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THE MEASUREMENT OF THERMAL CONDUCTIVITY BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The use of differential scanning calorimetry to measure thermal conductivity is discussed. A theory of the experiment is derived in which a first-order correction is made for lateral heat loss from the sample. The conventional approach in which this correction is ignored gives results with an accuracy of about 5%.

INTRODUCTION

The use of differential scanning calorimetry (DSC) to measure thermal conductivity has been described by a number of authors [1–5]. The emphasis is on a rapid and straightforward method which might be expected to have wide applicability. The technique most commonly used is to measure the thermal power needed to maintain a known temperature difference across the end-faces of cylindrical samples. However, implicit in the treatment of the experimental results has been the assumptions that both lateral heat loss from the surface of the cylinders and thermal impedance at the end-faces may be ignored. The purpose of the present work is to examine these assumptions. We set out a theory of the experiment and describe the extent to which it represents the results obtained using power-compensated DSC (Perkin-Elmer, Model 1b).

THEORY OF THE EXPERIMENT

The configuration of a single cylindrical sample is shown in Fig. 1. The temperatures T_0 and T_1 refer to the lower and upper faces of the cylinder in contact with surfaces at T_h and T_c respectively. T_a is the ambient temperature. The equations describing the heat balance in the steady state are

$$\frac{d^2U}{dx^2} + \epsilon U = 0, \text{ along the cylinder, } 0 < x < l \qquad (1)$$

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$$\kappa \frac{\mathrm{d}U}{\mathrm{d}x} + H\{U_{\mathrm{h}} - U(0)\} = 0, \text{ lower end, } x = 0, \; U(0) = U(x = 0) \tag{2}$$

$$\kappa \frac{\mathrm{d}U}{\mathrm{d}x} + H\{U(l) - U_{\mathrm{c}}\} = 0, \text{ upper end, } x = l, \; U(l) = U(x = l) \tag{3}$$

The symbol κ denotes the thermal conductivity, ϵ and H are the lateral heat transfer term and the end-face heat transfer coefficient, respectively, and U is the temperature excess over the ambient value, i.e. $U = T - T_{\mathrm{a}}$. It is presumed that ϵ is small and the temperature is constant over any cross-section.

A solution to these equations may be found using a perturbation method in which we look for a temperature field $U(x)$ in the form $U(x) = U_0 + \epsilon U_1 + \epsilon^2 U_2 + \ldots$ The first perturbation equations

$$\left.\begin{aligned} &\frac{\mathrm{d}^2 U_0}{\mathrm{d}x^2} = 0 \\ &\kappa \frac{\mathrm{d}U_0}{\mathrm{d}x} + H\{U_{\mathrm{h}} - U_0(0)\} = 0 \\ &\kappa \frac{\mathrm{d}U_0}{\mathrm{d}x} + H\{U_0(l) - U_{\mathrm{c}}\} = 0 \end{aligned}\right\} \tag{4}$$

lead to a description of the temperature field in the absence of lateral heat loss. The solution of (4) is $U_0 = Ax + B$ where A and B are constants such that $\kappa A = H\{U_{\mathrm{h}} - B\} = 0$ and $\kappa A + H\{Al + B - U_{\mathrm{c}}\} = 0$. Thus we find $A = -(U_{\mathrm{h}} - U_{\mathrm{c}})/l(1 + 2\lambda)$ and $B = U_{\mathrm{h}} - \lambda(U_{\mathrm{h}} - U_{\mathrm{c}})/(1 + 2\lambda)$ where $\lambda = \kappa/Hl$.

The second perturbation equations lead to a first-order correction for lateral heat loss. We have

$$\left.\begin{aligned} &\frac{\mathrm{d}^2 U_1}{\mathrm{d}x^2} + U_0 = 0 \\ &\kappa \frac{\mathrm{d}U_1}{\mathrm{d}x} + H\{-U_1(0)\} = 0 \\ &\kappa \frac{\mathrm{d}U_1}{\mathrm{d}x} + H\{U_1(l)\} = 0 \end{aligned}\right\} \tag{5}$$

from which $U_1 = -\frac{1}{6}Ax^3 - \frac{1}{2}Bx^2 + Cx + D$. The constants C and D are related to A and B by the expressions $D = \kappa C/H$ and $(1 + 2\lambda)l^{-1}C = (\frac{1}{6}Al + \frac{1}{2}B) + \lambda(\frac{1}{2}Al + B)$.

We are now in a position to calculate the thermal power W at the lower face of the cylinder. The first-order temperature field is $U = U_0 + \epsilon U_1$ and hence

$$W = \kappa S\left[-\frac{\mathrm{d}U}{\mathrm{d}x}\right]_{x=0} = -\kappa S(A + \epsilon C) \tag{6}$$

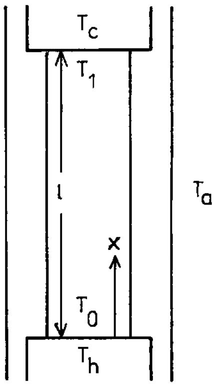

Fig. 1. Configuration of a single cylindrical sample.

where S is the cross-sectional area of the cylinder. Thus we find

$$\frac{W}{\kappa S\,\Delta U} \approx \frac{1}{l}\left(1 - \frac{l^2}{L^2} - \frac{l_0}{l}\right) \tag{7}$$

where $\Delta U = U_h - U_c = T_h - T_c$, $l_0 = 2\kappa/H$, $L^2 = (\epsilon X)^{-1}$ and $X = (U_h/2\Delta U) - \frac{1}{6}$. Equation (7) may be written in the form

$$W/\kappa S\,\Delta U\left(l^{-1} - l_0 l^{-2} + \tfrac{1}{6} l\epsilon\right) - \tfrac{1}{2} l\epsilon U_h \tag{8}$$

We observe that when $l_0 = 0$ and $\epsilon = 0$ the equation simplifies to $W = \kappa S \Delta U l^{-1}$ the elementary formula used to calculate κ without corrections.

RESULTS

Our measurements have been made on cylinders machined from perspex. The length of the cylinders was 6.01, 8.00, 10.00, 12.00 and 14.00 mm and the diameter 4.00 mm. The thermal conductivity of the perspex was known from precision-guarded, hot plate measurements made by the National Physical Laboratories. The long axis of the cylinders corresponded to the direction of heat flow in the hot plate experiments. Two cylinders were used in each measurement. Since the thermal conductivity and cross-sectional area are the same for both cylinders the differential thermal power $\Delta W = W_2 - W_1$ is given by

$$\Delta W/\kappa S = \Delta U\left\{\Delta(l^{-1}) - l_0 \Delta(l^{-2}) + \tfrac{1}{6}\epsilon\,\Delta l\right\} - \tfrac{1}{2}\epsilon U_h \Delta l \tag{9}$$

where $\Delta l = l_2 - l_1$ is the difference in length of the two cylinders. Other experimental configurations have been adopted by some authors: a single cylinder and an empty reference holder; two cylinders of different thermal conductivity. However, it is important to recognise that the use of two cylinders does not eliminate the need for corrections.

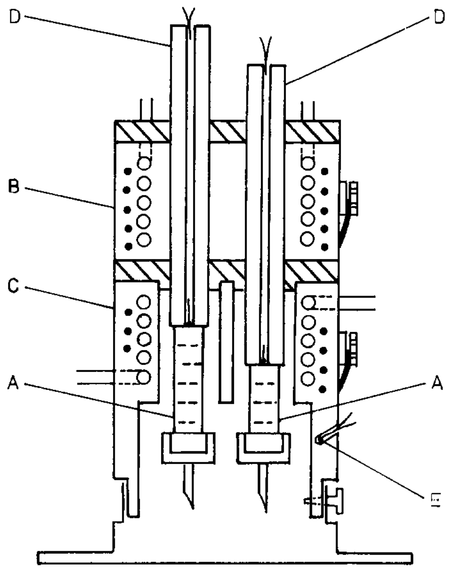

Fig. 2. Thermal conductivity apparatus.

The experimental arrangement is shown in Fig. 2. The cylindrical samples (A) are supported on silver discs which are a close fit in the specimen holders of the scanning calorimeter. The heat sink (B) and jacket (C) are also made of silver and are separated by a tufnol insulating disc. The silver rods (D) are a sliding fit in the heat sink and make contact with the top face of the samples. The temperature of the end faces of the rods was measured by thermocouples set in thermally conductive paste. A thermocouple (E) was used to measure the temperature of the jacket. The differential and average temperature calibrations of the calorimeter were established using gallium and indium with the thermal conductivity apparatus in position. Linearity between the instrument signal and thermal power was confirmed with sapphire discs.

We found it difficult to obtain consistent results when the measurements involved removing or replacing the sample cylinders in the apparatus. This was in spite of using thermally conductive paste on the end-face of the cylinders. The reference signal was obtained with either no cylinders in the apparatus or two cylinders of equal length. By rejecting the obviously erroneous results we used the elementary formula $\Delta W = \kappa S\ \Delta U\ \Delta(l^{-1})$ to obtain $\kappa = 0.182 \pm 0.015$ W m^{-1} K^{-1}. This result represents the mean from ten independent measurements. The certificated value at the mean temperature of the measurements (300 K) was 0.191 W m^{-1} K^{-1} with an accuracy considered better than $\pm 3\%$. The reproducibility of the hot plate measurements was better than 0.5%. The discrepancy between our result and the calibrated value was $\sim 5\%$ compared with the experimental error of $\sim 8\%$.

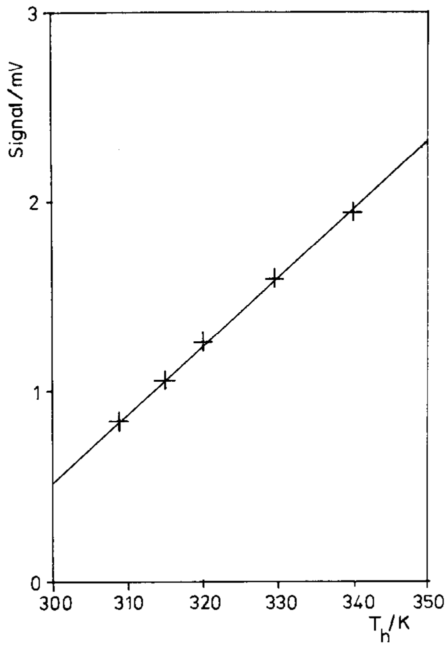

Fig. 3. Calorimetric signal as a function of the temperature T_h.

An alternative approach is to measure ΔW as a function of the temperature of the calorimeter, T_h. The advantage of this approach is that a knowledge of the reference signal is not needed. Figure 3 shows the results of one such experiment in which the temperature of the heat sink and jacket was maintained at 290 K. We emphasise that the linear relationship observed between the calorimetric signal and T_h does not imply the absence of lateral heat loss and thermal impedence at the end-faces of the samples. Thus from (9) we obtain

$$G_h = \frac{\partial \Delta W}{\partial T_h} = \kappa S\left\{\Delta(l^{-1}) - l_0\, \Delta(l^{-2}) - \tfrac{1}{3}\epsilon\, \Delta l\right\} \qquad (T_c,\, T_a \text{ constant}) \quad (10)$$

which is consistent with the linear relationship provided that any temperature dependence of ϵ and l_0 is small. The effect of changing T_c and T_a may be examined with the present apparatus which has been designed to allow the temperature of the heat sink and jacket to be varied independently. Both the heat sink and jacket are wound separately with electrical heaters and machined with channels through which water may be passed. Once again we observe a linear dependence of ΔW both on T_c and T_a with the magnitude of the gradient $\partial\, \Delta W/\partial T_c$ differing from that obtained from $\partial\, \Delta W/\partial T_h$. These observations are inexplicable in terms of the elementary theory but from (9) we have

$$G_c = -\frac{\partial\, \Delta W}{\partial T_c} = \kappa S\left\{\Delta(l^{-1}) - l_0\, \Delta(l^{-2}) + \tfrac{1}{6}\epsilon\, \Delta l\right\} \quad (T_h,\ T_a \text{ constant}) \tag{11}$$

and

$$G_a = \frac{\partial\, \Delta W}{\partial T_a} = \kappa S\left\{\tfrac{1}{2}\epsilon\, \Delta l\right\} \qquad (T_h,\ T_c \text{ constant}) \tag{12}$$

The gradients G_h and G_c provide a route to the absolute calculation of the thermal conductivity. Thus from (10) and (11) we derive

$$\tfrac{1}{3}(G_h + 2G_c)/\Delta(l^{-1}) = \kappa S - \kappa S l_0\left(l_1^{-1} + l_2^{-1}\right) \tag{13}$$

i.e. we predict that $y = \frac{1}{3}(G_h + 2G_c)/\Delta(l^{-1})$ is linear in $x = l_1^{-1} + l_2^{-1}$ with an intercept κS. Such an approach is neither rapid nor straightforward and the reliability of our results was diminished by the accumulated errors in the gradients and temperature dependences of the reference signal. The use of more precise calorimetric equipment may allow the approach to be adopted leading to an improvement in the accuracy of the results. The present work suggests that the effect of the corrections is likely to be small (< 5%). It may be that the cylinder lengths used in these measurements fortuitously represent a compromise in which the relative effect of thermal impedance at the end-faces is small without unduly increasing the effect of lateral heat loss.

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