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Note

Sample temperature lag in quantitative DTA (Dupont DSC)*

J. M. BARTON
Materials Department, Royal Aircraft Establishment, Farnborough, Hampshire (England)
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The presence of interfaces and the use of samples of finite dimensions and low thermal conductivity leads to significant thermal gradients in quantitative DTA and DSC experiments. Richardson et al.[1, 2] have dealt with this problem and have shown how the sample temperature lag may be estimated for a DSC of the differential power type. The present paper shows how similar methods may be applied to a scanning calorimeter of the differential temperature type (DuPont DSC).

EXPERIMENTAL, RESULTS, AND DISCUSSION

The instrument used was the DuPont 990 thermal analyser/DSC cell, operating with a nitrogen atmosphere (20 cm^3 min^{-1}), and attached to a digital voltmeter/data transfer unit/paper tape punch for readout of time, temperature, and heat flow data.

At the end of a temperature scan the instrument switches into an isothermal ("hold") mode at a preselected limit temperature, T_L, but the temperature continues to rise at a decreasing rate to reach an equilibrium final temperature, T_F. At any instant the heat flow, dq/dt, is related to the sample heat capacity, C_p, and the heating rate, dT/dt, by

$$\frac{dq}{dt} = C_p \cdot \frac{dT}{dt} \tag{1}$$

In the temperature range T_L to T_F for an infinitesimal sample with no temperature lag and constant heat capacity, from eqn (1):

$$\Delta q = \int_{t_L}^{t_F} dq = C_p \int_{T_L}^{T_F} dT, \tag{2}$$

where t_F and t_L are the elapsed times corresponding to temperatures T_F and T_L. For

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a finite sample with a temperature lag, ΔT, between the sample and the "sample" thermocouple:

$$\Delta q = C_p \int_{T_L - \Delta T}^{T_F} dT = C_p(T_F - T_L + \Delta T) \quad (3)$$

$$\therefore \Delta T = (\Delta q / C_p) - T_F + T_L \quad (4)$$

Now Δq is obtained from the area, A, under the plot of heat flow against time, bounded by the extrapolation of the final equilibrium baseline and the vertical line at time t_L as in Fig. 1. The quantity $\Delta q = AF/M$, where F is the instrument calorimetric calibration factor and M the sample mass. To a good approximation $C_p = Y \cdot F/M \cdot \phi$, where Y is the height of the curve above the baseline at or just before t_L and ϕ is the heating rate, so that

$$\Delta T = (A \cdot \phi / Y) - T_F + T_L \quad (5)$$

When there is a significant temperature gradient in the sample, the estimated temperature lag, ΔT, will be an average value.

A 6.8 mg sample of pure indium (Perkin-Elmer melting point standard, T_m° = 156.6°C) with a flat profile, encapsulated in an aluminium pan, was scanned through the melting range at 2 K min^{-1} and the apparent T_m from intersection of the baseline

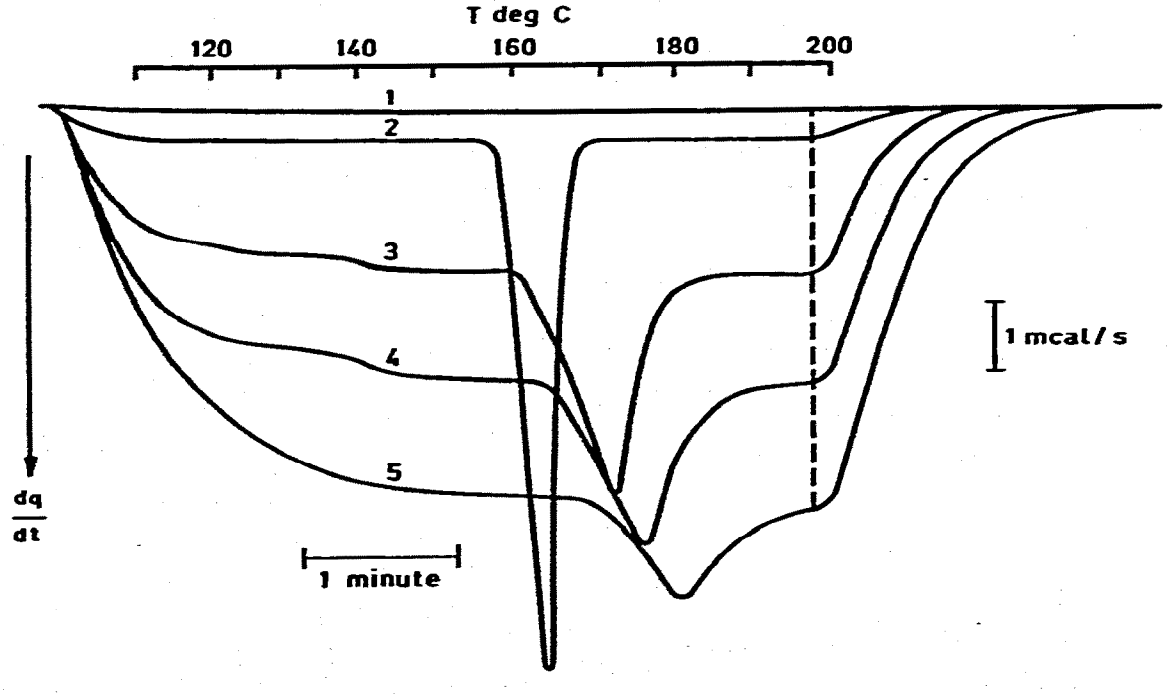

Fig. 1. DSC scans at 20 K min^{-1}. 1, empty pan; 2, In; 3, resin C + In; 4, resin B + In; 5, resin A + In. Dashed line at limit of scan is the boundary of the areas used for ΔT estimation.

and the extrapolated leading edge of the melting peak was 156.9°C. When the same sample was scanned at 20 K min^{-1} the apparent T_m was 157.7°C so that ΔT_m = 1.1K. The estimate of the temperature lag by area measurement as described above gave ΔT = 1.1K in excellent agreement with ΔT_m.

An aluminium sample pan containing an alumina disc (62.3 mg, 0.9 mm thick, 5 mm diameter) with a sample of pure indium (14.7 mg) placed directly on the top of the alumina was scanned at 20 K min^{-1}, the observed ΔT_m was 3.4K and ΔT determined from the area of the tail of the curve was 3.1K. This good agreement implies that there is not a steep thermal gradient through the alumina disc. For the pan containing the indium alone ΔT_m = 1.3K which is a measure of the lag due to the thermocouple/sample platform/pan/indium interfaces.

Further experiments involved an epoxy resin sample. The resin was bisphenol-A diglycidyl ether (Shell Epikote 825, 100 parts) cured with triethylenetetramine (CIBA MY 951, 14.0 parts) for 16 h at room temperature followed by 8 h at 160°C. The cured resin had a T_g of 131°C. Sample A was cut from a cast sheet and was approximately 3.5 × 3.0 × 2.38 mm thick.

The empty pan was scanned over the temperature range 100–200°C at 5, 10, and 20 K min^{-1}. These scans were repeated with the indium sample (14.6 mg) alone and then with the indium on the upper surface of resin sample A. The resin sample was then abraded down to a thickness of 1.50 mm to give sample B, and the scan with the indium was repeated at 20 K min^{-1}. Finally, sample B was abraded down to a thickness of 0.88 mm to give sample C for which the scan was again repeated at 20 K min^{-1}. The scans are illustrated in Fig. 1 and the results are summarised in Table 1. In Fig. 1 the broadening of the indium fusion peak and the increasing area of the tails of the curves with increasing sample thickness can clearly be seen.

The variation in temperature lag with sample depth for the epoxy resin is shown in Fig. 2. The intercept at zero depth, ~1K, can be attributed to the lag due to the sample/pan/instrument interfaces. The lag at the upper surface of the sample and that due to the resin/indium interface is given by ΔT_m. For a linear temperature gradient and neglecting interface effects the average lag in the sample should be

TABLE 1

ESTIMATED TEMPERATURE LAGS

Sample	ϕ *(K min^{-1})*	T_m *(°C)*	ΔT_m *(K)*	ΔT *(area)* *(K)*
In	20	158.0	1.4	2.0
Resin (A) + In		169.4	12.8	6.8
Resin (B) + In		164.9	8.3	4.5
Resin (C) + In		161.9	5.3	3.0
In	10	157.7	1.1	1.5
Resin (A) + In		163.4	6.8	4.1
In	5	157.4	0.8	0.5
Resin (A) + In		160.3	3.7	1.6

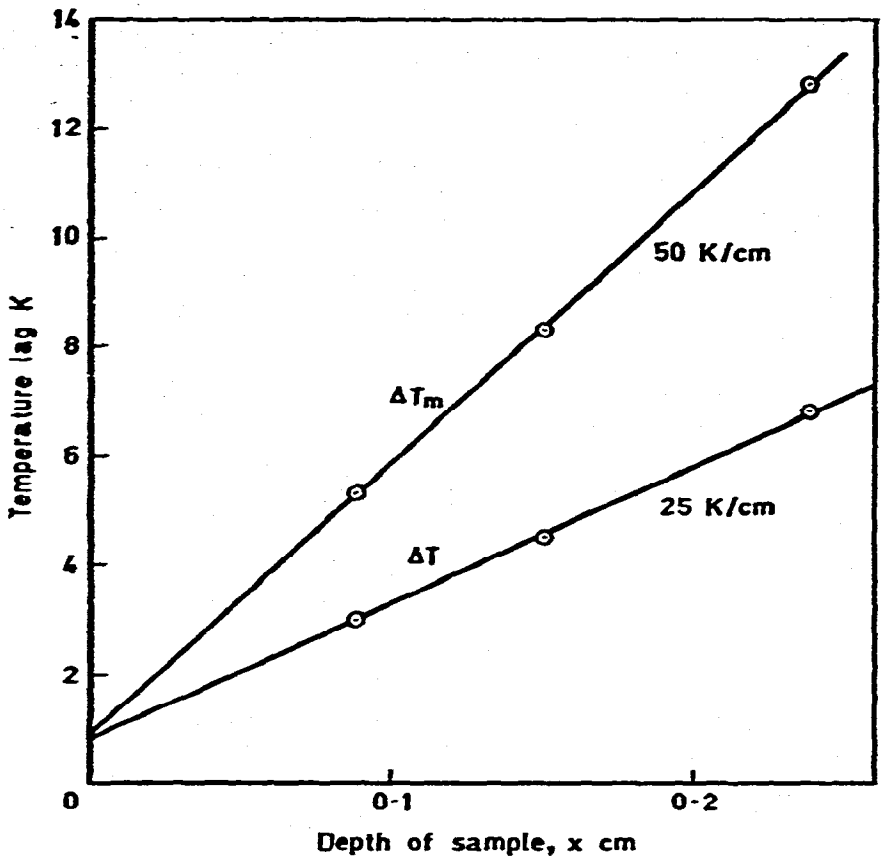

Fig. 2. Dependence of temperature lag on depth of resin sample.

$\Delta T \simeq 0.5\Delta T_m$. The ratio of the slopes of the lines in Fig. 2 is 0.50 which supports this simple model.

CONCLUSIONS

The average sample temperature lag under dynamic conditions in a DSC instrument of the differential temperature type may be estimated by a similar method to that described by Richardson. The estimated lags are consistent with shifts in the apparent melting temperature of indium in contact with the sample. Samples of low thermal conductivity can develop significant temperature gradients, which may be diminished by reducing the profile of the sample or the heating rate.

REFERENCES

1 M. J. Richardson and P. Burrington, *J. Therm. Anal.*, 6 (1974) 345.
2 M. J. Richardson and N. G. Savill, *Thermochim. Acta*, 12 (1975) 213.