PHYSICAL TRANSFORMATIONS IN DIFFERENTIAL SCANNING CALORIMETRY *

CONSTANTINE SANDU ** and RAKESH K. SINGH ***

Department of Food Science, Purdue University, West Lafayette, IN 47907 (U.S.A.)

(Received 14 December 1987)

ABSTRACT

The mathematical model for describing physical transformations in differential scanning calorimetry (DSC) encompasses by necessity, a series of assumptions. However, the procedure which involves the use of an empty reference pan and the analytical extrapolation of the data to zero heating rate allows for accurate results. Basically, this is the common practice in DSC studies. This paper offers mathematical and physical reasons for the justification of this practice. Any departure from the assumptions of the mathematical approach can introduce errors in the DSC analysis of physical transformations.

INTRODUCTION

Two of the corrections required by a DSC record, i.e. non-linearity and thermal lag corrections, are determined on the basis of measurements that involve physical transformations. Melting of various reference substances, for example, is a standard procedure for estimating these types of corrections [1]. However, using physical transformations for the purpose of DSC calibrations raises the question of the assumptions and errors contained in the model which describes these transformations.

During a chemical transformation, the temperature of the sample material follows the instrumentally programmed temperature, usually shown on the abscissa of the DSC record. In contrast, for physical transformations, the temperature history of the sample corresponds to the programmed temperature only in the pre-transition state. Once the instrument reaches the temperature of the phase transformation, the sample temperature remains constant until the transition state of the physical transformation is complete.

In the post-transition state, the sample temperature strives to match the instrumentally programmed temperature as fast as the heat transfer in the system allows. (Nevertheless, the temperature of the reference material is supposed to follow entirely the instrumentally programmed temperature in both chemical and physical transformations.)

The differential scanning calorimetric model previously used by Sandu and Lund [2] constitutes the basics in deriving the mathematics of physical transformations in DSC. Analytically, the entire approach will differ from that employed by Gray [3], although under particular considerations both sets of results are in agreement.

ASSUMPTIONS

The signal on the ordinate of the DSC record is the result of three effects: (a) an instrumental signal; (b) a signal due to the sensible-heat difference between sample and reference materials; and (c) a signal due to the chemical/physical transformation in the sample material (provided that the reference material is inert). In analytical terms [2], the ordinate signal has the expression

$$y = Y_0 + \alpha_s \left[C_s - C_r \left(1 + R_0 \frac{dq}{dT_s} \right) \right] \pm b \tag{1}$$

where y is the DSC ordinate signal (W), Y_0 is the instrumental signal (W), α_s is the instantaneous heating rate of the sample material (K s^{-1}), C_s and C_r are the mass of the sample and reference material, respectively, multiplied by heat capacity (J K^{-1}), R_0 is the heat transfer resistance (K W^{-1}), q is the difference in the heat flows to the sample and reference materials (W), T_s is the instantaneous temperature of the sample material (K), and b is the pure transformation signal (W). The $\pm$ sign depends on the conventional representation of the endothermic/exothermic effects on the DSC record.

At any time during the pre-transition and post-transition states of a physical transformation, the heating rate of the sample material relates to the heating rate of the reference material [2] via the relation

$$\alpha_s = \alpha_r / \left(1 + R_0 \frac{dq}{dT_s} \right) \tag{2}$$

where α_r is the instantaneous heating rate of the reference material (K s^{-1}). During the transition state of a physical transformation, eqn. (2) is no longer valid (see next section). (In the case of a chemical transformation, eqn. (2) is applicable over the entire range [2].)

Finally, for a given heating rate α (K s^{-1}) imposed by the DSC instrument at the sample platform, parameters Y_0, α_r, R_0, C_s and C_r in eqns. (1) and (2) are considered to be constants. Nevertheless, the heating rate a_s of

the sample material during a physical transformation changes from one state to the other, triggering a particular shape of the transformation signal (see next section).

TRANSFORMATION SIGNAL

In the pre-transition state, there is no pure transformation signal (that is, $\pm b = 0$) and the heating rate of the sample material assumes a finite constant value. Therefore, eqns. (1) and (2) combine into the following relation

$$y_1 = Y_0 + (\alpha_{s1}C_{s1} - \alpha_r C_r) \tag{3}$$

where 1 denotes the pre-transition state.

During the transition state of a physical transformation the heating rate of the sample material vanishes (that is, $\alpha_{s2} = dT_{s2}/dt = 0$, where t is the time (s)) because the temperature inside the sample remains constant. Equation (2) is not valid while the phase transformation occurs. Under these assumptions, eqn. (1) simplifies to

$$y_2 = Y_0 \pm b \tag{4}$$

where 2 denotes the transition state. Using basic assumptions in DSC (see ref. 2) it can be shown that

$$\pm b = q_2 = (T_r - T_{\text{trans}})/R_0 \tag{5}$$

where T_r is the instantaneous temperature of the reference material (K) and T_{trans} is the instantaneous temperature of the sample material (K) during the phase transformation, regarded as constant.

Let us fix the time zero at the moment when the transition state starts and let us assume that the reference material has the temperature T_{r0} at $t = 0$. As a result, the reference temperature during the transition and post-transition states can be described by the relation

$$T_r = T_{r0} + \alpha_r t \tag{6}$$

However, at $t = 0$, the condition $y_1 = y_2$ is fulfilled, so that it can be easily demonstrated that

$$T_{r0} = T_{\text{trans}} + R_0(\alpha_{s1}C_{s1} - \alpha_r C_r) \tag{7}$$

Combining eqns. (4)–(7) results in the DSC ordinate signal during the transition state

$$y_2 = Y_0 + (\alpha_{s1}C_{s1} - \alpha_r C_r) + \frac{\alpha_r t}{R_0} \tag{8}$$

that is, a straight line with the intercept y_1 and the slope α_r/R_0 (W s^{-1}). At

the end of the transition state, the difference in the heat flow reaches a maximum

$$q_{2\max} \equiv y_{2\max} - Y_0 = (\alpha_{s1}C_{s1} - \alpha_r C_r) + \frac{\alpha_r t_{\max}}{R_0} \tag{9}$$

where $t_{\max}$ is the time interval (s) on the DSC record required to bring the phase transformation to completion. Equation (9) is used later on in the mathematical model.

In the post-transition state, the pure transformation signal vanishes (that is, $\pm b = 0$), whereas the heating rate of the sample material changes according to eqn. (2). Under these assumptions, eqn. (1) becomes

$$y_3 = Y_0 + \frac{\alpha_r C_{s3}}{1 + R_0(dq_3/dT_{s3})} - \alpha_r C_r \tag{10}$$

Boundary condition at $T_{s3} = T_{trans}$, $q_3 = q_{2\max}$

where 3 denotes the post-transition state and the relation $y_3 - Y_0 = q_3$ holds (see ref. 2). After mathematical manipulations, the solution to this differential equation is (see ref. 4)

$$q_3 = [q_{2\max} - \alpha_r(C_{s3} - C_r)] \exp\left(-\frac{T_{s3} - T_{trans}}{\alpha_r R_0 C_{s3}}\right) \exp\left(\frac{q_{2\max} - q_3}{\alpha_r C_{s3}}\right)$$
$$+ \alpha_r(C_{s3} - C_r) \tag{11}$$

From basic assumptions in DSC (see ref. 2), it can be shown that

$$q_3 = (T_r - T_{s3})/R_0 \tag{12}$$

Further mathematical manipulations involving eqns. (6), (7) and (9)–(12) result in the DSC ordinate signal during the post-transition state

$$y_3 = Y_0 + \alpha_r(C_{s3} - C_r) + [q_{2\max} - \alpha_r(C_{s3} - C_r)] \exp\left(-\frac{t - t_{\max}}{R_0 C_{s3}}\right) \tag{13}$$

that is, an exponential curve. As time goes to infinity, eqn. (13) yields the asymptote

$$y_3^\star = Y_0 + \alpha_r(C_{s3} - C_r) \tag{14}$$

It can also be demonstrated that, at the beginning of the post-transition state, the heating rate of the sample material has the value

$$\alpha_{s3\max} = (q_{2\max} + \alpha_r C_r)/C_{s3} \tag{15}$$

followed by an exponential change until, at infinite time, it reaches the value α_r.

TRANSFORMATION PARAMETERS

The model developed so far is applicable to any type of physical transformation. Figure 1 represents the theoretical DSC record of a melting process.
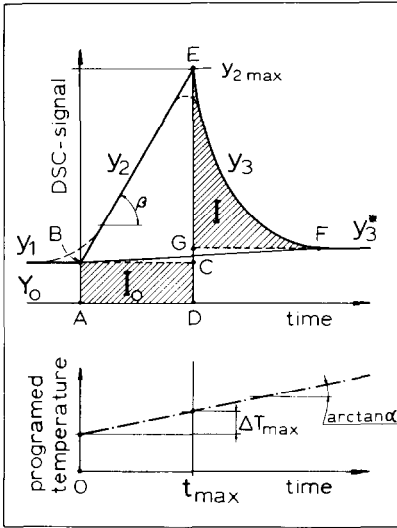
Fig. 1. Melting transformation in DSC. The onset point (B) and the end point (E) of a real DSC record are determined by extrapolation of the corresponding lines.

There are three parameters connected with physical change measurements in DSC that serve for calibration purposes: (latent) heat of transformation, transformation temperature and heat transfer resistance.

Consider that the following assumptions are perfectly valid for the relations derived in the previous section

$$\alpha_{sl} \simeq \alpha_r \simeq \alpha \tag{16}$$

$$T = T_{trans} + \alpha t \tag{17}$$

where T is the instrumentally programmed temperature (K) at the sample platform. Basically, although the developed model encompasses time as the independent variable, it is obvious that all relations can be easily expressed in terms of temperature by using eqn. (17).

From kinetic considerations (see ref. 5) it can be shown that

$$\int_0^{t_{max}} \pm b \; dt + \int_0^1 (\Delta H_R) m_0 \; df = (\Delta H_R) m_0 \tag{18}$$

where (ΔH_R) is the heat of physical transformation (J kg-mole^{-1}), m_0 is the amount of sample material (kg-mole) and f is the fraction conversion (dimensionless). Mathematical manipulations involving eqns. (3)–(5), (9), (16) and (18) result in

$$(\Delta H_R) = \frac{1}{m_0} \left[(y_1 - Y_0) t_{max} + \frac{(y_{2\,max} - y_1) t_{max}}{2} \right] \tag{19}$$

where the first term on the right-hand side represents the rectangular area ABCD and the second term is the triangular area BEC in Fig. 1. For a given

amount of sample material, the three parameters $y_1 - Y_0$, $y_{2\max} - y_1$ and $t_{\max}$ are measurable on the DSC record. If the abscissa of the DSC record is temperature, $t_{\max}$ is replaced by $\Delta T_{\max}/\alpha$ in eqn. (19), where $\Delta T_{\max}$ is the increase in the programmed temperature (K) corresponding to the transition state, also measurable on the record.

The instrumental signal Y_0 is the DSC ordinate when sample and reference platforms are loaded with empty pans under the same instrument settings as the DSC record considered. However, this implies a supplemental measurement, unless the rectangular area term in eqn. (19) can be replaced with an easy to measure counterpart. The only possibility is to evaluate the area EFG in Fig. 1, where point G $(t = t_{\max}, \ y = y_3^\star)$ is well defined, whereas point F is conventionally placed on the diagram. First, it can be demonstrated (from eqns. (3), (9) and (16)) that the integral corresponding to the area ABCD is

$$I_0 = R_0(C_{s1} - C_r)\left[y_{2\max} - Y_0 - \alpha(C_{s1} - C_r)\right] \tag{20}$$

where I_0 is in joules. Next, area EFG represents the integral of the exponential term in eqn. (13), from $t = t_{\max}$ to $t = \infty$. Further manipulations involving eqns. (3), (14) and (16) lead to the result (J)

$$I = R_0 C_{s3}\left[y_{2\max} - Y_0 - \alpha(C_{s3} - C_r)\right] \tag{21}$$

These last two equations are identical only if two conditions are fulfilled simultaneously: (a) the heat content of the reference material is negligible, that is, an empty reference pan ($C_r \simeq 0$), and (b) either the heat content of the sample material does not change significantly during the phase transition (that is, $(C_{s3} - C_{s1}) \to 0$) or the heating rate is very small (that is, $\alpha \to 0$).

With the assumption of an empty reference pan (condition (a)) in eqns. (20) and (21), it can be shown that

$$I_0 - I = R_0\alpha(C_{s3} - C_{s1})\left[(C_{s3} + C_{s1}) - \frac{y_{2\max} - Y_0}{\alpha}\right] \tag{22}$$

On the other hand, from eqns. (2), (14) and (16) one finds the relation

$$y_3^\star - y_1 = \alpha(C_{s3}C_{s1}) \equiv \alpha m_0(c_{s3} - c_{s1}) \tag{23}$$

where c_s is the heat capacity of the sample material (J kg-mol^{-1} K^{-1}). From the last two equations one can infer that condition (b) is always accomplished when the asymptote to the post-transition curve is a continuation of the pre-transition line (that is, $y_3^\star \simeq y_1$ or segment CG in Fig. 1 vanishes). The practical way to accomplish this requirement is to apply very small heating rates (that is, $\alpha \to 0$).

Consequently, under the assumption of an empty reference pan as well as sufficiently small heating rates, the area ABCD is approximated by the area EFG in Fig. 1. In this case, eqn. (19) becomes

$$(\Delta H_R) \simeq \frac{1}{m_0}(\text{area BEF})_{\text{at }\alpha \to 0} \tag{24}$$

where area BEF is measured in Fig. 1 in terms of Ws = J. A supplement error can always be connected with the ill-defined point F.

If only the assumption of an empty reference pan is taken into account in eqn. (19), the heat of physical transformation results as

$$(\Delta H_R) = \frac{1}{m_0} \left[\alpha C_{s1} t_{max} + \frac{\alpha t_{max}^2}{2 R_0} \right]$$ (25)

$$C_{s1} = c_{s1} m_0$$ (26)

$$\alpha / R_0 = \tan \beta$$ (27)

where $\tan \beta$ is the slope of the transition line (W s^{-1}) on the DSC record (Fig. 1). This solution requires a known heat capacity of the sample material during the pre-transition state.

From thermodynamic considerations, the heat capacity increases on melting of a solid substance; using the Nernst heat theorem (see ref. 6, p. 631) it can be shown that

$$(\Delta H_R) m_0 = T_{trans} (C_{s3} - C_{s1})$$ (28)

Combining eqns. (23) and (28) allows for another relation to calculate the heat of melting/solidification

$$(\Delta H_R) = \frac{T_{trans}}{m_0 \alpha} (y_3^\star - y_1)$$ (29)

For a given amount of sample material and for a given heating rate, the two parameters T_{trans} and $y_3^\star - y_1$ are measurable on the DSC record. Nevertheless, the use of eqn. (29) is limited by the fact that, at a given instrumental resolution of the ordinate signal, the parameter $y_3^\star - y_1$ cannot always be measured accurately on the record.

At a given pressure, the transformation temperature is an intrinsic property of the substance. Theoretically, the temperature at which the physical change takes place does not depend upon the heating rate imposed by the DSC instrument at the sample platform. Consequently, point B in Fig. 1 is always located at the intersection between the pre-transition line y_1 and the transition line y_2 (see ref. 1).

Finally, the heat transfer resistance is a property of the DSC instrument per se. This parameter changes with the heating rate and can be determined from the slope of the transition line of a physical transformation y_2 (Fig. 1 and eqn. (27)) (see ref. 7).

RESULTS

DSC records of melting transformation for phenyl ether and indium are reproduced in Figs. 2 and 3. The substances were provided by the United
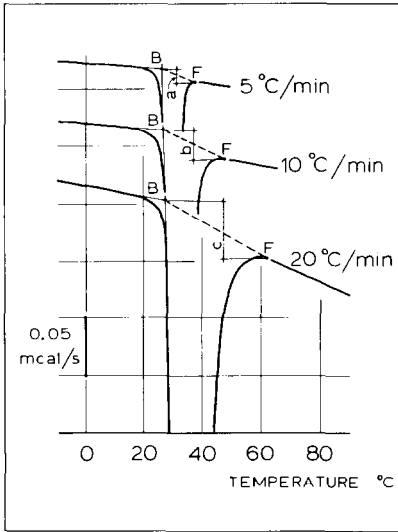
Fig. 2. Melting of phenyl ether at different heating rates. Amount of sample material, 15.0 mg. Empty reference pan.

States National Bureau of Standards. Measurements were carried out on a DuPont 990 thermal analyzer (E.I. DuPont de Nemours Co. (Inc.), Instrument Products Division, Wilmington, DE) using empty reference pans.
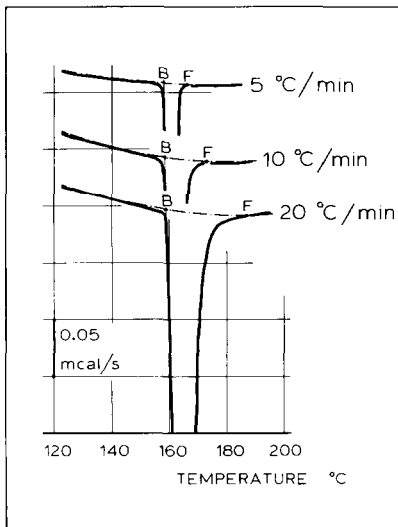

Fig. 3. Melting of indium at different heating rates. Amount of sample material, 14.95 mg. Empty reference pan.

DISCUSSION

The mathematical model implies two step changes in the heating rate of the sample material at points B and E (Fig. 1). These types of changes are rather features of an ideal stirred reactor and they cannot be approached by the sample pan in DSC. Temperature gradients are expected to be always present in a sample which is not subject to any agitation. A real DSC record implies gradual changes in heating fate of the sample around points B and E (broken lines in Fig. 1). Consequently, points B and E are to be found at the intersection of the corresponding extrapolations of the lines as shown in Fig. 1.

The records in Figs. 2 and 3 exhibit a slight change in the transformation temperature (also known as onset temperature) vs. heating rate. This behavior cannot be theoretically predicted. Simply, it is the byproduct of the assumptions contained in the mathematical model. Therefore, it is analytically necessary to extrapolate the onset temperature to the so-called zero heating rate.

Phenyl ether (Fig. 2) reveals an almost theoretical behavior. The post-transition curve rapidly reaches the asymptotic value. Consequently, point F can be graphically defined with accuracy. Line segments a, b and c in Fig. 2 represent the values for $y_3^\star - y_1$. At different heating rates (by applying eqn. (23)) these line segments are related as

$$b/a = 2; \quad c/b = 2; \quad c/a = 4 \tag{30}$$

These values are confirmed by the data in Fig. 2, which means that the melting of phenyl ether implies a measurable change in heat capacity of the sample material before and after the transition state.

Usually the DSC data measurements do not include the evaluation of the instrumental signal; as a result, it is not feasible to use eqn. (19) to compute the heat of physical transformation. However, on the other hand, if the reference pan is empty and the data are extrapolated to zero heating rate, eqn. (24) can give accurate results. This implies the measurement of the area BEF under the transformation curve, where line BF is graphically determined as in Fig. 2. Extrapolating to zero heating rate assures the condition $I_0 \simeq I$ in Fig. 1 (see eqn. (22)). Once the heat of physical transformation is determined, eqns. (23) and (25)–(27) can be used to calculate the heat capacities of the sample material before and after the transition state.

Indium (Fig. 3) proves to have a particular behavior in DSC due to negligible change in its heat capacity during melting. Graphically, it is shown that the asymptote to the post-transition curve is, within the resolution of the ordinate measurements in Fig. 3, a continuation of the pre-transition line, that is, $y_3^\star \simeq y_1$. In this case, eqn. (24) is readily applicable to determine the heat of transformation. An extrapolation to zero heating rate can improve the result, but it is not required when heat capacity does not change significantly.

CONCLUSIONS

DSC measurements of physical transformations allow the determination of the following: transformation temperature (onset temperature); (latent) heat of transformation; heat capacity of the substance before the transformation; heat capacity of the substance after the transformation. The purpose of these parameters is many-fold: characterization of substances, purity measurements, determination of kinetics and calibration of DSC instruments. In addition, there is another parameter of interest obtained from a physical transformation, that is, the heat transfer resistance in a DSC instrument. This parameter is needed in order to correct the DSC record of a chemical transformation.

LIST OF SYMBOLS

a, b, c	line segments in Fig. 2 representing the difference $y_3^\star - y_1$ for different heating rates (mcal s^{-1})
(area BEF)	area under the transformation curve in Fig. 1 (W · s) or (W · K)
b	pure transformation signal (W)
c	heat capacity (J kg-mol^{-1} K^{-1})
C	heat content (J K^{-1})
f	fraction conversion (dimensionless)
I	area EFG in Fig. 1 (W · s) or (W · K); with subscript 0 refers to the area ABCD in Fig. 1
m_0	amount of sample material (kg-mol)
q	difference in the heat flows to the sample and reference materials (W)
R_0	heat transfer resistance (K W^{-1})
t	time (s); zero time is fixed when the transition state starts
T	temperature (K)
y	DSC ordinate signal (w)
$y_3^\star$	asymptotic value of y_3 (W)
Y_0	instrumental signal (W)
α	heating rate (K s^{-1}); without a subscript refers to the heating rate instrumentally imposed at sample platform.

β arctan (α/R_0, angle defined in Fig. 1 (deg)

ΔH_R heat of transformation (J kg-mol^{-1})

Subscripts

0	at zero time
1	pertaining to the pre-transition state
2	pertaining to the transition state
3	pertaining to the post-transition state
max	pertaining to the end of transition state (curve maximum)
r	pertaining to the reference material
s	pertaining to the sample material
trans	transition or onset

REFERENCES

1 ASTM E474-80, 1982 Annual Book of ASTM Standards, Part 41, American Society for Testing and Materials, Philadelphia, 1982.
2 C. Sandu and D. Lund, Thermochim. Acta, 88 (1985) 453.
3 A.P. Gray, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 1, Plenum, New York, 1968.
4 E. Kamke, Differentialgleichungen. Lösungsmethoden und Lösungen, Band 1, Gewöhnliche Differentialgleichungen, Chelsea Publishing Company, New York, 1948.
5 C. Sandu, D. Lund and K.-H. Park, in X.J.R. Avula, R.E. Kalman, A.I. Liapis and E.Y. Rodin (Eds.), Mathematical Modeling in Science and Technology, Pergamon, New York, 1984.
6 J. Thewlis (Ed.-in-Chief), Encyclopedic Dictionary of Physics, Vol. 6, Pergamon, Oxford, 1962.
7 ASTM E698-79, 1982 Annual Book of ASTM Standards, Part 41, American Society for Testing and Materials, Philadelphia, 1982.