Measurement of Thermal Conductivity Using TMDSC: Solution to the Heat Flow Problem

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ABSTRACT: The dependence of the apparent heat capacity obtained from quasi-isothermal temperature-modulated differential scanning calorimetry (TMDSC) experiments and the thermal conductivity is determined for several cases. The relationships are based on the solution of the heat conduction equation which gives the temperature profile in the TMDSC sample. The temperature profile is then used to calculate the sinusoidal heat flow to the sample. We compare our results with those of other researchers. We also show the effect of thermal contact resistance on the results.

INTRODUCTION

TEMPERATURE-MODULATED DIFFERENTIAL SCANNING calorimetry (TMDSC) is a new technique in thermal analysis in which a sinusoidal temperature perturbation is used. The purported advantages of TMDSC include the ability to separate overlapping phenomena, as well as improved resolution and sensitivity [1]. There are problems associated with the interpretation of TMDSC data, especially when nonlinear processes, such as melting, reaction, or structural recovery [2,3] are involved. Thermal lag in the sample also presents problems for quantitative analysis of the heat capacity in TMDSC data since the apparent heat capacity de-

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creases as the thermal lag increases [3]. However, since the thermal lag and apparent heat capacity are directly related to the thermal conductivity of the sample, the thermal conductivity can, in principle, be determined from TMDSC measurements of the apparent heat capacity.

Here we question the method proposed by Marcus and Blaine [4] to obtain the thermal conductivity from TMDSC measurements. In their work, those researchers presented an equation to calculate the thermal conductivity from the apparent heat capacity based on their solution of the one-dimensional heat flow problem for a thick sample in an open pan. The derivation of the equation assumed that the bottom face of the sample (which is against the heat source) follows the applied temperature perturbation and the heat flow through the top of the sample is negligible. Based on this equation and TMDSC measurements, they calculated values of thermal conductivity for four materials that deviated from other literature values obtained by more conventional techniques by as much as 20%. In order to correct these results they accounted for radial heat losses in the relatively thick (>3 mm) samples used and then reported values that are within 3% of the literature values.

The equation derived by Blaine and Marcus [4] is:

$$\kappa = \frac{2\pi (mC_{app})^2}{C_p \rho A^2 P} \tag{1}$$

where m is the mass of the sample, C_{app} is the measured heat capacity of the thick sample, C_p is the heat capacity of the thin sample (assumed to be the true heat capacity), A is the area of the sample, and P is the period of modulation. We needed to include the mass in Equation (1) because we take the units of C_{app} to be J g^{-1} K^{-1}, whereas in their work, Marcus and Blaine defined C_{app} as having units of J K^{-1}. Substituting the modulation frequency $\omega = 2\pi/P$ and $\rho = m/AL$ (where L is the sample thickness), the equation of Marcus and Blaine reduces to:

$$\kappa = \rho C_p \omega L^2 \left(\frac{C_{app}}{C_p}\right)^2 \tag{2}$$

The equation they used to correct for radial losses is:

$$\kappa_{corr} = [\kappa - 2D + (\kappa^2 - 4D\kappa)^{0.5}]/2 \tag{3}$$

where D is typically 0.014 W/°C m [4].

One problem with the method Marcus and Blaine [4] proposed to obtain the thermal conductivity from TMDSC is that two samples are used, a thin sample enclosed in the typical aluminum pan in which no thermal lag is assumed to be present, and a thick sample, generally a 3–6 mm extruded rod which is placed in an open sample pan. The heat transfer coefficient between the sample and the furnace may vary between the two samples and this will affect the accuracy of the results. A more significant issue is the validity, or lack thereof, of their solution to the heat flow boundary value problem and the resulting equation relating the thermal conductivity to the apparent heat capacity as a function of experimental variables, such as sample thickness, and frequency and amplitude of modulation.

Here, we rederive the equation for κ as a function of the apparent heat capacity and compare the result to that of Marcus and Blaine [4]. To this end, we first obtain the time-dependent temperature profile in the sample and the sinusoidal heat flow by solving the one-dimensional heat conduction equation for the boundary conditions assumed by Marcus and Blaine [4]. Using the analytical expressions obtained, we proceed to derive the relationship between the thermal conductivity and the apparent heat capacity as a function of sample thickness, frequency, and the heat transfer coefficient. Our results indicate their equations are in error. The use of other boundary conditions are also examined and discussed.

ANALYTICAL SOLUTION OF THE HEAT FLOW PROBLEM FOR A THICK SAMPLE IN AN OPEN PAN

Temperature Profile in Sample

The one-dimensional heat conduction equation [5], in which radial heat transfer is neglected, given below, is solved to yield the temperature profile in the sample as a function of distance from the bottom of the sample x and of time t:

$$\frac{\partial}{\partial x}\kappa\frac{\partial T}{\partial x}=\rho C_p\frac{\partial T}{\partial t} \tag{4}$$

where T is temperature, κ is the thermal conductivity, ρ is the density, and C_p is the heat capacity of the material. If we assume that the thermal conductivity is not a strong function of temperature (and hence, x), the equation is simplified:

$$k\frac{\partial^2 T}{\partial x^2}=\frac{\partial T}{\partial t} \tag{5}$$

where $k=\kappa/\rho C_p$ is the thermal diffusivity. To solve Equation (5), the boundary and initial conditions need to be specified. We first examine the case considered by Marcus and Blaine [4] where the bottom of the sample (at $x = 0$) is assumed to follow the furnace temperature and there is no heat transferred from the top of the sample (at $x = L$):

$$T(x=0) = T_0 + A\sin(\omega t) \tag{6}$$

$$\frac{dT}{dx}(x=L) = 0 \tag{7}$$

$$T(t=0) = T_0 \tag{8}$$

The steady state (but oscillatory) solution is given by the following series:

$$T(x,t) = [T_0 + A\sin(\omega t)] - 2A\theta \sum_{n=1}^{odd} \frac{(\lambda_n \cos(\omega t) + \theta \sin(\omega t))}{\sqrt{\lambda_n}[\lambda_n^2 + \theta^2]} \sin\left(\sqrt{\lambda_n}\,\frac{x}{L}\right) \tag{9}$$

where λ_n are the eigenvalues given by $\sqrt{\lambda_n} = n\pi/2$. The parameter θ is a dimensionless parameter and is equal to $\omega L^2/k$. Equation (9) is obtained using a solution procedure similar to those commonly presented in textbooks [5], with the difference being the difficulties added by the presence of the time-dependent boundary condition. The application of the solution procedure to a DSC temperature ramp has been published [6].

Heat Flow in Sample

If one performs a TMDSC experiment under conditions such that there are no thermal events, such as structural recovery, melting or crystallization, or chemical reaction, then the heat flow to the sample depends on the sample geometry, heat capacity, mass, and the rate of temperature change. For the simplest case in which there is no thermal gradient in the sample and no heat loss, the heat flow is given by:

$$\dot{Q} = C_p \frac{dT}{dt} \tag{10}$$

When a thermal gradient exists, the heat flow is proportional to the average rate of temperature change in the sample:

$$\dot{Q} = C_p \int_0^1 \frac{dT}{dt} d\xi \tag{11}$$

where $\xi = x/L$ is a dimensionless sample thickness measured from the bottom of the sample.

We obtain an analytical solution for the steady-state sinusoidal heat flow for a thick sample in an open pan by taking the time derivative of Equation (9) for the temperature and then inserting this expression into Equation (11) and integrating over the thickness:

$$\dot{Q} = C_p A\omega \left\{ \cos(\omega t) + 2\theta \sum_{n=1}^{odd} \frac{\lambda_n \sin(\omega t) - \theta \cos(\omega t)}{\sqrt{\lambda_n}[\lambda_n^2 + \theta^2]} \right\} \tag{12}$$

The series in Equation (12) converges to within 1% of the limiting value in two terms for values of the parameters ω and θ examined; in some cases, for values of θ much less than $\pi^4/16$, the series may converge in one term.

Apparent Heat Capacity

Now that we have an analytical expression for the steady-state heat flow, we can obtain an expression for the apparent heat capacity, generally taken to be the amplitude of the sinusoidal heat flow, B, divided by the amplitude of the sinusoidal rate of temperature change $A\omega$:

$$C_{app} = \frac{B}{A\omega} = \frac{\dot{Q}_{\max}}{A\omega} \tag{13}$$

The amplitude of the heat flow is equal to the maximum in the heat flow $\dot{Q}_{\max}$, in our calculations because we assume no heat loss (i.e., we assume that the heat flow oscillates about 0 since dT/dt oscillates about 0). (It is noted that the apparent heat capacity is often taken to be a dynamic quantity and it is defined in Equation (13) similarly to the modulus of a dynamic heat capacity. We disagree with that interpretation in that we argue that the frequency-dependence lies in the enthalpy and is not inherent in the heat capacity [7].)

We can obtain an analytical expression for the amplitude of the heat flow by solving for the heat flow when the heat flow is a maximum. The value of ωt at which the heat flow is a maximum, $\omega t_{\max}$, is found through differentiation since:

$$\frac{d\dot{Q}}{d(\omega t)} = 0 \quad \text{when } \dot{Q} = \dot{Q}_{\max} \tag{14}$$

If the series in Equation (12) does not converge in one term, we find ωt_{max} from Equation (14) and the relationship between κ and C_{app} from Equations (12) and (13). If the series converges in one term, we can write an analytical expression for ωt_{max} and obtain an expression relating κ and C_{app}. For example, ωt_{max} and $\dot{Q}_{max}$ are given by the following when the series converges in one term:

$$\omega t_{max} = \tan^{-1}\left\{ \frac{2\theta\pi^2}{\pi^2\left(\frac{\pi^2}{16}+\theta^2\right) - 8\theta^2} \right\} \tag{15}$$

$$\dot{Q}_{max} = C_p A\omega \left\{ \cos(\omega t_{max}) + 2\theta \left(\frac{\frac{\pi^2}{4}\cos(\omega t_{max}) - \theta\sin(\omega t_{max})}{\frac{\pi}{2}\left[\frac{\pi^4}{16}+\theta^2\right]} \right) \right\} \tag{16}$$

Now we can insert our expression for the amplitude of the heat flow [Equation (16) for the one-term approximation] into the expression for the modulus of the complex heat capacity [Equation (13)]. For the one-term approximation we can re-arrange and solve the resulting quadratic equation for $\theta = \omega L^2/k$. We then rear-range and solve for $\kappa = k\rho\, C_p$:

$$\kappa = \frac{\rho C_p \omega L^2}{\theta} \tag{17}$$

where θ is given by:

$$\theta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{18}$$

and a, b, and c are given by the following:

$$a = \pi^2 \frac{C_{app}}{C_p} + (8 - \pi^2)\cos(\omega t_{max}) \tag{19}$$

$$b = -8\pi^2 \sin(\omega t_{\max}) \tag{20}$$

$$c = \frac{\pi^2}{16}\left\{\frac{C_{app}}{C_p} - \cos(\omega t_{\max})\right\} \tag{21}$$

Equation (17) cannot be solved explicitly for κ since the equation is nonlinear: κ depends on $\omega t_{\max}$ through Equations (19)–(21) for θ, and $\omega t_{\max}$ in turn depends on θ per Equation (15). However, simultaneous solution of the equations gives κ as a function of C_{app}.

RESULTS AND DISCUSSION

Relation Between κ and C_{app} for a Thick Sample in an Open Pan Assuming Perfect Heat Transfer

The equations we derived above relating κ and C_{app}/C_p for a thick sample in an open pan assuming perfect heat transfer at the bottom of the sample differ significantly from the solution obtained by Blaine and Marcus [4]. We compare our solution with theirs in Figure 1. We plotted C_{app}/C_p versus $1/\theta = k/\omega L^2 = \kappa/\rho C_p\, \omega L^2$ rather than versus κ at a given $\rho C_p\, \omega L^2$ in order to give the more general results. Two results are shown for our derivation: a four-term approximation and the one-term approximation [Equations (15), (17)–(21)]. The one-term and four-term approximations are identical (within less than 1%) and cannot be distinguished except at very small values of $k/\omega L^2$. Only Equation (2) from the work of Blaine and Marcus [4] is shown; the corrected result which presumably accounts for radial heat loss depends on the value of D in Equation (3), as well as the value of κ, and cannot be shown as a single curve as a function of the dimensionless variable $k/\omega L^2$. The results of Marcus and Blaine are in agreement with our solution at $k/\omega L^2$ less than approximately 0.2. The limiting behavior at high $k/\omega L^2$ differs significantly between their solution and ours. For our solution, the limiting value at high $k/\omega L^2$ is $C_{app}/C_p = 1.0$; whereas in the equation given by Marcus and Blaine [4], $C_{app}/C_p = 1.0$ at $k/\omega L^2 = 1.0$ and $C_{app}/C_p > 1.0$ for larger values of $k/\omega L^2$. Values of $C_{app}/C_p > 1.0$ are not theoretically possible unless the sample is undergoing an endothermic kinetic event.

The discrepancy between our result and that of Blaine and Marcus arises from the assumption made in their derivation [4,8] that the term[1]

[1]The term shown in Equation (22) is from Reference [8]; the factor of 2 preceeding the second term in the denominator is missing in Reference [4]. However the presence or absence of this factor is of minor importance and does not affect our arguments or conclusions.

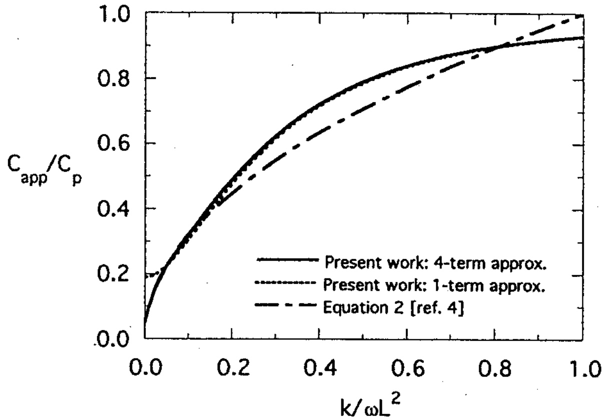

Figure 1. Apparent heat capacity versus k/ωL^2 for a thick sample in an open pan comparing our relationship with that in Reference [4].

$$\frac{1-2e^{2ZL}\cos(2zL)+e^{4ZL}}{1+2e^{2ZL}\cos(2zL)+e^{4ZL}} \tag{22}$$

can be set to unity, where $Z=(\omega/2k)^{1/2}$. Although this assumption is valid for very large e^{4ZL} at they note, errors above 10% are incurred for $k/\omega L^2$ values between 0.16 to 0.67, as shown in Table 1. The error in the apparent heat capacity will be half the

Table 1. Percent error in C_{app}/C_p due to assumption in derivation made in Reference [4].

$k/\omega L^2$	4ZL	e^{4ZL}	Equation (22)	% Error in Equation (22) when it is set to 1.0	% Error in C_{app}/C_p
0.05	12.65	311486	0.99	0.7	0.4
0.10	8.94	7664	1.01	−1.1	−0.5
0.15	7.30	1484	1.09	−8.7	−4.3
0.20	6.32	558	1.18	−15.6	−7.8
0.30	5.16	175	1.29	−22.6	−11.3
0.40	4.47	88	1.30	−23.1	−11.5
0.50	4.00	55	1.25	−19.9	−10.0
0.60	3.65	39	1.17	−14.7	−7.3
0.70	3.38	29	1.09	−8.2	−4.1
0.80	3.16	24	1.01	−0.8	−0.4
0.90	2.98	20	0.93	7.1	3.6
1.00	2.83	17	0.87	15.4	7.7
1.20	2.58	13	0.81	32.9	16.4
1.50	2.31	10	0.62	60.3	30.2

error incurred by assuming Equation (22) is unity since the term in Equation (22) is related to the square of the apparent heat capacity [8]. For example at a value of $k/\omega L^2$ of 0.4, the error in the C_{app}/C_p obtained from Equation (2) will be 11% too low (0.08 too low in terms of C_{app}/C_p), exactly the discrepancy observed. Interestingly, at a value of $k/\omega L^2$ near 0.8, the error incurred by assuming Equation (22) goes through zero and changes sign (see Table 1); this is responsible for the crossing of the two solutions in Figure 1 at $k/\omega L^2 = 0.81$. We note that Table 1 encompasses the range of e^{4ZL} between 40 and 3000 which Blaine and Marcus [8] state is the approximate range of application for their equation. Clearly, their statement is incorrect.

Effects of Heat Transfer on the Relationship between κ and C_{app} for a Thick Sample in an Open Pan

In addition to the apparent error in their derived equation, the methodology of Marcus and Blaine [4] has other problems. One issue is that perfect heat transfer between the furnace and sample is assumed. The effect of a finite heat transfer coefficient is a change in the boundary conditions at $x = 0$:

$$\frac{dT}{d\xi}(\xi = 0) = -H(T - T_p) \qquad (23)$$

where ξ is the dimensionless sample thickness, T_p is the furnace temperature [$= T_0 + A \sin(\omega t)$] and H is the dimensionless heat transfer coefficient ($H = h/\kappa L$, where h is the heat transfer coefficient with units of J m^{-2} s^{-1} K^{-1}, κ is the thermal conductivity, and L is the sample thickness). For this boundary condition at the bottom of the sample coupled with the original boundary condition at the top of the sample and the original initial condition, the heat flow problem can be solved. The solution for a thick sample in an open pan where there is thermal resistance between the sample and the furnace is given by:

$$\dot{Q} = C_p A\omega \left\{ \cos(\omega t) + 2\theta \sum_{n=1}^{odd} \frac{\sin^2\sqrt{\lambda_n}\,(\lambda_n \sin(\omega t) - \theta\cos(\omega t))}{\lambda_n[\lambda_n^2 + \theta^2]} \right\} \qquad (24)$$

where the eigenvalues are given by $\sqrt{\lambda_n}\tan\sqrt{\lambda_n} = H$ and where θ still equals $\rho C_p \omega L^2/\kappa$. The effect on the relationship between C_{app} and κ is that a smaller value of C_{app}/C is observed for the same value of $k/\omega L^2$ (or κ keeping the other variables the same), as shown in Figure 2. Hence, the ability to accurately determine κ based on the measurement of the apparent heat capacity depends on whether the heat transfer coefficient is adequately known.

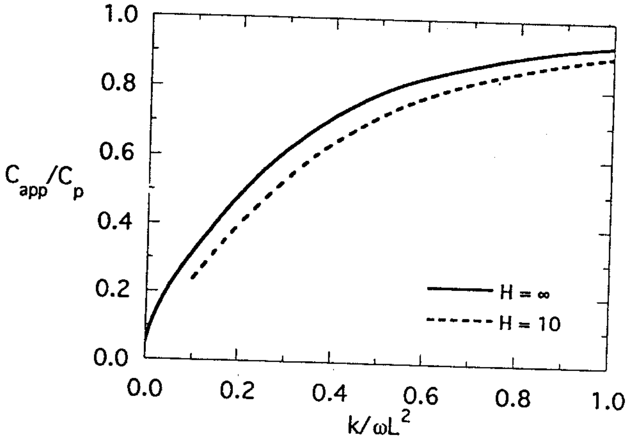

Figure 2. Apparent heat capacity versus $k/\omega L^2$ for a thick sample in an open pan showing the effects of thermal resistance between the furnace and the sample pan.

Solution for an Encapsulated Sample with and without Heat Transfer Limitations

Another problem in the method of Marcus and Blaine [4] is the use of a thick sample not enclosed in a sample pan. As they point out, thermal losses along the sides of the sample can be important and will result in a larger value of C_{app}/C for the same value of $k/\omega L^2$ (or κ keeping the other variables the same) since the heat flow into the sample will need to be higher to compensate for the losses (assuming that the losses are much greater for the sample than for the reference). For their thick sample, radial heat loss can be substantial because the radial surface area is 50% of the area of the top of the sample. Another factor that may be important for thick samples is the presence of a thermal gradient in the DSC furnace itself since a lower temperature in the furnace at the top of the sample will contribute to greater heat loss from the sample.

Incorporating heat loss due to a thick sample or due to a gradient in the DSC furnace into the heat flow problem is difficult. Hence, the empirical approach [Equation (3)] taken by Marcus and Blaine [4] is reasonable. However, an alternative approach is to exploit the fact that the apparent heat capacity depends on ω as well as on sample thickness. Hence, one can use a single nominal DSC sample encapsulated in an aluminum pan to determine thermal conductivity with measurements being performed over the frequency range available (approximately 0.06 rad/sec to 0.31 rad/sec).This approach mitigates the problems associated with radial heat loss and with the effects of gradients in the DSC furnace.

We now solve the heat flow problem for a thin encapsulated sample. We assume that when the sample is encapsulated, the temperature at the top of the sample is the same as at the bottom of the sample (i.e., the sample pan is assumed to have no thermal resistance and the thermal contact between the sample and the pan is assumed to be perfect). The boundary condition at the top of the sample then becomes:

$$T(x=L)=T(x=0) \tag{25}$$

or alternatively:

$$\frac{dT}{dx}(x=L/2)=0 \tag{26}$$

For the new boundary condition coupled with the original boundary condition at $x = 0$ and the original initial condition, the heat flow is given by:

$$\dot{Q}=C_p A\omega\left\{\cos(\omega t)+8\theta\sum_{n=1}^{odd}\frac{\lambda_n \sin(\omega t)-\theta\cos(\omega t)}{\sqrt{\lambda_n}\left[\lambda_n^2+\theta^2\right]}\right\} \tag{27}$$

where the eigenvalues are given by $\sqrt{\lambda_n} = n\pi$ rather than $n\pi/2$. For the case where there is thermal resistance between the sample bottom and the furnace but where the temperature profile in the sample is still symmetric (i.e., there is no thermal resistance between the pan and sample or within the pan itself) the heat flow is given by Equation (24) with θ being redefined as $\rho C_p \omega L^2/4\kappa$. Figure 3 shows how the apparent heat capacity is expected to vary with $k/\omega L^2$ for two values of H for a ther-

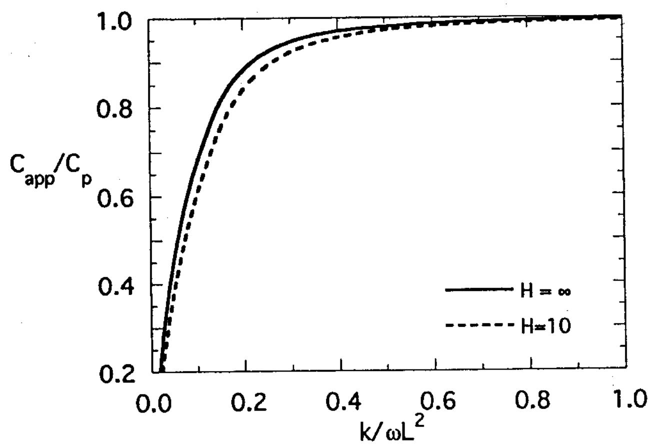

***Figure 3.** Apparent heat capacity versus k/ωL² for a thin encapsulated sample showing the effects of thermal resistance between the furnace and the sample pan.*

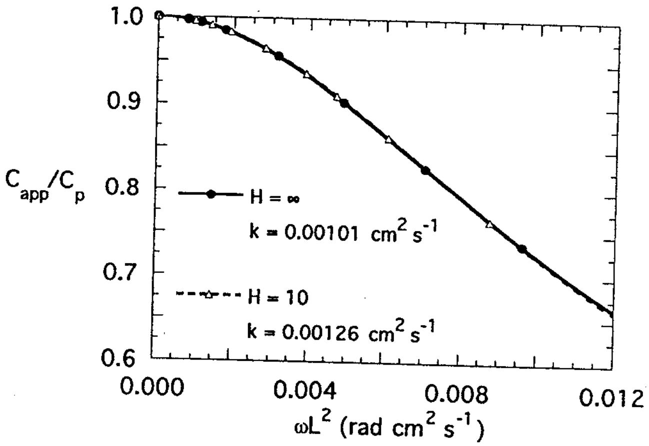

Figure 4. Apparent heat capacity as a function of ωL^2 for a thin encapsulated sample showing that the effects of k and H cannot be distinguished.

mal diffusivity ($k = \kappa/\rho C_p$) value of 0.001 cm s^{-1} (typical of polystyrene). The results show that the apparent heat capacity depends strongly on ω but also that without knowing the heat transfer coefficient, accurate prediction of k or κ is not possible. This is even more apparent in Figure 4. Here we plot the apparent heat capacity versus ωL^2 over the typical range of ωL^2 for two cases: $k = 0.00101$ cm s^{-1} with $H = \infty$ (no thermal resistance), and $k = 0.00126$ cm s^{-1} with $H = 10$. The curves for these two cases are identical. It is evident that the thermal diffusivity or thermal conductivity cannot be determined unless the heat transfer coefficient is known.

CONCLUSIONS

The analytical solution to the heat flow problem for a thick unencapsulated sample demonstrates that the equation relating the apparent heat capacity to the thermal conductivity proposed by Marcus and Blaine [4] is incorrect due to an approximation made in their derivation. In addition, examination of boundary conditions which assume some thermal resistance between the sample and the furnace show that thermal resistance can have a significant effect on the measured apparent heat capacity. The heat flow problem was also solved for a nominal DSC sample encapsulated in an aluminum pan. The thermal conductivity can be easily obtained from a single sample run at several frequencies if the heat transfer coefficient is known; however, if the heat transfer coefficient is not known, an accurate value of κ cannot be obtained.

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