in Fig. 1. Here the basic experimental quantities were T_m(isothermal = stepwise) $= 425.8$, $T_e(2.5) = 426.2$, $T_e(20) = 428.8$ (β in brackets, the instrument had been approximately set up for $\beta= 20\,K$ min^{-1} and a lower ambient temperature). In Fig. 1 all temperatures have been increased by $+4.0$ to give a corrected isothermal scale and the two 'onset' values now represent corrections of -0.4 and -3.0, the respective corrections for thermal lag are -0.5 and -3.0 showing, in this case, the equivalence of the two methods. (It could be anticipated that the large indium sample used (needed to give a reasonable c_p signal at the lowest β) would lead to an overcompensation – large δT – but separate experiments show that the mass effect is very small for this metal.)

In c_p work it is generally sufficient to use the average thermal lag from sample and calibrant rather than correcting each individual data set to common temperatures. In fact, experience quickly leads to sample sizes and geometries that approximate to those of the calibrant. Changes in δT with instrumental and material conditions are readily demonstrated. For example, granular samples have, as expected, relatively large values of δT and the improved contact on melting is clearly shown, there are particularly interesting effects for polymers [15]. Even the indium results discussed here show changes: the sample of Fig. 1 was a flattened pellet – without this precaution δT can increase by 50% and this remains after melting because an aluminium pan is not wetted by indium.

Some emphasis has been placed on the combination of an isothermal calibration with a dynamic thermal lag contribution. Together, they give an individual calibration for each run at any β. In particular, they are also suitable for work in cooling – a mode of operation that should be much more widely used to simulate the many material-forming processes that involve solidification from the molten state. Conventional calibration is impossible in cooling because supercooling is not a reproducible phenomenon and crystallisation temperatures cannot be certified with any precision.

Temperatures in cooling are often based on the assumed symmetry of the heating calibration – that the $T_e(\beta)$ vs. β curve can be extrapolated to negative values of β. Direct experimental confirmation is difficult to obtain except in the relatively narrow temperature region where liquid crystals are found. These appear to show negligible supercooling (on the 0.1 K scale that is significant for DSC) and have been carefully investigated as potential calibrants [16,17]. They work well although it is uncertain whether the 'onset' or 'peak' temperature is the relevant quantity: the peak can be used because many liquid crystal transitions involve only low energies and the signal remains linear throughout the transition. The assumption of symmetry is found to be justified both by work on liquid crystals [17] and by measurements of thermal lag. The lines for alumina in Fig. 3 are least-squares fits that include δT for both $\pm\beta$, all pass within 0.1 K of the origin.

3.3. Size effects

The small samples used in DSC can lead to a variety of anomalous temperature effects, both instrumental and material. In power compensation DSCs there is a small (tenths of a degree) temperature gradient between the centre (hotter) and outside of the sample holder [11]. A centrally placed and well-compacted sample may, because of surface tension, melt to form an annulus within the circumference of the pan: the subsequent T_m may therefore appear to be slightly higher.

A quite different effect is the stabilisation of metastable phases as the sample size decreases [18]. For many substances, it is a common observation that, on solidification, the stable form is only achieved after passing through one or more polymorphic transformations, in accordance with Ostwald's rule. Small samples emphasise this effect, structures may appear in the DSC that are otherwise difficult to observe but which provide valuable information about the solidification process. The T_m of such a structure will naturally differ from that of the more usual phase. Metastable p-nitrotoluene, for example, melts 6.2 K below the normal T_m of 324.7 K [19]. p-Nitrotoluene is cheap and easily purified and would be a useful DSC calibrant if either phase transition were reproducible. It could still be included as one member of a multiple point calibration (when an apparent error of 6 K would be obvious and immediately suggest that the 'wrong' polymorph was present) but there could be large errors when using the two point ASTM method [7]. A similar problem is found with the solid/solid transition (II/I or III/I) at ca. 400 K for potassium nitrate, one of the ICTAC temperature calibrants [8]. The structure (II), that is stable at room temperature, transforms to a high temperature phase (I) at 402.9 K. Subsequent cooling gives a metastable form (III) that converts to I at 402.0 K. There is clearly much potential for confusion here unless ICTAC recommendations (which feature the III/I transition) are followed exactly. Fortunately, enthalpies – even if only qualitative – can provide valuable supplementary information: the enthalpy for the III/I transition is only about half that for II/I – such a difference is obvious by inspection alone and the phase present, and relevant T_t, can be immediately identified.

3.4. Concluding remarks on temperatures

Many qualifications are needed before DSC temperature measurements can be said to have thermodynamic validity. Isothermal values, determined either directly or by extrapolation, are the most accurate. Conventional 'onset' values are appropriate for pure materials with narrow melting ranges – but problems with heat transfer mean that calibration curves at 'normal' values of β are material-dependent. A simple correction for thermal lag can be made and has been found suitable even for very high values of β (up to 80 K min^{-1}). This procedure is also valid for cooling and should encourage the more widespread use of this important facility which is not readily accessible by other forms of calorimetry.

4. Calorimetric data

The most basic form of a DSC curve is a plot of differential power or differential temperature against time – which is easily transformed to temperature for linear heating/cooling rates. The area enclosed by a power-time curve describes an energy and most calorimetric applications of DSC are based on the transformation of some area (exactly *what* is all too rarely discussed) to the energy associated with a process such as fusion, transition, reaction, etc. Calibration, using known $\Delta_{fus}h$ for example, gives quantitative legitimacy to the ordinate (differential power/temperature) axis but I have never found a scale labelled 'milliwatts' particularly helpful when investigating the properties of a particular material. A specific heat ordinate is generally much more relevant. The peaks and troughs corresponding to various thermal events can be looked upon as regions of unusual c_p that eventually lead to $\Delta_{fus}h$, etc. (Although beyond the scope of this paper, there are exciting possibilities that additional information can be derived in these regions using temperature-modulated DSC [3].) An area defined by a c_p vs. T curve is, again an energy – an enthalpy change – and the calorimetric applications of DSC are critically dependent upon the specification of areas that correspond to real thermodynamic quantities. A single DSC curve does not, by itself, define an area. Either a 'baseline' must be drawn for a peak or trough or an additional run made for the empty sample pan. Subtraction of the latter from the 'pan + sample' gives the desired sample contribution. In principle, temperature uncertainties (thermal lag, etc.) are minimised for a change from one iso-thermal temperature to another [20] – a complete run – and we used this approach in work on indium [21] to obtain a $\Delta_{fus}h$ that has since been shown to be 2% high [22]. Reexamination of our data shows that the discrepancies can be traced to the start-up and end periods, when going from isothermal to scanning modes or vice versa. When these are ignored and, instead, data taken from steady-state scanning regions, results are in good agreement with more recent values. There are unusual DSC power requirements in the start-up and end regions and the experience with indium has led us to concentrate on enthalpy changes between one

dynamic temperature and another $(T_1 \rightarrow T_2)$. Of course, the 'end' region has already been proposed (see above) as the source of a thermal lag term but the errors implied by the indium results have a negligible (ca. ± 0.02 K) effect on δT.

When there is any kind of thermal event between T_1 and T_2, the enthalpy of fusion, transition, reaction (or whatever) is included in the overall enthalpy change $h_b(T_2) - h_a(T_1)$, where subscripts 'a' and 'b' refer to the initial and final states. The usual practice is to ignore the 'empty' curve and extract the heat of fusion (say) directly by drawing some baseline to the melting curve. The major problem is to define an area that is thermodynamically meaningful. The normal proce-dure is to join two temperatures (on either side of the event) that are chosen for purely cosmetic reasons – so that the baseline merges smoothly with the DSC curve at T_1 and T_2. The baseline may have to span many tens of degrees, as in the melting of a polymer or an alloy, so to what temperature does the resultant quantity $(\Delta_{fus}h')$ refer? The disquieting answer is that $\Delta_{fus}h'$ is related to no particular temperature and has *no* direct thermodynamic significance: those who query the quantitative value of DSC rightly emphasise this problem. An examination of the literature for, say, adiabatic calorimetry shows that the derivation of $\Delta_{fus}h$ from the raw calorimetric data requires some effort – c_p and $\Delta_{fus}h$ contributions to the overall enthalpy change are intimately linked and care is needed to separate them [23].

The procedures that must be used (and are discussed below) are simple and give well-defined quantities. In fact, although, as already seen, temperatures must be approached with caution, *less* care is needed to obtain enthalpy data. This statement, the reverse of conventional thinking, becomes increasingly true as modern methods of data treatment supersede chart recorders and, particularly important, the thinking associated with them. Enthalpies (i.e. areas) were considered 'difficult' because they had to be measured by planimetry or 'cutting and weighing' which were time-consuming and added an additional uncertainty of at least $\pm 2\%$ to the actual experimental error. With personal computers this area measurement error is essentially eliminated and there is little prac-tical distinction between determining the corrected temperature of a point on a DSC curve and some area, however defined, beneath such a curve.

Table 1
Enthalpy changes $h(T_2) - h(T_1)$ (in J g^{-1}, T in K) for various heating rates β

$\beta/(\text{K min}^{-1})$	Mercury (NIST) (melt)		o-Terphenyl (ICTAC) (melt)		KClO$_4$ (ICTAC) (solid/solid)	
	$T_1=230$;	$T_2=245$;	$T_1=320$;	$T_2=340$;	$T_1=570$;	$T_2=585$;
2.5	13.64		104.4		118.7	
5	13.63		104.9		119.6	
10	13.62		104.8		119.5	

4.1. Enthalpy changes

Although the appearance of a DSC melting curve is very much a function of experimental conditions, the total specific enthalpy change, $hl(T_2) - h_s(T_1)$, through the melting region should be constant if the instrument is behaving as a calorimeter – and if T_1 and T_2 are chosen to be in thermally inert regions, respectively, below and above the melting region (subscript s = solid, l = liquid). Some enthalpy changes for different materials and transitions are given as functions of heating rate in Table 1. They are based on c_p vs. T curves (discussed later, the implicit baseline is the line $c_p = 0$). It is clear from Table 1 that overall enthalpy changes are independent of heating rate, separate experiments demonstrate that they are also unaffected by sample mass. These results show that the DSC is at least formally behaving as a calorimeter and it is realistic to proceed further and resolve the overall enthalpy change into specific heat and $\Delta_{fus}h$ terms – either of which (but traditionally the latter) can then be compared with literature values to give a quantitative description of the calorimetric performance of a DSC.

Calorimeters can only supply (or remove) heat. They are unable to differentiate between a requirement that involves heat capacity alone ($c_p\Delta T$ for a temperature increment ΔT) or one that needs the additional energy, $\Delta_x h(T)$, associated with a phase change or reaction, although an examination of the overall curve often allows a distinction to be made. The heat of fusion, reaction, etc. at any temperature T is defined as:

$$\Delta_x h(T) = h_b(T) - h_a(T) \tag{1}$$

where x refers to the transition from 'a' to 'b' which may be a physical or chemical 'event'. In the former case T will most often refer to a particular melting or transition temperature but data are sometimes needed at other temperatures – such as when comparing results within a homologous series or heats of crystallisation and subsequent fusion. The last two are often claimed to be equal with the equality being used to show the quantitative nature of the measurements. However, unless $\Delta c_p \equiv c_{pl} - c_{ps} = 0$, the two must differ, because of supercooling prior to solidification.

Table 1 demonstrated that enthalpy changes are readily obtained by DSC and Eq. (1) can be expressed in this form by

$$\Delta_x h(T) = [h_b(T_2) - h_a(T_1)] - [h_b(T_2) - h_b(T)] - [h_a(T) - h_a(T_1)] \tag{2}$$

$$= I - II - III \tag{2a}$$

I is equivalent to the quantity given in Table 1, II and II are obtained from the c_p vs. T curves for the high- and low-temperature states, respectively. They define the stepped baseline (with a step of Δc_p at T) that should be constructed on any DSC curve. Extrapolation into the peak area is required but for a physical change, with a specific value of T (= T_m, say) the predominant extrapolation is from high to low temperature – the temperature calibration has already fixed the 'onset' temperature as T_m or a close approximation thereto. The quantities I, II, III are shown in Fig. 5 from which it is clear that a full c_p vs. T curve is not required, the area differences can be defined from a single DSC curve. Discussion in terms of c_p, however, clearly indicates the principles behind the final geometric construction.

Normal DSC procedures do not use the discontinuous (at AB) baseline shown in Fig. 5 but a line that joins any two arbitrarily selected points in the low- and high-temperature regions. This is acceptable when $\Delta c_p \approx 0$ (AB) but not otherwise and it is instructive to examine the quantitative consequences.
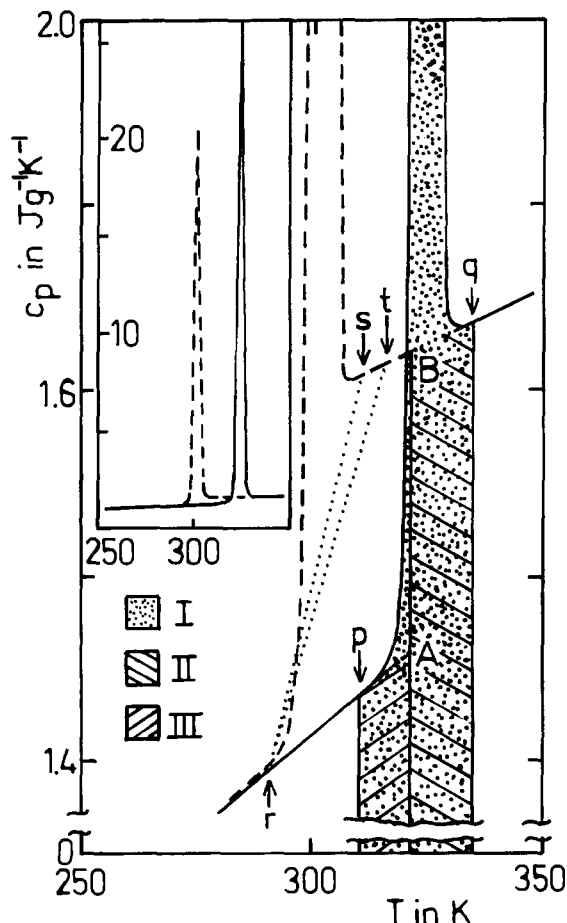
Fig. 5. The melting of two forms of benzophenone showing the complete curves (inset) and how the baselines (expanded scale) of Eqs. (2) and (2a) are defined for the stable phase (full curve): $T_1 = 310(\text{p})$, $T = T_\text{m} = 321.3(\text{AB})$, $T_2 = 335$ K(q). For the metastable phase (broken curve) two baselines IV (Eqs. (3) and (3a)) are drawn with $T_1 = 290(\text{r})$ and $T_2 = 310(\text{s})$ or 315 K(t).

The 'arbitrary' baseline joins points at T_1 and T_2, temperatures that are selected to ensure that all $\Delta_x h$ is

included (there is a natural tendency to err on the side of caution and make T_1 lower and T_2 higher than perhaps necessary to be certain of full integration). The measured quantity $\Delta_x h'$ (Fig. 5) is given by

$$\Delta_x h' = I - 0.5(T_2 - T_1)\{c_\text{pa}(T_1) + c_\text{pb}(T_2)\} \tag{3}$$

$$= I - IV \tag{3a}$$

where IV shows how the 'baseline' represents an average heat capacity. The differences between Eqs. (2) and (3) are best illustrated by a real example. Benzophenone (Fig. 5, Table 2) exists in (at least) two forms. Crystallisation from the melt (after supercooling some 50–60 K) gives a metastable structure that can be melted directly or annealed to the more stable form; the two, and the liquid, have heat capacities given by

$$\text{stable } c_\text{p} = -0.0101 + 0.004127T$$
$$\text{J g}^{-1}\text{K}^{-1}, \ T \text{ in K} \tag{4}$$

$$\text{metastable} = 0.0364 + 0.003942T \tag{5}$$

$$\text{liquid} = 0.8666 + 0.002426T \tag{6}$$

Enthalpy changes (I) are 124.7 (315 → 330 K, stable) and 102.2 J g^{-1} (295 → 310 K, metastable) and terms II and III may be calculated from Eqs. (4) and (6) or Eq. (5). $\Delta_\text{fus}h'$ depends on the values chosen for T_1 and T_2 and some effects are shown in Table 2(a) and (b). There are systematic changes in $\Delta_\text{fus}h'$ that cannot be dismissed as trivial. No 'best' values of T_1 and T_2 can be recommended because the procedure is simply wrong. At times errors may, fortuitously, cancel but it is clear from Table 2 (and Fig. 5) that high values of T_2 inevitably give large $\Delta_\text{fus}h'$. High T_2 (long baselines) are needed for high heating rates and/or sample masses and systematic work gives an apparent dependence of $\Delta_\text{fus}h'$ on these parameters. These remarks

Table 2
Baseline dependence of the apparent heats of fusion ($\Delta_\text{fus}h'$, in J g^{-1}) for two forms of benzophenone

(a) Stable				(b) Metastable			
($T_\text{m} = 321.3$ K, $\Delta_\text{fus}h(T_\text{m}) = 102.1$ J g^{-1})				($T_\text{m} = 298.6$ K, $\Delta_\text{fus}h(T_\text{m}) = 79.6$ J g^{-1})			
T_1	$T_2 = 330$	$T_2 = 335$	$T_2 = 340$	T_1	$T_2 = 310$	$T_2 = 315$	$T_2 = 320$
305	100.9	101.8	102.7	285	79.3	80.2	81.2
31	101.7	102.6	103.5	290	80.3	81.2	82.2
315	102.5	103.3	104.2	295	81.4	82.4	83.4

are valid when $\Delta c_p > 0$ but, although probably the most general case, there are many examples when the converse applies. The resultant confusion does not advance the reputation of DSC as a calorimetric technique. It is – and can – so easily be used as one! Extrapolation of low- and high-temperature baselines to T_m is a trivial operation for the computing aids that have so transformed modern scanning calorimetry (although we should not forget that the calorimeters themselves are little changed). It is not the fault of the 'instrumentation' but of ourselves for leading it astray with incorrect programs!

The examples of Table 2 are fairly typical of an organic material for which it might be claimed that an uncertainty of ±2% is acceptable. It must be emphasised that the changes shown in Table 2 represent self-inflicted errors, unrelated to instrumental performance. They are magnified as Δc_p increases and $\Delta_x h$ decreases. We are fortunate that Δc_p is negligible for indium so that this popular calibrant does not contribute to this source of uncertainty – but not all reference materials are so well-behaved. In any case, in the real world we are interested in a whole range of materials for which Δc_p may even change sign or the step height may be a significant fraction of the peak height: the transitions in rubidium nitrate (Fig. 6), for example, require great care in their analysis, linear baselines can grossly distort the enthalpies for liquid crystal transitions [24]. There is no need to degrade instrumental performance by faulty data treatment – nor is the thermal-analysis community helped in its efforts to associate itself with the final letter of its global organisation ICTAC.

There can be times when it is unclear how an extrapolation should be made – it may be difficult to decide if c_p curvature is due to 'premelting' (or some equivalent phenomenon) or is an inherent material property. This is a problem that is not unique to DSC but one that is met with in most forms of calorimetry (again, modulated DSC offers exciting possibilities for the resolution of overlapping events). Earlier work [25] showed that the transition temperature (942 K) of ICTAC potassium chromate could be determined to a few tenths of a degree using both heat flux and power compensation DSC. $\Delta_{trans}h$ for this compound presents some problems because there is curvature in the low-temperature heat capacity (Fig. 7). The enthalpy change over the transition range
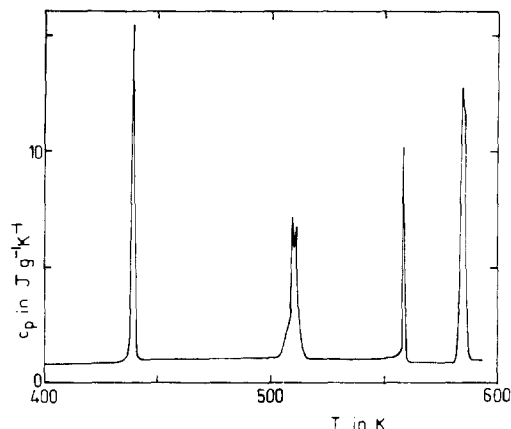

Fig. 6. Phase changes in rubidium nitrate showing Δc_p of both signs.

shows excellent reproducibility for this high temperature (e.g. $h(960) - h(930) = 73.2 \pm 1.3$ J g^{-1} from 11 runs using a range of heating and cooling rates and sample sizes). This gives $\Delta_{trans}h(942) = 39$ J g^{-1} using a linear low temperature (to 910 K) baseline but this can be decreased to < 37 J g^{-1} [26] by reducing the pretransitional region. The problem is one of material science rather than calorimetry. Calorimetrists must explain their procedures so that, as our structural knowledge improves, calculations may be modified to partition gross enthalpy changes between competing phenomena. Even data derived using conventional linear baselines could be given meaning at some future date if T_1 and T_2 are also quoted so that, when the relevant c_p data become known, $\Delta_x h'$ can be transformed to I (Eq. (3)) and even $\Delta_x h$ (Eq. (2)).

4.2. Specific heat capacity

This basic application of DSC was first suggested by Wunderlich as long ago as 1965 [27] – would that it were more widely used! As it is, and mainly due to Wunderlich [28], our knowledge of the thermodynamic properties of polymers, some quite exotic, is better than that for many far simpler compounds. There is much DSC information for the latter but, unfortunately, of dubious value. The emphasis tends to be on 'events' – often misinterpreted as discussed above – when a few additional measurements would have given fundamental data, including the 'events', covering a wide range of temperature.
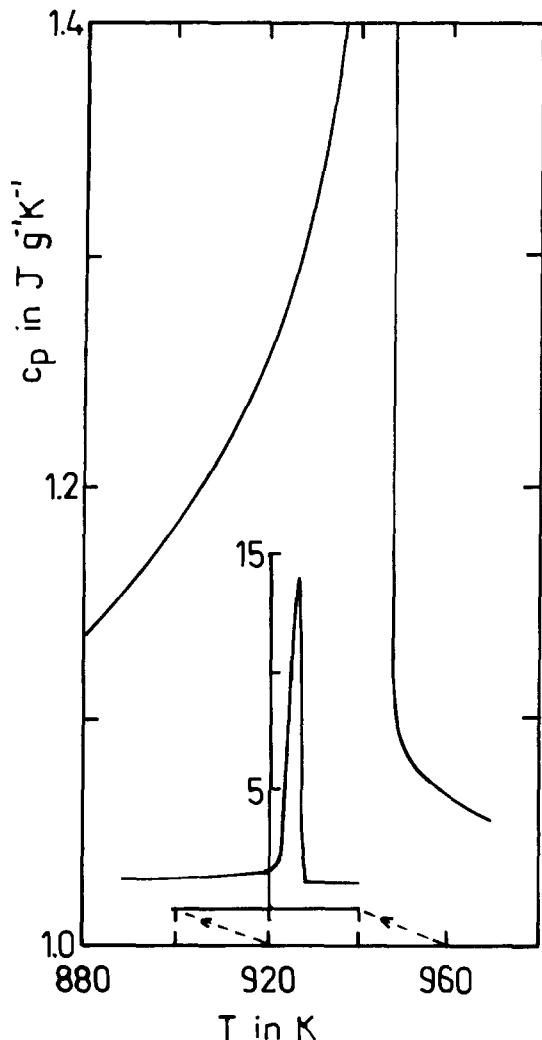
Fig. 7. The 942 K solid/solid transition for potassium chromate. Although the overall enthalpy change is very reproducible, $\Delta_{trans}h$ is extremely sensitive (see text) to the chosen baseline.

Whenever possible, all our DSC work is made in the c_p mode of operation [29]. This means that, in principle, there is no need for area calibration – the ordinate is calibrated as c_p (Figs. 1, 5–7) with respect to the reference material used (normally alumina, synthetic sapphire).'In principle' should be emphasised because a distinction between the results for heat-flow rate and area calibrations has been made [30]. Our experience has been that practical differences are small, at least for the power compensation DSC used. Based on the alumina calibrant we have

reproduced, to within 1%, $\Delta_{fus}h$ for all the organic and metallic reference materials supplied by the UK Laboratory of the Government Chemist[31]. The two curves of Fig. 1, for example, used LGC indium and $\Delta_{fus}h = 28.68(2.5)$ and 28.59 (20 K min^{-1}) J g^{-1} (LGC certificate value [22] 28.71 J g^{-1}).

This type of calibration routinely gives ordinate-to-c_p conversion factors (F) for a wide range of instrumental conditions – heating/cooling rates, temperatures (both sample and ambient) – all of which influence F in some way. Changes are not large, a few per cent from one extreme to another [29], but they must be recognised for the most precise work. They emphasise the dangers of mixing measurements that have been made under different conditions.

4.3. Consistency tests

Confidence in any technique is always enhanced if different procedures can be shown to give similar results. In Table 1 enthalpy changes were seen to be independent of heating rate and several other examples, of varying sophistication, can be given.

The simplest quantity is c_p itself in a region that is thermally inert – free from transitions and/or reactions. Again, this should be independent of sample mass, rate (whether heating (+) or cooling (−)) and, as implied in the previous section, experimental conditions. Results were given in Ref. [29] to illustrate these points: even though the c_p conversion factor F varied as mentioned in Section 4.2, the final c_p was essentially independent of experimental parameters for a wide range of materials. This certainly raises confidence in the quantitative validity of the experimental and computational procedures used.

The calculation of $\Delta_{fus}h$ requires a clear definition of the liquid heat capacity (leading to II in Eq. (2a)). Some values, determined at rates of ± 10 K min^{-1}, for a molten aluminium/7% silicon alloy are $1.183(+)/1.175(−)$ at 900 and $1.175(+)/1.157(−)$ J g^{-1} K^{-1} at 960 K. This is excellent agreement for measurements near the upper limit (1000 K) of power compensation DSC (and confirms the observation [32] that many molten metals and alloys have a negative value of dc_p/dT in the vicinity of T_m). Other examples have been given showing that c_p is independent of β and
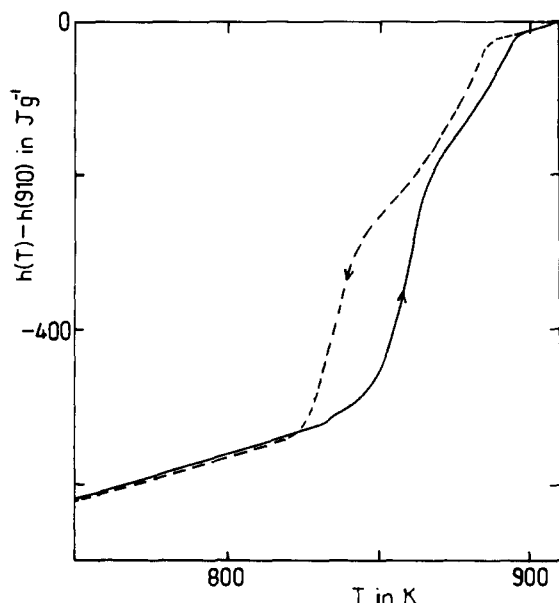
Fig. 8. Enthalpy changes in an aluminium/7% silicon alloy (± 10 K min^{-1}). The greatest change is at the eutectic temperature, both this and the liquidus temperature show some degree of supercooling.

of sample mass [33,34]. It must be emphasised that successful results always depend on intelligent use of equipment so that extremes of mass and/or rate (leading to problems caused by small signals or excessive thermal lag) cannot be expected to give c_p data comparable with results obtained under better conditions – say half full pans and rates of 5–20 K min^{-1}.

A natural progression is to combine enthalpy changes in cooling and subsequent heating modes to investigate the closure (or otherwise!) of the enthalpy cycle liquid(T_2) $\rightarrow$ solid(T_1) $\rightarrow$ liquid(T_2). The cycle should go from liquid to liquid because this is thermodynamically well-defined, any solid can anneal and an 'as received' material may be in an ill-defined state. The minimum temperature T_1 must be such that the solid is stable (no isothermal drift) on at least the time scale needed to equilibrate after cooling and prepare for the subsequent heating. Enthalpy changes for the alloy described above (liquidus temperature 887 K), and shown in Fig. 8, are 626(−)/621(+) J g^{-1} (750–910 K) showing that the enthalpy cycle is effectively closed. The dangers of using an uncharacterised solid state are revealed when the alloy is allowed to cool to ambient temperature between measurements – the enthalpy change on heating rises to 640 J g^{-1} after low temperature annealing. Closed enthalpy cycles (and, by implication, calorimetric performance) have been reported for polymers [9,15] and low-molar-mass organic compounds [24].

5. Quantitative differential scanning calorimetry

This paper has shown that, although DSC is only a relative, rather than abslute, method, when correctly calibrated it is possible to obtain results of calorimetric significance. With little effort c_p data can be determined with an accuracy of $\pm (1–2)\%$ as judged by measurements on materials of known c_p. Precise c_p data are rare and DSC could greatly enlarge our background knowledge of this fundamental quantity. Although calorimetric 'events' may be perturbed by instrumental limitations so that melting *appears* to extend over many degrees (Fig. 1), overall enthalpy changes are unaffected and $\Delta_{fus}h$ is readily derived. In fact, with some effort a melting curve can be 'desmeared' [35] to give a good approximation to a more realistic enthalpy/temperature distribution. Generally, however, sufficiently precise information can be derived from the initial 'c_p' curve. Other thermodynamic functions follow in the usual way, the entropy of fusion [24], $\Delta_{fus}h/T_m$ ($\beta = 0$), neglects premelting effects but these are usually less than experimental errors. At present, minimum DSC temperatures are far from zero (100 K is generally given but 150 K is probably more realistic for accurate work) so that only entropy changes can be derived. These, however, still lead to free energy changes relative to some reference state – say the supercooled liquid – so that the true thermodynamic stability of polymorphs can be determined [24].

The transition of DSC from a qualitative 'pictorial' technique to a precise thermodynamic method can be considered to be complete when free energies become available. The route is not unduly arduous and, although greater effort is certainly needed, the addition to our knowledge of material properties more than compensates for this – consider how much more basic information we should have if even only 10% of DSC work had produced truly quantitative data!

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