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EVALUATION OF HEATS OF TRANSITION IN SCANNING CALORIMETRY

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ABSTRACT

A procedure for the evaluation of heats of transition in scanning calorimetry has been developed. A formula for evaluation of the energy of fusion of a compound at its melting point is derived that takes into account the baseline shift that is attributable to the heat capacity change on melting. Several other calorimeter parameters of importance are discussed. These include heat exchange between calorimeter vessel and jacket, the time constant of the instrument, the scanning rate, and the heater placement.

I. INTRODUCTION

Thermal analysis devices of various designs and constructions have been widely used for the determination of heats of transition[1-7]. Although the accuracy obtained in these devices has not as yet been as high as that obtained in carefully constructed adiabatic calorimeters[8], they generally do have the advantage of ease of operation and they can yield rapid results on small amounts of material.

Recently, this laboratory had the occasion to measure some heats of fusion using a thermal analysis method[9]. One ambiguity we encountered, however, was in the treatment of the data—namely, in how to draw the baseline under the transition peak. The common and customary practice has been simply to draw a straight line under the peak[7]. However, if there was a baseline shift, there was an uncertainty as to just how the baseline should be drawn. A search of the literature indicated that this problem had, with the exception of a few workers[10-12], been ignored.

In an effort to solve this problem and to lay a theoretical foundation for this type of calorimetry, we have developed a one-body model treatment for phase transition data obtained from scanning calorimetry. Our theory predicts that a correct treatment of the experimental data involves an extrapolation of the baseline obtained on completion of the transition and the application of a correction term involving the scanning rate, the magnitude of the baseline shift, and the temperature difference and heat conduction constant between the calorimeter vessel and its jacket.

II. THE IDEALIZED HEAT CONDUCTION CALORIMETER IN THE SCANNING MODE

The discussion and analysis of calorimetric methods frequently idealizes the separation of the calorimeter proper into two regions: namely, the calorimeter vessel or cell, within which the process of interest occurs, and the calorimeter surroundings or jacket (see Fig. 1). The ratio of the heat capacity (C) of the calorimeter cell and contents to the heat conduction constant (h) between jacket and cell defines the time constant (τ) of the calorimeter. Heat conduction calorimeters are characterized by a small time constant unlike adiabatic and isoperibol calorimeters which generally have larger time constants, although the distinction between these various types of calorimeters must also depend on the mode of operation of the instrument and on which physical variables are kept constant[13]. The theory and practice of adiabatic and isoperibol calorimetry has been discussed elsewhere[7,13,14], and in this paper we shall be concerned only with heat conduction calorimeters. Later, we shall return to a discussion of the importance of the time constant.

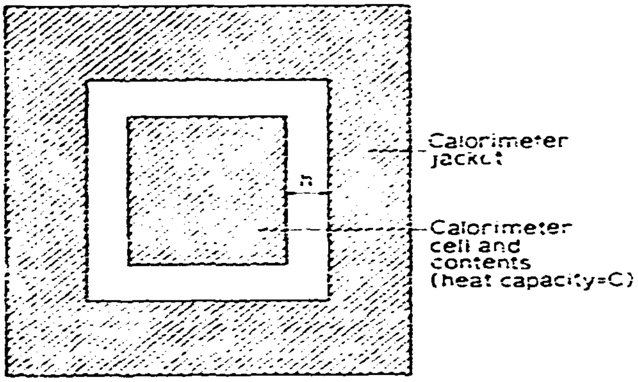

Fig. 1. One-body model of calorimeter where h is the heat conduction constant between calorimeter cell and jacket.

For purposes of this paper, we define a scanning calorimeter as a heat conduction calorimeter, where the temperature of the jacket is changing with time. The temperature of the calorimeter cell may then either lag behind the temperature of the jacket or may be made very nearly equal to it by means of an electrical heater contained within the cell. Since accurate calorimetric measurements require an accounting for heat exchange between calorimeter cell and jacket, it is required that this heat exchange be known or calculable. For conduction* or for radiation heat exchange across small temperature differences one can write

$$dQ/dt = h(\theta_j - \theta_c) = h\Delta\theta \quad (1)$$

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*See assumption 3, Section III.

where dQ/dt is the rate of heat exchange between calorimeter and jacket, h is the heat conduction constant, and θ_j and θ_c are the temperatures of jacket and calorimeter cell, respectively.

There are several possible arrangements and modes of operation of scanning calorimeters. For example, one may measure the temperature difference between the jacket and the calorimeter cell (*e.g.* by means of thermocouples), or one may just measure the temperature of the cell itself, knowing the temperature of the jacket as a function of time. One may have single cell or double cell operation (differential arrangement). One may also apply electrical heating to a cell to compensate for endothermic effects. A summary of several possible types of scanning calorimeters is given in Table 1.

TABLE 1

POSSIBLE ARRANGEMENTS AND MODES OF SCANNING CALORIMETERS

I. Single cell
- A. Measure $(\theta_j-\theta_c)$ and θ_j as functions of time.
  - 1. No electrical compensation
  - 2. Electrical compensation
- B. Measure θ_c and θ_j as functions of time.
  - 1. No electrical compensation
  - 2. Electrical compensation

II. Double cell[a]
- A. Measure $[(\theta_j-\theta_c)-(\theta_j-\theta_c')]$ and θ_j as functions of time.
  - 1. No electrical compensation
  - 2. Electrical compensation
- B. Measure $(\theta_c-\theta_c')$ and θ_j as functions of time.
  - 1. No electrical compensation
  - 2. Electrical compensation

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[a] θ_c and θ_c' are the temperatures of the working and auxiliary cells, respectively

III. A SIMPLE ONE-CELL CASE

We shall proceed by working out a simple case—one in which the calorimeter consists of a single cell in which one measures the temperature difference between the jacket and the cell as well as the temperature of the jacket, both as functions of time. We shall consider the cell to contain a known mass of a substance that melts at temperature θ_m. The energy of fusion of this mass of material at this temperature is given by $\Delta U_{f,\theta_m}$.

In general, the heat capacity of the solid (C_s) will not be equal to the heat capacity of the liquid (C_l). No electrical energy is applied to the cell during the experiment. We shall consider the cell to be a closed system made of rigid walls so that there can be no exchange of matter with the surroundings or work done by the system on the surroundings. The object of the experiment is to determine the energy of fusion at the melting temperature.

We state the following assumptions:

1. The substance is pure and melts at a constant temperature and has negligible vapor pressure.
2. The heat capacity of the cell (C_c) and the heat capacities of the liquid and solid are constants, independent of temperature.
3. The heat exchange between cell and jacket is given by eqn. (1) where the heat conduction constant (h) is known and is independent of temperature over the range of the experiment. Implicit in eqn. (1) is the assumption that the heat capacity of any material between jacket and calorimeter cell is negligible.
4. The temperature of the jacket is uniform at all times and changes linearly with time

   $$\theta_j = \theta_j(0) + \alpha t \tag{2}$$

   where $\theta_j(0)$ is the value of θ_j at time (t) equal to zero, and α is the programming or scanning rate of the jacket.
5. The temperature of the cell and its contents is uniform at all times.*

After this simple case has been worked out, the other possible arrangement and modes will be discussed. Finally, some of the possible consequences due to the above assumptions not holding will be considered.

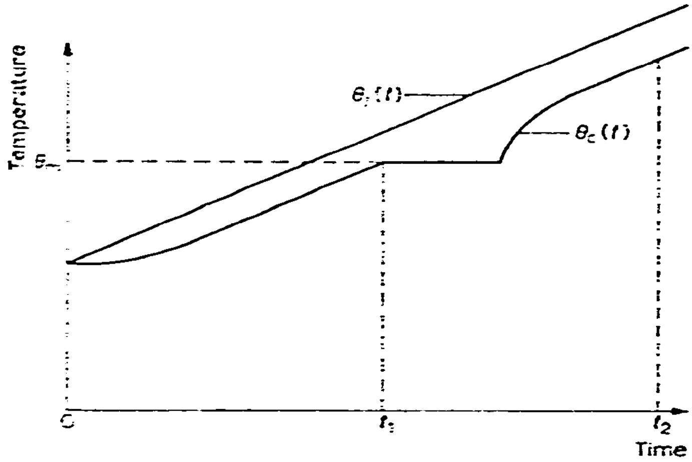

Fig. 2. Temperature of calorimeter jacket (θ_j) and calorimeter cell (θ_c) as functions of time for a melting process. θ_m is the melting temperature; $C_l > C_s$.

In Figs. 2 and 3 are shown qualitative pictures of the data one would expect to obtain for our simple case (IA1 in Table 1). Initially, the jacket and the cell with its contents are at the same temperature, $\theta_j(0) = \theta_c(0)$ at $t = 0$. The temperature of the

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*The last three statements are one-body model assumptions[14]. Clearly, it is impossible to build a perfect one-body calorimeter.

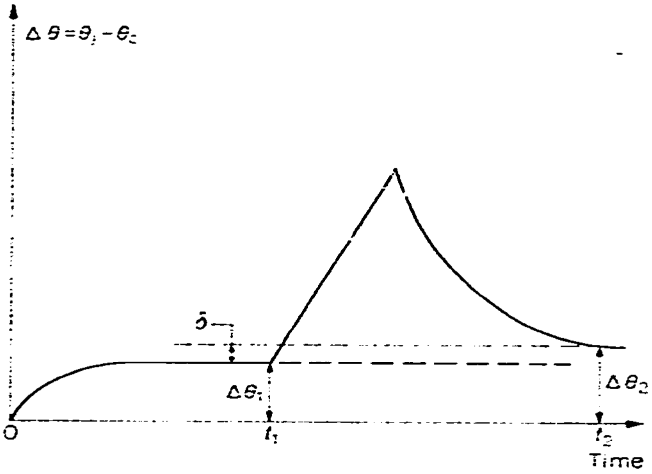

Fig. 3. Temperature difference ($\Delta\theta$) between calorimeter jacket and cell as a function of time during a melting experiment. $\Delta\theta_1$ and $\Delta\theta_2$ are the steady state temperature differences prior to and after melting, respectively; $\delta = \Delta\theta_2 - \Delta\theta_1$.

jacket is then increased at the rate α, according to eqn. (2). Since the heat flowing from the jacket to the cell is given by eqn. (1) we can write

$$C_1(\mathrm{d}\theta_c/\mathrm{d}t) = h(\theta_j - \theta_c) = h\Delta\theta \tag{3}$$

where C_1 is the heat capacity of the cell and the solid sample (the initial system). We solve eqn. (3) for θ_c and $\Delta\theta$ to obtain

$$\theta_c = (\theta_j(0) + \alpha t) + \frac{\alpha C_1}{h}(\mathrm{e}^{-ht/C_1} - 1) \tag{4}$$

$$\Delta\theta = \frac{\alpha C_1}{h}(1 - \mathrm{e}^{-ht/C_1}) \tag{5}$$

After the exponentials in eqns. (4) and (5) have died out for large t, we find that $\mathrm{d}\theta_c/\mathrm{d}t$ becomes equal to α and that

$$\Delta\theta = \Delta\theta_1 = \alpha C_1/h = \alpha\tau \tag{6}$$

The time during which $\Delta\theta_1$ is a constant constitutes the fore period baseline. At temperature θ_m, corresponding to time t_1 in Figs. 2 and 3, the sample will start to melt and the cell and its contents will remain at a constant temperature until the melting process is complete. Then, the temperature of the cell will catch up rapidly with the temperature of the jacket until a new after period baseline is achieved where, by reasoning similar to that given above, one can show that

$$\Delta\theta_2 = \frac{\alpha C_2}{h} \tag{7}$$

where C_2 is the heat capacity of the cell and the liquid sample (the final system). $\Delta\vartheta_2$ corresponds, like $\Delta\theta_1$, to the temperature difference between the jacket and the cell after the exponential term has become insignificant. In Figs. 2 and 3 the baseline shift due to the change in heat capacity has been exaggerated. The magnitude of the baseline shift is defined by the quantity δ, where

$$\delta = \Delta\theta_2 - \Delta\vartheta_1 = \frac{\alpha}{h}(C_2 - C_1). \tag{8}$$

At time t_1 in Figs. 2 and 3 our calorimeter cell contains the pure solid at temperature $\theta_{c1} = \theta_m$. This can be expressed as

$$\theta_{c1} = \theta_m = \theta_j(0) + \alpha t_1 - \Delta\theta_1 \tag{9}$$

By time t_2, the melting process has been completed and we now have cell and liquid sample at temperature θ_{c2}, which is given by

$$\theta_{c2} = \theta_j(0) + \alpha t_2 - \Delta\theta_2 \tag{10}$$

In eqns. (9) and (10), θ_{c1} and θ_{c2} are the temperatures of the cell at times t_1 and t_2, respectively, while $\Delta\theta_1$ and $\Delta\theta_2$ are the temperature differences between jacket and cell at these respective times. From the First Law of Thermodynamics, the total quantity of heat (Q) that has entered the sample cell, given by eqn. (11)

$$Q = h \int_{t_1}^{t_2} \Delta\theta \, \mathrm{d}t \tag{11}$$

is also equal to the change in internal energy for the process

$$\text{cell(at } \theta_{c1}) + \text{solid(at } \theta_{c1}) \rightarrow \text{cell(at } \theta_{c2}) + \text{liquid(at } \theta_{c2}). \tag{A}$$

But (A) may be treated as the sum of the two step process

$$\text{solid(at } \theta_{c1}) \rightarrow \text{liquid(at } \theta_{c1}) \tag{B}$$

$$\text{cell(at } \theta_{c1}) + \text{liquid(at } \theta_{c1}) \rightarrow \text{cell(at } \theta_{c2}) + \text{liquid(at } \theta_{c2}). \tag{C}$$

One may then deduce that

$$Q = h \int_{t_1}^{t_2} \Delta\theta \, \mathrm{d}t = \Delta U_{f,\theta_m} + (C_l + C_c)(\theta_{c2} - \theta_{c1}). \tag{12}$$

Eliminating the last term in eqn. (12) by means of eqns. (7), (9), (10), and the previous definition of the term δ, we obtain an expression for $\Delta U_{f,\theta_m}$ in terms of *experimentally measureable* quantities, namely

$$\Delta U_{f,\theta_m} = h \left[\int_{t_1}^{t_2} \Delta\theta \, \mathrm{d}t - \Delta\theta_2 (t_2 - t_1) + \left(\frac{\Delta\theta_2}{\alpha} \right) \delta \right]. \tag{13}$$

Equation (13) is a "prescription" for determining the energy of fusion of a pure compound for our simple case and within the context of the assumptions given above. Geometrically, the first two terms in the brackets of eqn. (13) represent the area *abc* minus the area of the triangle *acd* shown in Fig. 4. To this resultant area must be added the term $(\Delta\theta_2/\alpha)\delta$. The sum of these terms is then multiplied by the heat conduction constant h.

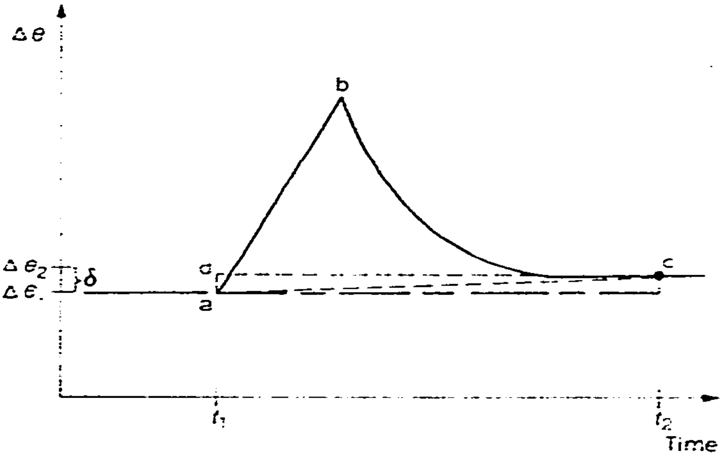

Fig. 4. Temperature difference between jacket and vessel as a function of time during a melting process using the single-cell mode of operation. The relevant areas that must be measured to obtain the energy of fusion ($\Delta U_{f,\theta_m}$) at the melting point are indicated on the figure.
$\Delta U_{f,\theta_m} = h(\text{area-}abc - \text{area-}acd + (\Delta\theta_2/\alpha)\delta)$.

We note that the choice of the time t_2 is immaterial provided that it is any time on the new baseline established after completion of the melting. However, the choice of the time t_1 is seen to be of consequence.

Physically, the last term in eqn. (13) multiplied by h is equal to $(C_l + C_c)\delta$ and corresponds to the quantity of heat required to raise the temperature of the cell and liquid sample over the temperature interval δ.

The assigned temperature of transition is θ_{c1}, given by eqn. (9).

Our treatment confirms that if there is no heat capacity change on melting, δ is equal to zero, and the correct area to be used in the calculation is the area above the baseline and under the peak due to the transition. In such a case, the heat of fusion is independent of temperature and the choice of t_1 and t_2.

The extension of our treatment to the experimental situation where θ_c and θ_j are measured as functions of time (case IB1 in Table 1) is trivial in that if one knows both these quantities as functions of time, this information can be combined to yield $\Delta\theta$ as a function of time, namely,

$$\theta_c = f(t) \tag{14}$$

$$\Delta\theta = \theta_j(0) + \alpha t - f(t) \tag{15}$$

The treatment of these data is then identical to that given in Section III above. If electrical compensation is used (case IB2) the treatment of the data would be as given in Section IV.

IV. CASE OF ELECTRICAL COMPENSATION

Case IA2 in Table 1 differs from the case just considered in that now electrical power, $P(t)$, is being provided by a heater contained within the cell. We will assume that the power is known accurately as a function of time and that proper accounting has been made for power generated in the heater leads[15]. If electrical heating is used only between the times t_1 and t_2 (see Fig. 3), the energy of fusion will then be given by

$$\Delta U_{f,\theta_m} = h\left[\int_{t_1}^{t_2} \Delta\theta \,\mathrm{d}t - \Delta\theta_2(t_2-t_1) + \left(\frac{\Delta\theta_2}{\alpha}\right)\delta\right] + \int_{t_1}^{t_2} P(t)\,\mathrm{d}t. \tag{16}$$

Since electrical compensation is being provided, the magnitude of the $\int_{t_1}^{t_2} \Delta\theta \mathrm{d}t$ term in eqn. (16) will be smaller than the same term in eqn. (13) where no compensation was provided. The principal advantage of electrical compensation is that electrical power can be measured very accurately and precisely when proper care is taken.

When total electrical compensation is attempted, one must demonstrate that the sum of the negative and positive heat exchange between calorimeter cell and jacket is negligible.

V. DOUBLE CELL OPERATION

In double cell, or differential operation, we have a "twin" cell contained within the jacket. Although the heat capacity (C') and the heat conduction constant (h') of the twin are approximately equal to that of the working cell, it does not contain a material that will undergo a thermal transition. It is evident that all of the equations developed earlier will apply to the twin cell. Thus, after the decay of an initial exponential term (eqn. 5), the temperature difference between the twin cell and jacket will be

$$\Delta\theta' = \frac{\alpha C'}{h'} \tag{17}$$

If one measures the quantity $(\Delta\theta - \Delta\theta')$, corresponding to case IIA1 in Table 1, one would obtain data of the sort shown in Fig. 5. The energy of fusion at temperature θ_{c1} would be given by eqn. (13) which is (by reference to Figs. 4 and 5) equivalent to

$$\Delta U_{f,\theta_m} = h\left[\text{area-}abc - \text{area-}acd + \left(\frac{\Delta\theta_2}{\alpha}\right)\delta\right]. \tag{18}$$

The quantity δ and the areas *abc* and *acd* are known from the data in Fig. 5, but the value of $\Delta\theta_2$ is not. We, therefore, conclude that double cell operation is feasible provided that the quantity $\Delta\theta_2$ (or $\Delta\theta_1$) is also measured, as in the single-cell mode of operation.

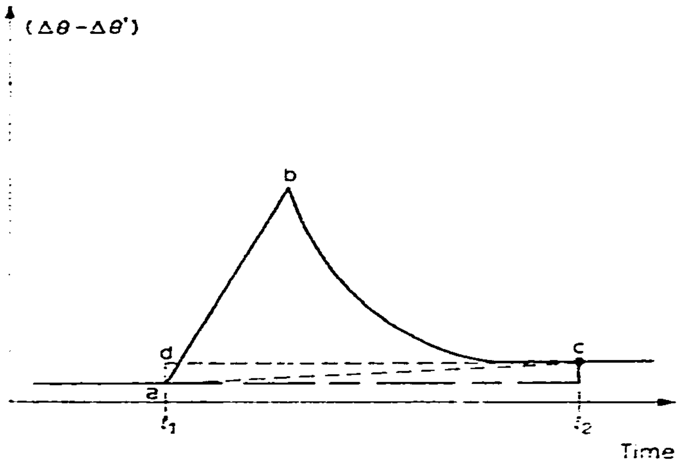

Fig. 5. Plot of $(\Delta\theta-\Delta\theta')$, the differential temperature difference, as a function of time for a melting process utilizing differential operation. In this experiment, the quantity δ and the areas *abc* and *acd* are measured, but the value of $\Delta\theta_2$ must be obtained by a separate measurement.

If electrical compensation is applied to the working cell, eqn. (16) would then be applicable. Again, the quantity $\Delta\theta_2$ must be measured.

If the difference in temperature of the individual cells $\theta_c - \theta_c'$, is measured (cases IIB1 and IIB2), this is equivalent to measuring the quantity $\Delta\theta - \Delta\theta'$ under our assumption of uniform jacket temperature. The treatment of the data would then follow the prescription given above.

The only reason for using differential operation would be to cancel out curvature in the baseline due to non-linear temperature programming of the jacket. Otherwise, differential operation should not be necessary.

VI. THE REAL SCANNING CALORIMETER

The treatment given above is based upon the assumptions stated in Section III. The real calorimeter, however, presents a much more complicated and difficult problem, and it is not the purpose of this paper to present a complete and rigorous solution for this problem. Nevertheless, we shall discuss in a qualitative way some of the consequences due to departures from the assumptions made earlier.

If the compound contained within the calorimeter has a vapor pressure, a correction to the measured energy of fusion can be applied using the procedure derived by Hoge[16]. A correction of this sort becomes necessary only in the case of highly accurate work or when the compound has a large vapor pressure. High accuracy work would also necessitate a correction for any impurities contained within the sample.

There are several effects that can make eqn. (3) non-linear. These effects are due to temperature dependencies of (1) the heat capacity of the calorimeter cell, (2) the heat conduction constant (h), and (3) the heat capacity of the sample itself. It is our belief that there are experimental remedies available that will help to minimize these difficulties although not entirely eliminate them. For example, if one provides electrical compensation during a melting experiment (see Section IV), the correction for heat exchange to the jacket is smaller and hence any temperature dependence of h becomes less important. It should also be possible to insure that the heat capacity of the calorimeter cell is reasonably constant over a small temperature range. Differential operation and a slow scanning rate should also help to minimize the above non-linear effects as well as non-linear temperature programming of the jacket. We note that if a transition occurs over a wide temperature range, as is frequently the case with protein denaturations[3], a very slow scanning rate may not be feasible.

If the equation for heat exchange between cell and jacket were by some chance different than eqn. (1), one would then have to modify all of the equations in the subsequent treatment. The difficulties and dangers inherent in a procedure of this sort can be avoided experimentally by (1) design of a calorimeter in such a way that most of the heat exchange is by conduction and (2) operation of the instrument in such a way that the temperature difference between jacket and cell is never excessively large.

As stated earlier, one cannot build a perfect one-body calorimeter. Gradients will always exist on the jacket and on and within the calorimeter cell. These gradients can be minimized, however, by means of vanes and by the use of materials having a high thermal diffusivity. We also note that all calorimetric measurements are comparison measurements between a known and an unknown quantity of heat and that meaningful calorimetric measurements can be made if the gradients on the surface of the calorimeter cell are the same for both the known and unknown heats. A test that has been proposed[17] to check the accuracy of calorimetric measurements is that of heater placement. To perform this test, one moves the heater about within the calorimeter cell and determines the effects of these operations on the experimental results. In an accurate calorimeter, heater placement should make little or no difference.

An additional effect of lags in the calorimeter would be to distort the shape of the scanning curve from that predicted by the one-body model. Thus, one should expect to find a rounded curve rather than a curve of the type depicted in Fig. 4 which demonstrates abrupt changes corresponding to the onset and end of melting.

Equation (13) was derived, in part, in order to be able to account for the baseline shift encountered in scanning calorimetry. Recently, Guttman and Flynn[18], have developed a treatment specifically for the type of scanning calorimeter developed by Watson *et al.*[2]. It is hoped that as scanning calorimetry becomes more accurate treatments of this sort will come into wider usage.

Earlier in this paper it was stated that the time constant was an important characteristic of the calorimeter. It is our contention that, for heat conduction calorimetry, it is desirable to have a small time constant. The reason for this lies in the fact that the experiment is not completed until the curve has reached the after-period baseline. For example, if we have a calorimeter with a time constant of 100 seconds, a peak on its decay to the baseline will fall to half of its value in 69 seconds. If we consider the curve to have returned to its baseline when it has fallen to one one-thousandth of its maximum value, we calculate that we must wait approximately ten half-times for this to happen, which in the case of our example corresponds to 690 seconds. We feel that a time constant of about this order of magnitude probably constitutes a practical upper limit for scanning calorimetry. If it is exceeded, not only does one lose the advantage of speed, but if one wishes to measure small heat effects, one must contend with the variety of thermal disturbances that can occur during this long wait for a return to baseline.

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