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FREE ENERGY CHANGES BY DIFFERENTIAL SCANNING CALORIMETRY: APPLICATION TO A LOW ENERGY BUT METASTABLE FORM OF *p*-NITROTOLUENE

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ABSTRACT

With decreasing sample size, a metastable form of *p*-nitrotoluene persists for increasing periods; for weights of 1 mg or less this form effectively supersedes the stable structure. It is unusual in having a lower enthalpy than the latter but this is offset by a lower melting point and the free energy is indeed greater than that of the stable form.

INTRODUCTION

Recent improvements in the quantitative performance of DSC and DTA instruments are such that meaningful results can now be obtained on sub-milligram quantities of materials and the purpose of this paper is to draw attention to the unusual polymorphs which can arise when such small samples are used. Anomalous phase behaviour first became apparent during a DSC investigation of the heat of fusion of *p*-nitrotoluene, the original aim of which was a comparison within this laboratory of DSC and adiabatic calorimetry. An "in house" comparison is essential because published data, even for pure metals, show variations of several percent[1].

Comparative DSC and adiabatic calorimetry results for *p*-nitrotoluene are briefly given here but the main emphasis is on the unusual phase behaviour. This is so pronounced that, for sufficiently small samples, a metastable state effectively replaces the normal form. The latter can be identified by its lower free energy but this can only be considered after a discussion of the seemingly contradictory requirement of dynamic calorimetry (a finite heating rate) and reversible thermodynamics (equilibrium conditions).

EXPERIMENTAL

p-Nitrotoluene was zone refined and had an estimated purity of 99.9 %. Measurements were made in a Perkin Elmer DSC 2 using sealed sample pans. Quantitative operation of the DSC has already been described[2, 3]. Only relevant details will be emphasised here. Isothermal temperatures were calibrated using a slow stepwise melting procedure[2]; calibrants were a variety of materials, the melting points of which had been determined in this laboratory using platinum resistance thermometry. Thermal lag was calculated from individual DSC curves[4]. The lag correction so obtained is valid for "steady state" conditions but in a melting region there is a perturbation in the linear heating rate because instrumentation is such that the momentary, near-infinite amount of power needed to suddenly melt a pure material is spread out over a finite time. Thus, although it *appears* (curve 1, Fig. 1) that the sample has superheated, this is really a manifestation of the nonlinear heating rate in the melting region. The effect can be minimised by using smaller samples and/or heating rates (curve 1a, Fig. 1).

The power (ordinate) scale was calibrated using synthetic sapphire as a reference material.

The ultimate product of a quantitative DSC experiment is the heat capacity as a function of temperature (Fig. 1). This can be obtained in either a heating or a cooling experiment and data treatment is such that equilibrium values are obtained under steady state conditions (i.e. "heating" and "cooling" values superimpose in the absence of "thermal events") but transition temperatures *appear* high on heating (the instrumental effect mentioned above) or *are* low on cooling (a true supercooling effect in the material itself). With modern computational techniques, the specific heat–temperature data can be manipulated to produce enthalpy and entropy changes but the latter will be in error as considered in more detail later.

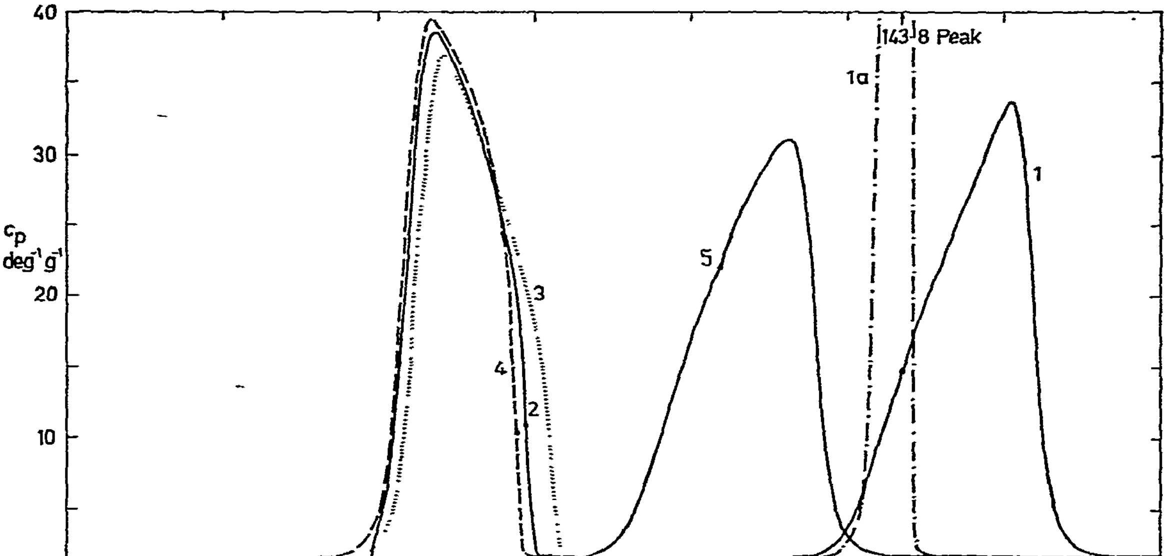

Fig. 1. Heat capacity curves (1–5) for 15.38 mg *p*-nitrotoluene obtained at + or − 5 K min^{-1} (arrows indicate heating or cooling). Curve 1a is for 1.83 mg heated at 2.5 K min^{-1}.

RESULTS

Phase behaviour

Figure 1 shows how heat capacity curves reflect the phase behaviour of *p*-nitrotoluene. For consistency, all curves (1a excepted) refer to a given sample (15 mg) and heating or cooling rate (+ or -5 K min^{-1}). 15 mg is unusually large for a heat of fusion determination and smaller samples and/or slower temperature changes give sharper and more elegant curves (1a, Fig. 1). No smaller sample, however, revealed the variety of effects so clearly. Normal melting behaviour is shown by curve 1 and if melting is carried out using the stepwise technique[2] the equilibrium value, 324.7 ± 0.1 K, agrees exactly with reported values[5]. The melt supercools to 315 K and subsequent crystallisation (curve 2) is unexceptional until near the end when a small endotherm is observed[*]. Remelting follows curve 1 exactly but subsequent cooling is less reproducible especially with regard to the endotherm which is well resolved in 3 but does not appear in 4. In the last case, remelting, curve 5, shows that the product of crystallisation melts several degrees (318.5 K on stepwise melting) below that of the normal material. At this point, it should be emphasised that whilst curves 1–5 in Fig. 1 were being produced, the sample remained undisturbed and the only alterations to the DSC settings were those required for cycling from 300 → 340 → 300 K. Residence times at the maximum and minimum temperature were always the same so that nucleation conditions were kept constant. In spite of these precautions, it is clear that crystallisation is a relatively random process when compared with melting. (For this sample, and on the scale of Figure 1, all melting curves exactly superimpose on either 1 or 5.) This randomness characterises the crystallisation behaviour of *p*-nitrotoluene although certain trends can be identified. With small samples (up to, say, 2 mg) the endotherm is generally absent and the product melts at the lower temperature (318.5 K). The converse usually holds when the mass is greater than 10 mg, with the endotherm appearing as an appendage to the much larger exotherm as in curve 2, Fig. 1 (although here 3 and 4 emphasise that this is only a generalisation, not a rule). Irrespective of the behaviour of a given sample, it is clear that the initial product of crystallisation is the 318.5 K melting form and conversion of this to the more normal, higher melting material only occurs after a small *uptake* of energy. This can occur at a variety of temperatures and Fig. 2 shows examples that are well below those of Fig. 1. The heating curve for the 2.87 mg sample (broken lines) was obtained by stopping cooling at 288 K (i.e. before the onset of the transition on cooling alone) and reheating. The larger sample (full line, Fig. 2) was unique among those of > 10 mg in remaining untransformed to such low temperatures. Irrespective of the detailed geometry of the transition it will be seen later (Fig. 5) that transition enthalpies are smooth functions of temperature showing

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[*] In a "cooling" experiment, both sample and calibrant show "negative" power requirements. The overall result is a positive heat capacity for the exotherms (crystallisation) of curves 2–4. The opposite sign of the minor peak indicates an endotherm.

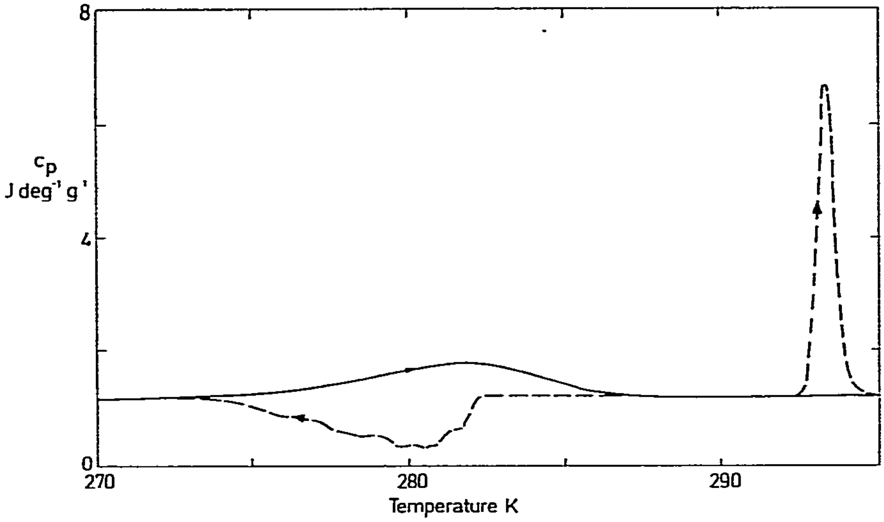

Fig. 2. The metastable → stable transition at relatively low temperatures. Broken line: 2.87 mg at + or − 5 K min^{-1} (arrows indicate heating or cooling). Full line: 17.65 mg after quenching from melt into liquid nitrogen and heating at 20 K min^{-1}.

that a given phase refers to a thermodynamically well-defined form. In only one out of some ten independent samples examined was multiple melting found and this was attributable to the sample pan configuration which allowed material to segregate into two distinct regions.

Heat capacities

The coarse ordinate scales of Figs. 1 and 2 conceal significant differences between the heat capacities of the two solid phases (designated u or s for untransformed (metastable) or stable, respectively). Relevant data from Fig. 1 are therefore shown in more detail in Fig. 3. The direction of the arrows indicates heating or cooling experiments and these are in good agreement. All curves (e.g. those giving Fig. 2) show that the difference $C_{pu} - C_{ps}$ is independent of temperature and about equal to 0.04 J deg^{-1} g^{-1}. A more accurate value, 0.048 J deg^{-1} g^{-1}, has been obtained from the slope of the enthalpy of transition–temperature curve (see Fig. 5) and this figure has been used [eqn. (2)] to calculate C_{pu} from C_{ps} rather than using the relatively sparse C_{pu} data alone. The information available for C_p (solid) is heavily biased towards C_{ps} as this is favoured (see above) by large samples (the DSC signal is directly related to sample mass) whereas for *systematic* work on C_{pu}, samples must be reduced to about 1 mg. All data for C_{ps} are given to better than ±1% by

$$C_{ps} = 0.132 + 3.77 \times 10^{-3} T \text{ J deg}^{-1} \text{ g}^{-1} \qquad (270 < T < 318 \text{ K}) \qquad (1)$$

whence

$$C_{pu} = 0.180 + 3.77 \times 10^{-3} T \text{ J deg}^{-1} \text{ g}^{-1} \qquad (270 < T < 314 \text{ K}) \qquad (2)$$

Data for the liquid, for which heating and cooling curves are again indistinguishable, are given by

$$C_{pl} = 0.964 + 2.00 \times 10^{-3} T \text{ J deg}^{-1} \text{ g}^{-1} \qquad (315 < T < 340) \qquad (3)$$

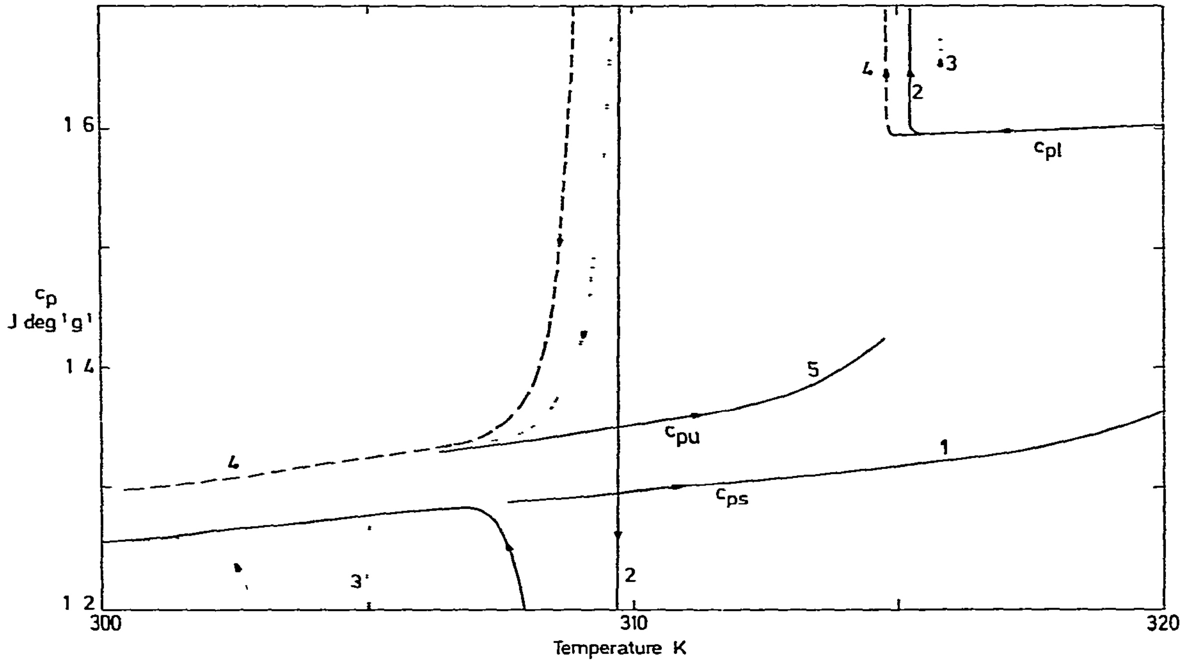

Fig. 3. As Fig. 1 but showing the heat capacity difference between the stable (C_{ps}) and metastable (C_{pu}) forms

Temperature limits refer to the range over which measurements were made. The upper limits for (1) and (2) indicate (Fig. 3) that premelting was observable above these temperatures. Specific runs can be represented by linear temperature equations to within a few tenths of one per cent. The figure of $\pm 1\%$ refers to the overall reproducibility of the DSC results but, as the instrument is directly calibrated, this should also give an idea of the overall accuracy. This can be confirmed by comparison with results from these laboratories[6] using adiabatic calorimetry. The latter gives slightly lower values for both C_{ps} (0.5%) and C_{pl} (1.1%, 325 K; 0.7%, 340 K) when compared with (1) and (3), respectively (the metastable phase does not appear when tens of grams are used, as in adiabatic calorimetry).

Heats of fusion and transition

A major benefit of computerised treatment of DSC data is the ease with which the heat capacity, the normal end product, can be transformed into other thermodynamic functions. Although the resultant entropy changes, say, must be hedged with qualifications (see Discussion), enthalpy (H) changes present no problems and if a convenient temperature in the liquid is used as a common reference state, differences between phases are readily seen. Figure 4 shows how the heat capacity curves of Fig. 1 transform to enthalpy curves with respect to H_l (340 K) $= 0$. Although the variables of a DSC experiment (sample mass and heating or cooling rate) affect the geometry and apparent location of the change from solid to liquid (or vice versa), enthalpy curves for solid and liquid represent equilibrium (or metastable) conditions. In particular, the vertical displacement gives the heat of fusion and the value at the

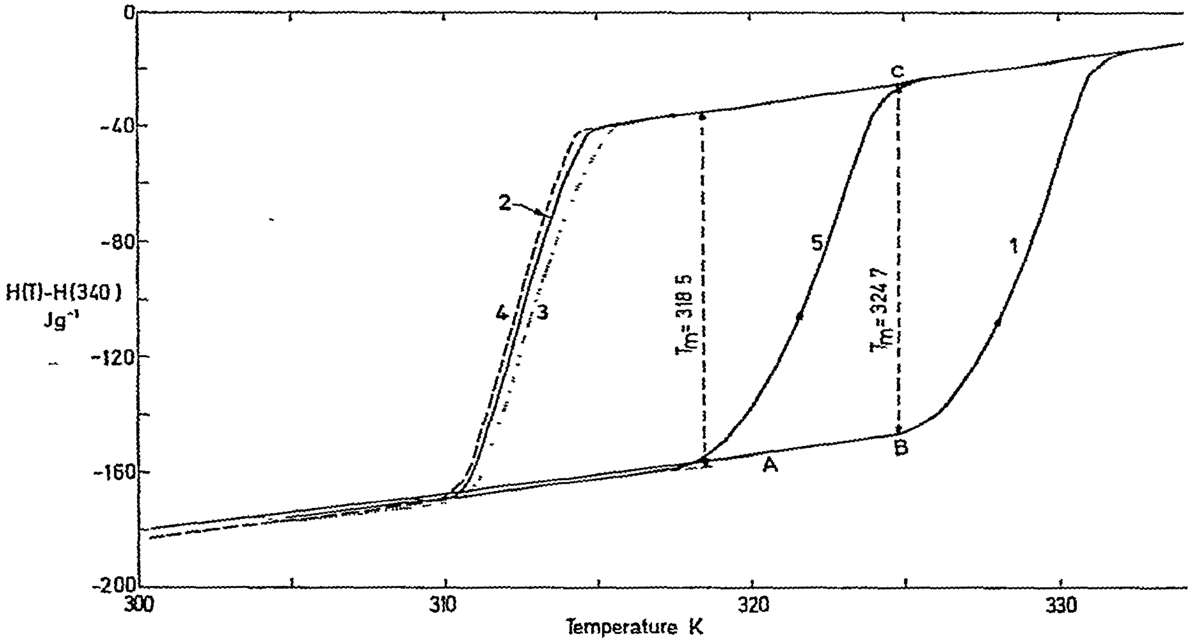

Fig. 4. Enthalpy changes with respect to H_l (340 K) = 0 derived from the heat capacity curves of Fig. 1.

melting point of the two forms under discussion here is indicated by the two vertical broken lines. These correspond to "ideal" behaviour in which both premelting (due to sample impurities, see 1 and 5 in Fig. 3) and apparent superheating (an instrumental artefact) are eliminated according to the equation

$$\Delta H(T_m) = H_l(T_m) - H_s(T_m) = [H_l(T_2) - H_s(T_1)] - [H_l(T_2) - H_l(T_m)] - [H_s(T_m) - H_s(T_1)] \quad (4)$$

Here T_2 is an arbitrary temperature (340 K in Fig. 4) in the liquid region and T_1 one below the onset of premelting (Fig. 3). With this definition, the first term in square brackets is an experimental quantity and the second and third, which follow from eqns. (3) and (1) [or (2)], respectively, extrapolate the *normal* liquid and solid behaviour to T_m. The heats of fusion of the two forms are

$\Delta H_u(T_m = 318.5 \text{ K}) = 123.3 \text{ J g}^{-1}$

$\Delta H_s(T_m = 324.7 \text{ K}) = 121.6 \text{ J g}^{-1}$

These are the means of 7 and 11 determinations, respectively, both of which show standard deviations of 0.9 J g^{-1}. Agreement with the adiabatic value[6] of ΔH_s, 122.6 J g^{-1}, is satisfactory although it should be noted that the relative magnitude (adiabatic > DSC) is reversed with respect to the heat capacity results previously discussed. ΔH values are unusual in that the metastable form has the lower energy and transition to the stable structure calls for an uptake of energy. This effect is emphasised when the comparison is made at the same temperature; because $\Delta C_p = C_{pl} - C_{ps} \neq 0$, ΔH_s (318.5 K) must be reduced by $6.2\Delta C_p = 1.6$ J g^{-1} with respect to ΔH (324.7 K) to give an apparent energy difference of 3.3 J g^{-1} at the melting point of the metastable form. As this figure is a small difference between two large

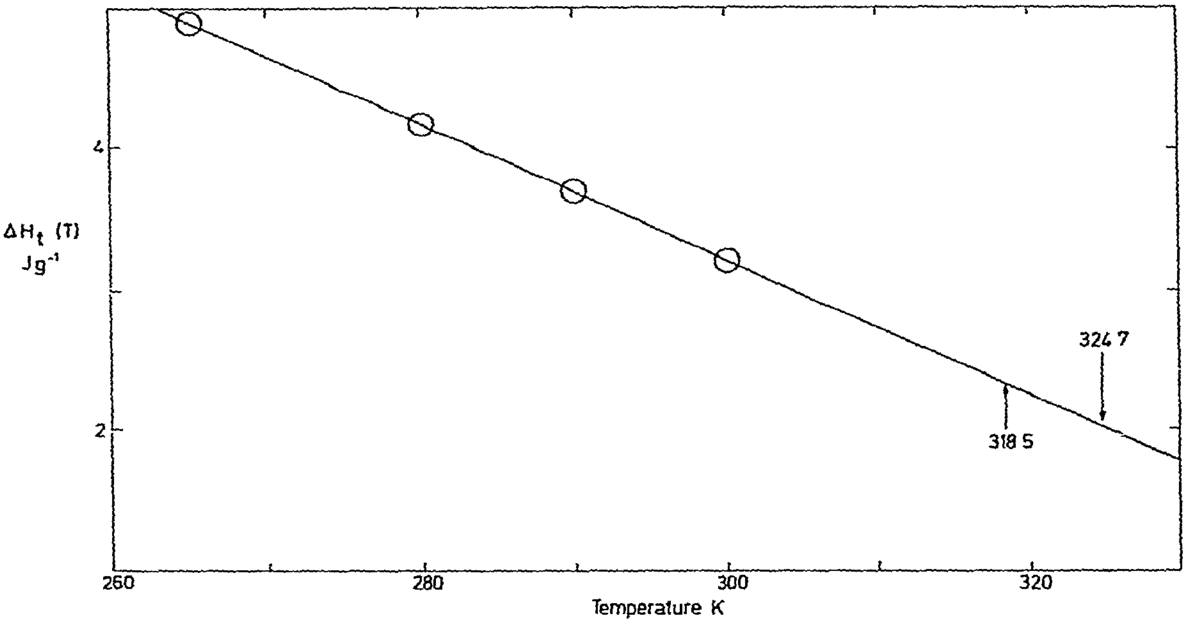

Fig. 5. The enthalpy of transition $\Delta H_t = H_s - H_u$ as a function of temperature.

quantities, it must be considered to be of limited accuracy. A better method is to use the directly observed enthalpy change through the transition region $H_s(T_4) - H_u(T_3)$ (the observed transition temperature is assumed to lie between T_3 and T_4). This is available over a wide range of temperature (see Figs. 1 and 2) and the isothermal enthalpy of transition ΔH_t is obtained as

$$\Delta H_t(T_3) = H_s(T_3) - H_u(T_3) = [H_s(T_4) - H_u(T_3)] - [H_s(T_4) - H_s(T_3)] \quad (5)$$

The second square bracketed term is given by (1). Figure 5 shows that there is an excellent linear relationship between ΔH_t and temperature over a wide range of temperature so the extrapolation to 318.5 (2.3 J g^{-1}) or 324.7 K (2.0 J g^{-1}) can be made with some confidence. At the same time, the slope of the curve, 0.048 J deg^{-1} g^{-1}, gives $C_{pu} - C_{ps}$ directly and this value has been used to generate (2) from (1).

DISCUSSION

It is now commonplace to use thermal methods (DTA, DSC) for the determination of heats of fusion or transition, but the physical significance of the quantity thus obtained is rarely considered. The basic operation is the transformation of an area into an enthalpy using calibration factors that have been determined in independent experiments. This paper may be considered to describe one such "independent experiment" and as some of the problems encountered are of a general nature, these will be discussed before those that are peculiar to *p*-nitrotoluene.

The major problem lies in defining the "area" portion of the area-to-enthalpy conversion factor. The heat of fusion is an isothermal quantity whereas any area in Fig. 1, for example, naturally covers a range of temperature. Figure 1 is unusual for a DSC or DTA curve in that the ordinate scale shows absolute values so that the *total* enthalpy change from solid to liquid (say from 320 to 335 K for curve 1) is easily defined. The simplest method for the subsequent decomposition of this quantity into heat capacity (solid and liquid) and isothermal heat of fusion terms is probably that exemplified by eqn. (4). This procedure does not call for any base line to curve 1 (in effect it uses $C_p = 0$) as is essential in the normal DSC/DTA method of comparing two curves (sample and calibrant) which have a common ordinate scale but an unknown zero. Various base line constructions have been described[7, 8] but the only truly general procedure must be based on the thermodynamic considerations discussed above[2, 9]. This is especially relevant for cooling experiments where crystallisation can occur at temperatures far below the equilibrium melting value and it is essential to recognise that the "area" thus measured refers to a heat of crystallisation that *must* (because $\Delta C_p = C_{pl} - C_{ps} \neq 0$, generally $C_{pl} > C_{ps}$), be lower than the equilibrium value. Another area in which difficulties can be encountered concerns the melting of polymers, a process which may occur over many tens of degrees; only enthalpy curves permit an unambiguous assignment of the heat of fusion at a given temperature.

We turn now to polymorphism, which is of immediate relevance to *p*-nitrotoluene but which may prove to be a more widespread phenomenon. "Metastable" and "stable" have been applied to the two forms on the basis of the apparent irreversibility of the metastable → stable transition and the higher melting point of the latter form. Against this must be set the lower energy of the metastable modification. The only true measure of stability is on the basis of the form with the lower Gibbs free energy (G). This demands equilibrium entropy (S) changes, a requirement that conflicts with the need, in dynamic calorimetry, for finite heating rates. The problem is easily seen by reference to Fig. 4; in an ideal experiment, curve 1 would follow ABCD and entropy changes could be calculated from

$$\delta S_s = S_l(T_2) - S_s(T_1) = \int_{T_1}^{T_m} C_{ps} \, \mathrm{dln}\, T + \Delta H(T_m)/T_m + \int_{T_m}^{T_2} C_{pl} \, \mathrm{dln}\, T \tag{6}$$

(symbols Δ and δ refer to isothermal and variable temperature processes, respectively). The C_p curves of Fig. 1 are made up of "point" values at intervals of a few tenths of a degree; the entropy increment corresponding to each "point" is $\bar{C}_p \Delta T/\bar{T}$ where $\Delta T = T_j - T_i$ and $\bar{C}_p$ and $\bar{T}$ are mean values over the range $T_i \rightarrow T_j$. Summation from T_1 to T_2 gives an *apparent* entropy change δS_{sa} and this is always $< \delta S_s$; similarly, $\delta S_{ua} < \delta S_u$.

In the present context, we require reversible entropy changes which are related to δS_{sa} and δS_{ua} by $\delta S_s = \delta S_{sa} + Z_s$ and $\delta S_u + Z_u$ where the terms in Z refer to errors due to the apparent superheating. As curves 1 and 5 of Fig. 4 can be superimposed rather well, it is reasonable to assume that $Z_s \sim Z_u$; if the approximation is exact $\Delta G(T_1)$ is unaffected by terms in Z [eqn. (9)] and some idea of the validity of the approximation can be obtained by comparison with data obtained assuming the ideal curve ABCD as well as noting any effects of heating rate and sample mass. Because all experimental quantities must be measured relative to some reference temperature (T_2) in the liquid, $\Delta G(T_1)$ must be expressed as

$$\Delta G(T_1) = [G_1(T_2) - G_u(T_1)] - [G_1(T_2) - G_s(T_1)] \qquad (7)$$

and is follows from the definition $G = H - TS$ that the first term

$$G_1(T_2) - G_u(T_1) = H_1(T_2) - H_u(T_1) - T_1\delta S - \delta T S_1(T_2) \qquad (8)$$

where $\delta S_u = S_1(T_2) - S_u(T_1)$ and $\delta T = T_2 - T_1$. As $S_1(T_2)$ is common to both phases, the final expression becomes

$$\Delta G(T_1) = [H_1(T_2) - H_u(T_1)] - [H_1(T_2) - H_s(T_1)] - T_1[\delta S_u - \delta S_s] \qquad (9)$$

Direct experimental results are shown in Fig. 6 which gives both ΔG and ΔH. The latter is the difference given by the first two square-bracketed terms of eqn. (9) and is a well-defined thermodynamic quantity as shown by the good agreement between results in the two "horizontal" regions where ΔH (<317 K) = 2–3 J g^{-1} or ΔH (321 → 324 K) = $-$(121–122) J g^{-1}. Although the phase changes appear to take very different thermal paths, the final effect on the overall entropy *difference* is very similar as shown by the near coincidence of ΔG values at temperatures below about 318 K. If "ideal" entropy changes are calculated according to eqn. (6), ΔG(316 K) decreases by 5% to 2.42 J g^{-1} (Fig. 6). Because of premelting, the equilibrium course of the enthalpy–temperature curve will not exactly follow the path ABC (Fig. 4) and in this sense, even eqn. (6) does not represent equilibrium conditions. Compared,

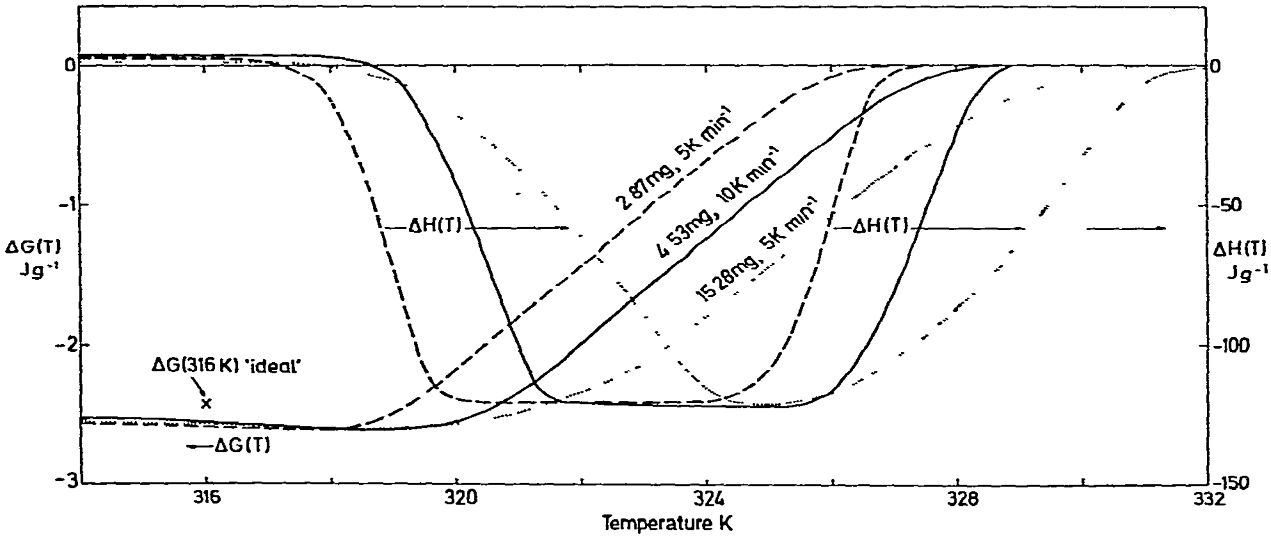

Fig. 6. Enthalpy ($X = H$) and free energy ($X = G$) differences $\Delta X(T) = X_s(T) - X_u(T)$ for several sample sizes and heating rates. The idealised value of ΔG (316 K), equivalent to all melting at T_m, is shown.

however, with the "superheating" effects under discussion here, the effect is trivial and we believe that 5% is a realistic estimate of the error in ΔG. This is a result of underestimating δS for either solid phase (by about 1% over the range 320–335 K) when using "observed" DSC C_p values, but it must be stressed that no attempt has been made here to minimise this error (relative stabilities only are sought) and it will be much reduced at the lowest heating rates which more closely approach reversible conditions. A full discussion of the errors that can arise in the calorimetric determination of entropy changes has been given by Goldstein[10]. For the present work, it is emphasised that "irreversibility" is an instrumental, rather than a material (annealing) effect.

Whatever the error in ΔG, there can be no doubt that $\Delta G = G_s - G_u < 0$ confirming the original assumption that the high melting, but high energy, modification is the stable form at room temperature. Because the enthalpy difference between the two forms increases with decreasing temperature (Fig. 5), ΔG slowly drops as the temperature is lowered but the effect is not large enough to define a temperature where the stabilities are reversed. In this respect, it should be emphasised that crystallisation is much affected by sample size and 2 mg of *p*-nitrotoluene only crystallise spontaneously below 300 K (compare the 315 K of Fig. 1). Future developments in thermal analysis will assuredly emphasise the trend to smaller sample sizes and it is possible that the polymorphism described in this paper may be more widespread than is currently appreciated. This is especially true of highly supercooled liquids when the relatively low temperatures involved may stabilise atypical structures. DSC investigations of potential calibrants should emphasise the widest possible range of sample sizes and geometries as well as instrumental parameters.

CONCLUSIONS

Specific heats and heats of fusion, determined to ±0.1% by adiabatic calorimetry, can be reproduced to ±1% by a DSC calibrated with synthetic sapphire provided that the thermodynamic significance of the ultimate DSC data is clearly recognised.

p-Nitrotoluene exhibits polymorphism, the metastable form being stabilised by smaller sample sizes. The free energy difference between the two forms can be found with an error of some 5% using relatively rapid (5–10 K min^{-1}) heating rates. With slower rates, DSC could become a powerful tool for the routine determination of free energy changes.

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