MODELING DIFFERENTIAL SCANNING CALORIMETRY *

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ABSTRACT

The present study is a unified mathematical approach to the analysis of DSC data. It addresses the baseline correction to the DSC record as well as the solutions of DSC curves of single or multiple, physical and chemical transformations. In this study, previous results in the pertinent literature become particular solutions of the general model.

The transition baseline in a physical transformation is identical with the instrumental signal. When an 'empty' reference pan is used and the results are extrapolated to zero heating-rate, a pseudo-baseline can be defined. Physical transformations in DSC display a straight line signal during transition, followed by an exponential curve during the post-transition state. The model gives solutions for temperature and heat of transformation in both single and multiple physical transformations.

The equation of the transition baseline in a chemical transformation accounts for: the pre-transition baseline; the heat-capacity change from that of the reactants to that of the products of the reaction; and the heating-rate difference between sample and reference materials. If there is no change in the heat capacities and either the reference pan is 'empty' or the thermal resistance is negligible, then the transition baseline is an extension of the pre-transition baseline. The DSC curve represents the corrected DSC record.

The DSC curve of a chemical transformation is a bell-shaped graph whose skewness depends on the order of reaction. From the distinctive features of the DSC curve (i.e., relations at curve peak, inflection points and curve-bounded area), the apparent kinetic parameters are calculated (order of reaction, activation energy, pre-exponential factor and heat of reaction). The parameters specifically involved in these calculations are: peak temperature, inflection point temperature(s), shape index, area before peak, area after peak, asymmetry index, peak area and partial areas. The larger the asymmetry index, the smaller the reaction order. Final solutions contain the heating rate and the initial concentration (initial amount of reactant) as parameters. A zero-order chemical reaction displays an exponential signal and its solutions are particular.

Two multiple reaction systems in DSC are analyzed: (a) two irreversible, first-order, parallel reactions, and (b) two irreversible, first-order, consecutive reactions. In the first case, the apparent kinetic parameters correlate with the area before the maxima/minima of the

DSC curve. In the second case, the main parameter is the deflection at the maxima/minima. General-order, mechanistically uncoupled reactions are also discussed.

Emphasis is placed on the assumptions and the analytical development as well as on the final solutions and their applicability range. The mathematics of physical transformations are referenced with time as an independent variable, whereas chemical transformations relate to temperature. No attempt was made to express the final solutions in both time and temperature coordinates.

DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) (Fig. 1) monitors the difference in heat flow between a sample (i.e., reacting system) and a reference (i.e., inert system) when both systems are subject to a controlled linear temperature change. With the onset of the physical/chemical transformation in the reacting system, the heat flow into the sample material adjusts to compensate for the exothermic/endothermic effects of reaction. Accordingly, the history of heat flow difference becomes a fingerprint for the transformation occurring in the sample material during heating.

For illustration purposes, it is assumed that the schematic in Fig. 1 refers to a DuPont 990 thermal analyzer (E.I. DuPont de Nemours Co., Inc., Instrument Products Division, Wilmington, Delaware). This particular instrument uses a constantan disc as the (electrical) heater, supplying energy to the sample and reference pans. At the same time, the constantan disc serves as one element of the temperature-measuring sensors (Fig. 1). Temperatures at the raised sample and reference platforms are monitored by chromel–constantan thermocouples, formed by the junction of the constantan disc with a chromel wire at each platform position. The output difference between these two thermocouples is monitored as the difference in energy flow (W) on the ordinate of the DSC record. The sample platform has an additional chromel–alumel thermocouple, whose output is monitored as temperature (K) on the abscissa of the DSC record.
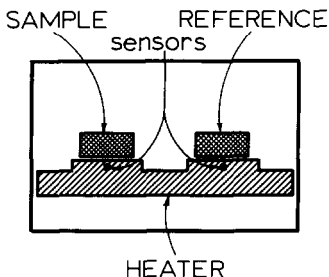

Fig. 1. Differential scanning calorimetry technique. Sample and reference are subject to a linear temperature change.

According to the design of the DSC instrument, the sample and reference heating platforms are expected to follow a linear temperature change (regardless of the instantaneous state of the sample or reference materials)

$$T = T_0 + \alpha t \tag{1}$$

where T is the abscissa parameter on the DSC record (K), T_0 is the initial temperature (K), α is the instrumentally imposed constant heating rate (positive or negative) for a given run (K s^{-1}), and t is time (s).

From Fig. 1, it is obvious that the heat transfer to the sample/reference pan occurs by conduction, where the contact zone may represent the controlling thermal resistance. The sensors are not located inside the sample/reference pan. The instantaneous temperature state of the sample material depends on the exothermic/endothermic effects. Under these conditions, the actual temperatures in sample and reference materials slightly differ from each other as well as from the temperature registered on the abscissa of the DSC record. The same is true for the actual heating rates of sample and reference materials versus the instrumentally imposed heating rate. It is the design, operation and control of the instrument that minimizes these effects. With good contact between the sample/reference pan and the heating platform (Fig. 1), and by using very thin and highly thermally conductive metal pans, the temperature inside the sample/reference material will be reasonably well represented by the abscissa of the DSC record (physical transformations being an exception).

At any time, the signal on the ordinate of the DSC record is the result of three effects: an instrumental signal; a signal due to the sensible heat difference between sample and reference materials; and a signal due to the physical/chemical transformations of the sample material (provided the reference material is inert). The sum of the first two effects represents the baseline of the DSC record.

To assess the real signal produced by the physical/chemical transformations in the reacting system, the DSC record requires a series of corrections: the non-linearity correction (referring to the signal output from the thermocouple giving the temperature on the abscissa of the DSC record); the heating rate correction; the thermal lag correction (due to thermal resistance in the heat transfer from the heating platform to the sample/reference pan); and the baseline correction (connected with the variation in heat capacity during the transformation from the reactants to the reaction products). The first two corrections are technical problems (successfully solved by modern electronically equipped DSC instruments), whereas the last two are analytical and are inherent in every model used for evaluating DSC data.

The heat capacity of the sample material changes from that given by the mixture of the reactants, before the physical/chemical transformation, to that given by the mixture of the products of reaction after the transformation. During the transformation, the heat capacity is that of a mixture of

reactants and products of reaction corresponding to the instantaneous progress of the reaction. The DSC record reveals three distinct states: pre-transition, transition, and post-transition.

During a chemical transformation, the temperature of the sample material 'closely' follows the instrumentally programmed temperature. 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 phase transformation, the sample temperature remains constant until the transition state is complete. In the post-transition state, the sample temperature strives to recover and to match the instrumentally programmed temperature. Nevertheless, the temperature of the reference material follows the instrumentally programmed temperature in both chemical and physical transformations.

Based on previous work by Sandu et al. [1–4], the authors present here the mathematical modeling of differential scanning calorimetry with emphasis on corrections to the DSC record, the physical/chemical transformations in DSC, and the apparent reaction-kinetic parameters derived from DSC data.

CORRECTIONS TO THE DSC RECORD

The non-linearity correction is usually performed by running standard materials whose melting points are very well established [5]. Once the non-linearity correction is accomplished, the heating-rate correction encompasses the direct checking of the instrument performance at different heating-rate settings [6]. Therefore, the only correction to the DSC records that needs to be analytically performed is the baseline correction. Thermal resistance (NB, thermal lag correction) is one of the parameters used in the baseline equations of the DSC record.

The DSC record is a graph of the difference in energy flow (W) plotted on the ordinate, for a conventional representation of the exothermic/endothermic effects, versus temperature (K) or time (s) on the abscissa. Besides the baseline equation, analysis of the DSC record requires the definition of the onset (beginning) and end points of a transformation (see Fig. 3, later).

Selected references treating various aspects related to the mathematics developed in this section include: Heuvel and Lind [7], Brennan et al. [8, 9], Richardson and Burrington [10], McNaughton and Mortimer [11], Holba et al. [12], and Gorbachev [13].

Baseline assumptions and equations

(a) The heating source (Fig. 2) is characterized by a uniform (time dependent) temperature, T_{source}.
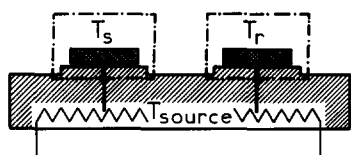
Fig. 2. Heat flow in DSC. Heat transfer to the sample/reference occurs by conduction.

(b) The thermal resistance, R_0, is the same for both platform–pan systems and is assumed to be constant for a given heating rate, α, imposed by the instrument.

(c) There are no thermal gradients inside the sample/reference materials. The sample and reference materials are described by instantaneous temperatures T_s and T_r, respectively

$$T_s = T_0 + \alpha_s t \tag{2}$$

$$T_r = T_0 + \alpha_r t \tag{3}$$

where α_s and α_r are instantaneous heating rates of sample/reference materials (K s^{-1}), and subscripts s and r refer to sample and reference.

The inertness of the reference material facilitates a precise control of its temperature. For $\alpha_r \simeq \alpha$, eqns. (3) and (1) are identical, that is, the reference material follows a linear time–temperature change. In contrast, exothermic/endothermic effects in the sample material induce instantaneous variations in its heating rate, that is, α_s is a function of time. This implies that the sample material follows a complex time–temperature change (eqn. (2)). Furthermore, sample and reference materials are instantaneously at different temperatures, a state that generates the difference in heat flow between the two systems which is the principle of DSC.

One can define the holding pans together with the corresponding platforms (Fig. 2) as two closed systems at uniform temperatures T_s and T_r, respectively. The heat flow from the heating source to both the sample and reference systems (Fig. 2) is the result of heat transfer by conduction

$$q_s = (T_{source} - T_s)/R_0 \tag{4}$$

$$q_r = (T_{source} - T_r)/R_0 \tag{5}$$

where R_0 is the thermal resistance (K W^{-1}), assumed constant for a given instrumental heating rate. The difference in heat flow readily results as

$$q \equiv q_s - q_r = (T_r - T_s)/R_0 \tag{6}$$

while the following equation gives its variation versus the temperature of the sample material

$$(dq/dT_s)\alpha_s = (\alpha_r - \alpha_s)/R_0 \tag{7}$$

The difference in heat flow is due to the difference in sensible heat between sample and reference materials as well as the heat effect due to the

physical/chemical transformation in the sample material (provided the reference material is inert)

$$q = (C_s \alpha_s - C_r \alpha_r) \pm b \tag{8}$$

where C_s and C_r are the mass of the sample and reference material, respectively, multiplied by the corresponding heat capacity ($J\ K^{-1}$), and b is the pure transformation signal (W). The $\pm$ sign depends on the conventional representation of the exothermic/endothermic effects on the DSC record.

The actual signal on the ordinate of the DSC record also encompasses the instrumental signal

$$y \equiv Y_0 + q = Y_0 + (C_s \alpha_s - C_r \alpha_r) \pm b \tag{9}$$

where Y_0 is the instrumental signal (W). The instrumental signal is the DSC ordinate when sample and reference platforms are loaded with empty pans under the same instrument settings as the DSC record under consideration. This particular term takes into account eventual design/control imbalances between sample and reference systems, as well as the pan heat-capacity and the thermal resistance changes with temperature. Eliminating α_r between eqns. (7) and (9) results in the DSC ordinate signal

$$y = Y_0 + \alpha_s \{ C_s - C_r [1 + R_0 (dq/dT_s)] \} \pm b \tag{10}$$

where the sum of the first two terms on the right-hand-side represents the baseline of the DSC record.

Equations (9) and (10) are valid at any time during a physical/chemical transformation, that is

$$y_1 = Y_0 + q_1 \tag{11}$$

$$y_2 = Y_0 + q_2 \tag{12}$$

$$y_3 = Y_0 + q_3 \tag{13}$$

$$y_1 = Y_0 + \alpha_s \{ C_{s1} - C_r [1 + R_0 (dq_1/dT_s)] \}; \qquad b = 0 \tag{14}$$

$$y_{trans} \equiv (y_2 - (\pm b)) = Y_0 + \alpha_s \{ C_{s2} - C_r [1 + R_0 (dq_2/dT_s)] \}; \qquad b > 0 \tag{15}$$

$$y_3 = Y_0 + \alpha_s \{ C_{s3} - C_r [1 + R_0 (dq_3/dT_s)] \}; \qquad b = 0 \tag{16}$$

where the subscripts 1, 2 and 3 refer to pre-transition, transition and post-transition states, respectively; and y_1, y_{trans}, and y_3 are the baseline equations in the three states of a physical/chemical transformation.

Chemical transformations

According to the type of transformation, physical or chemical, the transition baseline (eqn. (15)) requires different analytical interpretations. In this

section, we develop the baseline equation for a chemical transformation. (The issue of a physical transformation is the subject of the next section.)

The term C_{s2} in eqn. (15) can be expressed by an additive relation describing the mixture of reactants and reaction products corresponding to the instantaneous progress of the reaction

$$C_{s2} = C_{s1}(1 - f) + C_{s3}f \tag{17}$$

where f is fraction conversion (dimensionless). After mathematical manipulations of eqns. (11)–(17), the transition baseline takes the relation

$$y_{\text{trans}} = y_1 + \{(y_3 - y_1) + \alpha_s C_r R_0 [d(y_3 - y_1)/dT_s]\} f$$
$$- \alpha_s C_r R_0 [d(y_2 - y_1)/dT_s] \tag{18}$$

The first term in eqn. (18) represents the pre-transition baseline. The second term describes the heat-capacity change from that of the reactants to that of the products of reaction, and implies that the post-transition baseline may not be an extension of the pre-transition baseline. The third term is the result of the heating rate for the sample material which differs from that of the reference material.

If the term $\alpha_s C_r R_0$ in eqn. (18) vanishes, the equation of transition baseline simplifies to

$$y_{\text{trans}} \simeq y_1 + (y_3 - y_1) f; \qquad \alpha_s C_r R_0 \to 0 \tag{18a}$$

In practice, this is possible when the reference pan is 'empty' (i.e. $C_r \simeq 0$) or the thermal resistance is negligible (i.e. $R_0 \simeq 0$). In the first case, the reference pan may be filled with air. The second case may be accomplished through proper design and operation. Nevertheless, a combination of 'empty' pan and negligible thermal resistance would technically justify eqn. (18a).

If, in addition to a vanishing $\alpha_s C_r R_0$ term, the change in heat capacity of the reaction products versus the reactants is negligible (i.e. $y_1 \simeq y_3$), the equation of transition baseline is an extension of the pre-transition baseline

$$y_{\text{trans}} \simeq y_1; \qquad \alpha_s C_r R_0 \to 0 \text{ and } y_1 \simeq y_3 \tag{18b}$$

While eqns. (18a) and (18b) may be used in many DSC studies, let us consider the implications of applying the complete solution, eqn. (18).

(a) Functions describing the pre-transition baseline (y_1), DSC ordinate signal during transition (y_2), and post-transition baseline (y_3) are linear and/or polynomial fittings of the DSC record data (Fig. 3); y_1 and y_3 represent extrapolations to the transition range.

(b) The term C_r is a known quantity derived from the available information on the reference material (i.e. mass and heat capacity, where the latter can be a function of temperature).

(c) For a given instrumental heating rate α, the thermal resistance R_0 is measurable from a physical transformation (see next section).
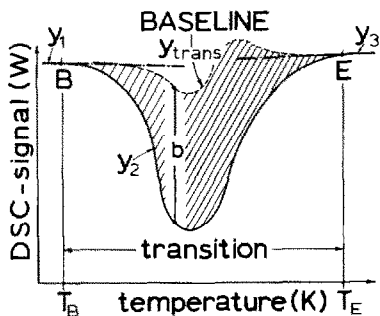
Fig. 3. DSC record of a chemical transformation (endotherm). Transition baseline results from change in heat capacities.

(d) From eqns. (7) and (12), one can derive the relation

$$\alpha_s = \alpha_r / \left[1 + R_0 d(y_2 - Y_0)/dT_s \right] \tag{19}$$

where Y_0 is a linear/polynomial fitting of the instrumental signal, and T_s is approximated through the corresponding instrumental parameter, T. If the thermal resistance is negligible (i.e. $R_0 \simeq 0$), eqn. (19) would predict

$$\alpha_s \simeq \alpha_r \simeq \alpha; \qquad R_0 \simeq 0 \tag{20}$$

Under the conditions of eqn. (20), the parameters in eqn. (18) referring to the sample material can be replaced by the corresponding instrumental quantities, α and T.

(e) Fraction conversion in eqns. (18) and (18a) requires a trial-and-error procedure. First, line BE in Fig. 3 is assumed to be the transition baseline. This allows the definition of the DSC curve and the estimation of the apparent reaction-kinetic parameters (see later). Second, fraction conversion is related to the kinetic parameters via a relation derived from eqn. (47) (see later)

$$(1 - f)^{-n} df = C_0^{n-1}(A/\alpha) \exp(-E/RT) dT \tag{21}$$

where C_0 is the initial concentration of the reactant (kg-mol m^{-3}), n is the apparent order of reaction (dimensionless), A is the apparent pre-exponential factor [(kg-mol m^{-3} s^{-1})/(kg-mol m^{-3})^n], E is the apparent activation energy (J kg-mol^{-1}), and $R = 8314$ J kg-mol^{-1} K^{-1}, the gas law constant.

Heuvel and Lind [7] used a statistical approach to determine the onset temperature of the transformation (point B in Fig. 3). A linear or second-order polynomial is fitted to the estimated pre-transition baseline, and the standard deviation of the point extrapolated to the abscissa at the peak of the DSC record (Fig. 3) is calculated. The procedure is repeated, while the end of the pre-transition baseline is shifted along the DSC record towards the transition range. The minimum value of the standard deviation at the extrapolated point will occur at a given temperature which is designated as the onset temperature of the transformation (point B in Fig. 3). A similar

procedure is used to define the end temperature of the transformation (point E in Fig. 3), where the estimated post-transition baseline is shifted along the DSC record towards the transition range.

At the onset point, the fraction conversion has a constant value, actually close to zero. Similarly, at the end point, the value of the fraction conversion approaches unity. Assuming that the term $1 - f_{B,E}$ has a corresponding finite value (Gorbachev [13]), where the subscript (B, E) denotes onset or end point, eqn. (21) can be integrated

$$f_{B,E}(1 - f_{B,E})^{-n} \simeq C_0^{n-1}(A/\alpha)\left[RT_{B,E}^2 \exp(-E/RT_{B,E})/E \right] \qquad (22)$$

where an approximate solution to the temperature integral was used (see eqn. (52a)). Although it implies a trial-and-error procedure to estimate the apparent reaction-kinetic parameters, eqn. (22) contains known data to solve for the onset or end temperature $T_{B,E}$. Actually, this approach is related to the general solution to the transition baseline, eqn. (18).

PHYSICAL TRANSFORMATIONS IN DSC

During a phase transformation, the temperature of the sample material remains constant (at constant pressure) as the reference material continues to follow the instrumentally programmed temperature. When the phase transformation is completed, the sample temperature changes as fast as the heat transfer in the system allows to match the state of the reference sample. As a result, physical transformations in DSC have a unique signal output (Fig. 4). Their mathematics were recently advanced by Sandu and Singh [2].

This section summarizes previous work for systems involving single physical transformations in DSC [2], and extends the modeling to include systems encompassing multiple physical transformations. The analytical approach to a single physical transformation [2] differs from that employed by Gray [14], although under particular considerations both sets of results are in agreement.
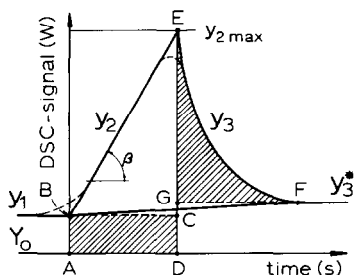

Fig. 4. DSC record of a physical transformation (exotherm). B–F defines the pseudo-baseline of the transformation.

Single physical transformations

A physical transformation in DSC (Fig. 4) is characterized by an ordinate signal that follows a straight line with slope α/R_0 during the transition state, and an exponential curve whose argument is directly proportional to $1/R_0$ during the post-transition state [2]. The signs of both the slope and the argument depend on the exothermic/endothermic effects of the transformation. In contrast with a chemical transformation (see later), the 'curve peak' in Fig. 4 marks the completion of the physical transformation.

Assumptions
(a) Equation (10) applies over the entire range of the DSC record of a physical transformation

$$y = Y_0 + \alpha_s \{ C_s - C_r [1 + R_0 (dq/dT_s)] \} \pm b \tag{10}$$

where the pure transformation signal during both pre-transition and post-transition states vanishes (i.e. $b = 0$).

(b) The heating rate of the sample material, generally expressed by a relation derived from eqn. (7)

$$\alpha_s \equiv dT_s/dt = \alpha_r / [1 + R_0 (dq/dT_s)] \tag{23}$$

takes distinct values during the transformation. In the pre-transition state, eqn. (23) predicts a finite value

$$\alpha_{s1} \simeq \alpha_r \simeq \alpha; \qquad dq_1/dT_s \simeq 0 \tag{24}$$

According to eqn. (23), in the transition state, the heating rate of the sample material vanishes

$$\alpha_{s2} = 0; \qquad dT_{s2}/dt = 0 \tag{25}$$

because the instantaneous temperature is constant. During post-transition, the sample heating-rate starts at a maximum value [2]

$$\alpha_{s3,\text{max}} = (q_{2,\text{max}} + \alpha_r C_r)/C_{s3} \tag{26}$$

followed by an exponential decrease, until it matches the reference heating rate, where $q_{2,\text{max}}$ is the difference in heat flow (W) at the end of transition (Fig. 4).

(c) For a given instrumental heating rate α, parameters Y_0, α_r, R_0, C_{s1}, C_{s3} and C_r in eqns. (10) and (23) are assumed to be constant.

(d) Equations of physical transformations have time as the independent parameter [2], whose origin is established at the onset of the transition state (point B in Fig. 4). By comparison, the mathematics of chemical transformations is more conveniently developed in terms of temperature as the independent variable.

Transformation signal

With the assumptions outlined above, the DSC ordinate signal of a physical transformation (Fig. 4) is described by three equations [2]

$$y_1 = Y_0 + \alpha_r(C_{s1} - C_r) \tag{27}$$

$$y_2 = y_1 + (\alpha_r/R_0)t \tag{28}$$

$$y_3 = [q_{2,\max} - (y_3^\star - Y_0)] \exp\left(-\frac{t - t_{\max}}{R_0 C_{s3}}\right) + y_3^\star \tag{29}$$

where the time parameter originates at the onset of the transformation (Fig. 4), $y_3^\star$ is the post-transition baseline (W), and $t_{\max}$ is the time interval (s) required to bring the physical transformation to completion. The two parameters in eqn. (29) are defined [2]

$$y_3^\star = Y_0 + \alpha_r(C_{s3} - C_r) \tag{30}$$

$$q_{2,\max} = y_1 + (\alpha_r/R_0)t_{\max} \tag{31}$$

where $y_3^\star$ is the asymptotic value of the DSC ordinate signal during the post-transition state (that is, the post-transition baseline).

The ordinate signal during pre-transition, eqn. (27), is a constant; y_1 is implicitly the pre-transition baseline. Equations (28) and (29) are unique to a physical transformation (Fig. 4). During transition, eqn. (28), the ordinate signal, is a straight line with intercept y_1 and slope α_r/R_0. In the post-transition state, eqn. (29), the ordinate signal is an exponential function with a negative argument. The slope in eqn. (28) is totally independent of the physical/kinetic parameters of the sample material. In contrast, the argument of the exponential function depends on sample material parameters as well as parameters linked to the instrument operation. The smaller the thermal resistance R_0 in eqn. (29), the faster the sample material reaches the instrumentally programmed temperature, once the physical transformation has been completed.

From eqns. (15) and (25), the transition baseline of a physical transformation takes a particular form

$$y_{\text{trans}} = Y_0; \qquad \alpha_{s2} = 0 \tag{32}$$

Combining eqns. (18), (25), (17), (27) and (30) results in the relation

$$y_{\text{trans}} = Y_0 + \alpha_r(C_{s2} - C_r); \qquad \alpha_{s2} = 0 \tag{18c}$$

In fact, both expressions are identical as the term $\alpha_r(C_{s2} - C_r)$ in eqn. (18c) is zero (i.e. no sensible heat-exchange is involved during the transition state of a physical transformation).

The heating rate of the sample material is subject to step changes (eqns. (24)–(26)) at the onset and end of a physical transformation. However, a real DSC record implies gradual changes of the heating rate around points B and E (Fig. 4). Consequently, the onset and end points are established at the

intersection of the corresponding extrapolated lines (points B and E in Fig. 4). The final point of a physical transformation (point F in Fig. 4) does not have a counterpart in a chemical transformation. Point F is conventionally placed on the DSC record at the position where the post-transition ordinate signal 'practically' reaches its asymptotic value.

Transformation parameters

There are two important results associated with the DSC analysis of physical transformations: the heat and temperature of the transformation. In addition, the slope of the DSC signal during transition state is used in calculating the thermal resistance term.

The area under the transition ordinate signal (corrected for the instrumental signal) represents the total amount of heat involved in a physical transformation (Fig. 4)

$$(\Delta H_R)m_0 = \int_0^{t_{max}} (y_2 - y_{trans}) \, dt \tag{33}$$

where (ΔH_R) is the heat of transformation (J kg-mol^{-1}), m_0 is the amount of sample material (kg-mol), and the transition baseline is given in eqn. (32). After mathematical manipulations, the result is [2]

$$(\Delta H_R) = (1/m_0)\{(y_1 - Y_0)t_{max} + [(y_{2,max} - y_1)t_{max}/2]\} \tag{34}$$

where the first term in the braces on the right-hand-side represents the rectangular ABCD area (W s) and the second term is the triangular BEC area (W s) in Fig. 4. For a given amount of sample material, all parameters in eqn. (34) are measurable on the DSC record. In fact, one needs to evaluate the total ABED area (W s), corresponding to the term in braces in eqn. (34).

Combining eqns. (27), (28) and (34), another analytical relation is derived for the heat of transformation. If one assumes an 'empty' reference pan (i.e. $C_r \simeq 0$) as well as the approximation $\alpha_r \simeq \alpha$, the heat of transformation can be calculated using the relation

$$(\Delta H_R) = (1/m_0)[\alpha C_{s1} t_{max} + (\alpha t_{max}^2/2R_0)]; \qquad C_r \simeq 0 \text{ and } \alpha_r \simeq \alpha \tag{35}$$

$$C_{s1} = c_{s1} m_0 \tag{36}$$

$$\alpha/R_0 = \tan \beta \tag{37}$$

where c_{s1} is the heat capacity of sample material (J kg-mol^{-1} K^{-1}) during the pre-transition state, and $\tan \beta$ is the slope (W s^{-1}) of the transition BE line in Fig. 4.

It can be demonstrated mathematically [2] that the term in braces in eqn. (34) is approximately equal to the total BEF area (W s) in Fig. 4. This approach is convenient because it does not require the definition of the instrumental signal Y_0. However, the error is minimized only when both an

'empty' reference pan is used (i.e. $C_r \simeq 0$) and the result is extrapolated to zero heating rate

$$(\Delta H_R) \simeq (1/m_0) \text{ (area BEF)}_{\text{at } \alpha \to 0}; \qquad C_r \simeq 0 \qquad (38)$$

where (area BEF) is confined between the transition and post-transition ordinate signal and a pseudo-baseline BF (Fig. 4).

The temperature of transformation corresponds to the transformation onset (point B on Fig. 4). Real DSC records exhibit a slight dependency of the transformation onset on the heating rate. This behavior cannot be theoretically predicted; it originates with the thermal lag, the thermodynamics of physical transformations, etc. As a result, it is recommended that the onset temperature is extrapolated to zero heating rate. As a common practice, the transformation temperature in the melting of various standard substances is used to calibrate the temperature on the abscissa of the DSC record.

The thermal resistance is an intrinsic property of the DSC instrument that depends on the design and operation of the equipment. This parameter changes with the heating rate and can be determined from the slope of the transition line of a physical transformation (Fig. 4 and eqn. (37)). The smaller the thermal resistance, the easier the interpretation of the DSC records and the more accurate the parameters associated with physical/chemical transformations.

Multiple physical transformations

Assume a mixture of two solid substances (fine powders) subject to heating in DSC. Assume also that no chemical reaction between the two substances occurs. DSC records of such systems usually reveal "curve peaks and shoulders" that suggest a series of melting transformations corresponding to the number of phases formed. The location and magnitude of "curve peaks and shoulders" depend on the heats and temperatures of transformations as well as on the amount of each phase in the system.

In this section, we analyze a simplified system of two interfering physical transformations as the basis for modeling more complex systems. The purpose is to determine the parameters of the transformations.

Assumptions
(a) Two solid substances are mixed together to form a uniform sample material. During the melting process, the sample material is a two-phase system (going from solid–solid to liquid–solid to liquid–liquid state), without formation of any new phases. The two substances will reveal the transformation parameters of the pure compounds.

(b) There are no temperature gradients inside the sample material; this is equivalent to perfect mixing and heat transfer between the two phases.
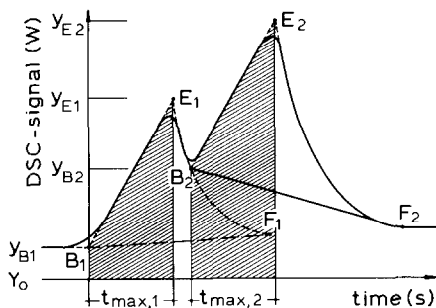
Fig. 5. DSC record of two physical transformations (exotherm). Temperature of sample is delayed until both transformations have been completed.

(c) According to Fig. 5, when the sample material reaches the onset temperature of the low-melting-point substance, the system remains at constant temperature until the first transformation is completed. While the system undergoes the post-transition state of the first transformation, the sample material reaches the onset temperature of the high-melting-point substance. The system remains at constant temperature until the second transformation is completed.

(d) The quantitative relations developed for single physical transformations apply in modeling multiple physical transformations. It is important that the temperature of the sample material is delayed with respect to the reference temperature until both physical transformations have been completed. This creates analytical problems, particularly in determining the onset temperature of the second transformation (Fig. 5).

Transformation parameters

If the ordinate signal at point B_2 verifies eqn. (30)

$$y_{B2} = Y_0 + \alpha C_{s3,1}; \qquad C_r \simeq 0 \text{ and } \alpha_r \simeq \alpha \tag{39}$$

where subscript 1 refers to the low-melting-point substance, then the pseudo-baseline $B_1 F_1$ is identical with the line $B_1 B_2$ (Fig. 5). Under any other circumstances, it is incorrect to approximate the pseudo-baseline of the first transformation with the line $B_1 B_2$. It is consistent with the model developed in this study to define the pseudo-baseline $B_2 F_2$ of the second transformation as depicted in Fig. 5.

Equation (34) is the recommended solution for the calculation of the heats of transformation

$$(\Delta H_{R1}) = (1/m_{0,1})\{(y_{B1} - Y_0)t_{max,1} + [(y_{E1} - y_{B1})t_{max,1}/2]\} \tag{40}$$

$$(\Delta H_{R2}) = (1/m_{0,2})\{(y_{B2} - Y_0)t_{max,2} + [(y_{E2} - y_{B2})t_{max,2}/2]\} \tag{41}$$

where subscripts 1 and 2 refer to the low-melting-point and high-melting-point substances, and both the heat-flow and time parameters are defined in

Fig. 5. The terms in braces in eqns. (40) and (41) originate with the integrals under the transition state lines $B_1 E_1$ and $B_2 E_2$ in Fig. 5.

The transformation temperature for the low-melting-point substance is determined as in the case of a single physical transformation, that is, the onset corresponds to the abscissa of point B_1 in Fig. 5. In contrast, the sample temperature at point B_2 (the onset of the high-melting-point substance) is behind the reference material

$$T_{transf,2} = T_{B2} - R_0(y_{B2} - Y_0) \tag{42}$$

where T_{B2} is the temperature (K) on the abscissa corresponding to point B_2 in Fig. 5. The relation was derived from eqns. (6) and (9).

Discussion

(a) Note that the transition-state lines of multiple physical transformations are parallel lines with slope α/R_0.

(b) For a series of physical transformations whose signals interfere, the onset temperature of the first transformation, the final point and the pseudo-baseline of the last transformation in the series are directly located on the DSC record. The remaining transformation parameters are analytically estimated.

(c) The location and magnitude of "curve peaks and shoulders" depend on the temperature and heat of the transformations as well as on the amount of each phase in the system. Figure 6 is an illustration of the DSC record when the signal of the high-melting-point transformation is much smaller than that in Fig. 5.

CHEMICAL REACTION KINETICS IN DSC

The purpose of defining the transition baseline is to calculate the pure transformation signal, that is, the DSC curve
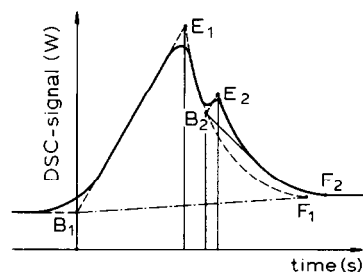
$$\pm b = y - y_{trans} \tag{43}$$

Fig. 6. DSC record of two physical transformations (exotherm). Second transformation yields a smaller signal output.

where y is the ordinate signal of the DSC record, and y_{trans} is the transition baseline expressed by eqns. (18), (18a) or (18b).

The DSC curve stays for the corrected DSC record. Equation (43) is implicitly defined over the transition state of a chemical transformation (between the onset and end temperature points).

This section is based on previous work by Sandu et al. [3,4], and addresses systems involving single and multiple reactions. Selected references treating aspects similar to those analyzed here include Borchardt and Daniels [15], Kissinger [16], Horowitz and Metzger [17], Rogers and Smith [18], Ozawa [19], and Balarin [20].

Single chemical reactions

The DSC curve of a chemical transformation (Fig. 7) is uniquely characterized by a bell-shaped graph that displays a peak (maximum or minimum) and two inflection points. The features of the DSC curve directly relate to the nature of the chemical transformation in the sample material during heating. As a result, the mathematics of the DSC curve allows the calculation of the apparent reaction-kinetic parameters. It is correct to define them as 'apparent' parameters as modeling implies that a series of assumptions are required to obtain the analytical solutions.

Assume a homogeneous chemical reaction in a liquid phase, where species C undergoes an (apparent) transformation of the form

$$n\,C \rightarrow \text{products of reaction} \tag{44}$$

Its reaction rate follows a typical Arrhenius behavior, as described by the relation

$$dC/dt = -A\,\exp(-E/RT)C^n \tag{45}$$

where C is the concentration (kg-mol m^{-3}), and the apparent order of reaction can take any positive value, $n \geqslant 0$.
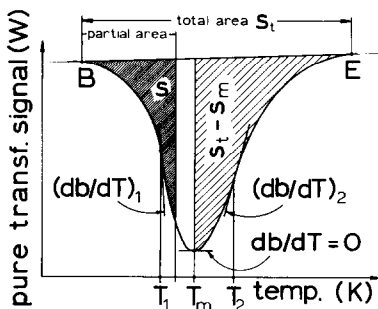

Fig. 7. DSC curve of a chemical transformation (endotherm). The larger the asymmetry index, the smaller the reaction order.

If the change in the volume of the reacting system is negligible, the fraction conversion is used to describe the concentration of the limiting reactant [21]

$$f = 1 - C/C_0 \tag{46}$$

From eqns. (1), (45) and (46), the progress of the reaction is expressed

$$df/dT = C_0^{n-1}(A/\alpha) \exp(-E/RT)(1-f)^n \tag{47}$$

where the heating rate takes only positive values, $\alpha > 0$.

The pure transformation signal (that is, the deflection of the DSC curve) is a measure of the heat of reaction

$$\pm b = (\Delta H_R) m_0 (df/dt) \tag{48}$$

where the deflection of the DSC curve (W) is proportional to the rate of change of the fraction conversion, and m_0 is the initial amount of reactant in the sample material (kg-mol). In terms of temperature as independent parameter, it is easy to show that eqn. (48) becomes

$$\pm b = \alpha(\Delta H_R) m_0 (df/dT) \tag{49}$$

$$= (\Delta H_R) m_0 C_0^{n-1} A \exp(-E/RT)(1-f)^n \tag{50}$$

According to eqn. (50), the pure transformation signal vanishes at the onset point (that is, at a temperature low enough such that the relation $\exp(-E/RT) \simeq 0$ is true) as well as at the end point where the reaction is completed (that is, the relation $1 - f \simeq 0$ is verified). The exponential term increases with temperature, whereas the binomial term in eqn. (50) decreases. As a result, the DSC curve of a chemical transformation has a bell shape with a maximum or minimum, depending upon the exothermic/endothermic effects. In contrast to the physical transformation, the curve peak does not correspond to the end of the chemical transformation (NB, except for zero-order reactions).

A zero-order chemical reaction has a particular behavior

$$\pm b = [(\Delta H_R) m_0 A/C_0] \exp(-E/RT); \qquad n = 0 \tag{51}$$

where the DSC curve is an exponential function that does not display a maximum/minimum or inflection points (Fig. 8). The apparent "curve peak" in Fig. 8 corresponds to the end of the reaction. In contrast with physical transformations: (1) the sample material in a zero-order chemical reaction does follow the programmed temperature during the transition state; (2) the onset temperature is determined according to the analysis at chemical transformations (eqn. (22), for instance); and (3) at the end of transition, the pure transformation signal undergoes a step change (compare Figs. 4 and 8).

Assumptions
(a) Equation (50) applies to the DSC curve of a chemical reaction (including zero-order reaction). Assuming a known, pure transformation
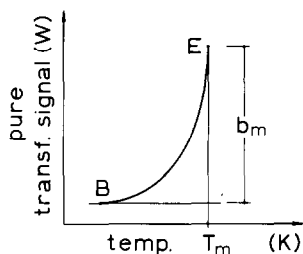
Fig. 8. DSC curve of a zero-order chemical transformation (exotherm). Its solutions are particular.

signal (eqn. (43) and Fig. 7) as well as defined parameters m_0 (initial amount of reactant in the sample material) and C_0 (initial concentration of reactant in the sample material), eqn. (50) provides the basis to analytically determine the apparent reaction-kinetic parameters (order of reaction, activation energy, heat of reaction, and pre-exponential factor).

(b) The 'temperature integral' present in the mathematics of DSC curves, that is

$$\theta = \int_{T_0}^{T} \exp(-E/RT)\, \mathrm{d}T \tag{52}$$

is approximated by the expression

$$\theta \simeq (RT^2/E)\exp(-E/RT) \tag{52a}$$

where, for practical values of E/RT (that is, 10–50), the error in eqn. (52a) is negligible [22].

There are three features of a DSC curve that can be uniquely identified and used to develop the mathematics of chemical reaction kinetics: the position of the curve peak (maximum or minimum); the shape of the curve (inflection points); and the area bounded by the curve.

Curve peak

The solution to zero-order chemical reactions is distinct. Assume $n = 0$ in eqn. (47), and integrate for the boundary conditions $f = 0$ at T_0 and $f = 1$ at T_m; the result is

$$1 = (AR/C_0 E)(T_m^2/\alpha)\exp(-E/RT_m); \qquad n = 0 \tag{53}$$

where subscript m refers to the maximum/minimum of the curve (Fig. 8). Taking logarithms of eqn. (53) reveals a linear relationship

$$\ln\left[\alpha/T_m^2\right] = \ln(AR/C_0 E) - (E/R)(1/T_m); \qquad n = 0 \tag{54}$$

Combining eqns. (51) and (53), one derives the expression

$$\pm b_m = (E(\Delta H_R)m_0/R)(\alpha/T_m^2); \qquad n = 0 \tag{55}$$

where b_m is the signal (W) at curve peak, and T_m is the peak temperature (K).

Unlike physical and zero-order chemical transformations, the DSC curve of a general-order chemical reaction ($n > 0$) is mathematically a continuous function at the peak (Fig. 7), that is, $[db/dT]_m = 0$. This leads to the analytical condition (derived from eqn. (49))

$$[d^2f/dT^2]_m = 0; \qquad n > 0 \tag{56}$$

By substituting eqn. (47) into eqn. (56), the relation that defines the kinetics at the curve peak is

$$\alpha/T_m^2 = (nC_0^{n-1}AR/E)(1-f)_m^{n-1}\exp(-E/RT_m); \qquad n > 0 \tag{57}$$

where f_m is the fraction conversion (dimensionless) at the maximum/minimum of the curve, i.e. $0 < f_m < 1$. The binomial term in eqn. (57) results from integrating eqn. (47) for the boundary conditions $f = 0$ at T_0 and $f = f_m$ at T_m

$$(1-f)_m^{1-n} = 1 + [(n-1)C_0^{n-1}AR/E](T_m^2/\alpha)\exp(-E/RT_m); \qquad n \neq 1 \tag{58}$$

Note that, when $n = 1$, there is no need for an analytical expression of the binomial term in eqn. (57).

From eqns. (57) and (58), the peak temperature changes with heating rate

$$\ln[\alpha/T_m^2] = \ln(C_0^{n-1}AR/E) - (E/R)(1/T_m); \qquad n > 0 \text{ and } n \neq 1 \tag{59}$$

If the order of reaction is unity, one finds from eqn. (57)

$$\ln[\alpha/T_m^2] = \ln(AR/E) - (E/R)(1/T_m); \qquad n = 1 \tag{60}$$

an equation previously developed by Murray and White [23] and Rogers and Smith [24].

As stated by eqns. (54), (59) and (60), the graph of $\ln[\alpha/T_m^2]$ versus $1/T_m$ is a straight line for chemical transformations in DSC, regardless of the reaction order. While all the equations have similar slopes $-E/R$, the intercepts relate to the order of reaction

$$\Lambda = \ln(AR/E) = \text{const.}; \qquad n = 1 \tag{61a}$$

$$\Lambda = \ln(AR/E) - \ln C_0; \qquad n = 0 \tag{61b}$$

$$\Lambda = \ln(AR/E) + (n-1)\ln C_0; \qquad n > 0 \text{ and } n \neq 1 \tag{61c}$$

where Λ is the intercept of the graph $\ln[\alpha/T_m^2]$ versus $1/T_m$.

Discussion

(a) Although the solutions originate with different assumptions in the analytical model, eqns. (59) and (61c) can be considered general relations,

valid for any order of reaction

$$\ln\left[\alpha/T_m^2\right] = \ln\left(C_0^{n-1}AR/E\right) - (E/R)(1/T_m); \qquad n \geqslant 0 \qquad (62)$$

$$\Lambda = \ln(AR/E) + (n-1)\ln C_0; \qquad n \geqslant 0 \qquad (63)$$

Equation (62) agrees with previous results by Kissinger [16].

(b) DSC data that relate the peak temperature to the heating rate and initial concentration, eqns. (62) and (63), allow calculation of three apparent kinetic parameters: the order of reaction, the activation energy, and the pre-exponential factor. The basic procedure is linear regression analysis. In addition, eqn. (55) is used to estimate the heat of reaction for zero-order transformations.

(c) For a zero-order reaction, the absolute value of the deflection at curve peak is directly proportional to the α/T_m^2 term in eqn. (55).

Inflection points

The DSC curve of a chemical transformation (other than a zero-order reaction) has two inflection points (see solution to eqn. (66)). According to Kissinger [16], the shape index of the DSC curve is defined as the absolute value of the ratio of slopes at the inflection points (Fig. 7)

$$\phi = |(db/dT)_1/(db/dT)_2|; \qquad n > 0 \qquad (64)$$

where subscripts 1 and 2 refer to the first and second inflection points and one always considers $T_1 < T_2$. Analytical manipulations of eqns. (49), (47) and (64) result in the expression

$$\phi = \left| \frac{(df/dT)_1\{(E/RT_1^2) - [n/(1-f)_1](df/dT)_1\}}{(df/dT)_2\{(E/RT_2^2) - [n/(1-f)_2](df/dT)_2\}} \right|; \qquad n > 0 \qquad (65)$$

The second derivative of the DSC curve at the inflection point vanishes, that is, $[d^2b/dT^2]_i = 0$. This leads to the analytical condition (derived from eqn. (49))

$$\left[d^3f/dT^3\right]_i = 0; \qquad n > 0 \qquad (66)$$

where subscript i refers to the first/second inflection point. After mathematical manipulations of eqns. (47) and (66), one finds a quadratic expression

$$[2 - (1/n)] X_i^2 - \left(3E/RT_i^2\right) X_i + \left(E/RT_i^2\right)[1 - (2RT_i/E)] = 0;$$
$$n > 0 \qquad (67)$$

$$X_i = [n/(1-f)_i](df/dT)_i \qquad (68)$$

whose solutions serve to estimate the corresponding terms in eqn. (65).

It is assumed that the relation $2RT/E \ll 1$ is always true [16]. In this case, eqn. (67) can be solved for the stated unknown, eqn. (68), to obtain

$$[n/(1-f)_i](df/dT)_i = \left(E/RT_i^2\right)[(3 \pm \gamma)/\delta]; \qquad n > 0 \text{ and } n \neq 0.5$$

$$\gamma = (1 + 4/n)^{1/2}; \qquad \delta = (4 - 2/n) \qquad (69)$$

where the major issue is to define the $\pm$ sign association with the right inflection point of the DSC curve. The analytical approach starts from the observation that the following inequality is always verified

$$(1 - f)_1 > (1 - f)_2 \tag{70}$$

Next, eqn. (47) is integrated for the boundary conditions $f = 0$ at T_0 and $f = f_i$ at T_i, where subscript i refers to any one of the inflection points. The result can be brought to the form

$$(1 - f)_i^{1-n} = 1 + [(n - 1)RT_i^2/E](1 - f)_i^{-n}(df/dT)_i; \qquad n \neq 1 \tag{71}$$

Combining eqns. (69) and (71), one finds that the binomials in the inequality (70) are solely functions of the reaction order

$$(1 - f)_i = \{1 - [(n - 1)(3 \pm \gamma)/n\delta]\}^{1/(n-1)}; \qquad n > 0, \; n \neq 0.5 \text{ and } n \neq 1 \tag{72}$$

For a realistic range of the reaction order (e.g. $0.5 < n \leqslant 3$), the right-hand-side of eqn. (72) can be calculated numerically. It follows that inequality (70) is verified only when the first inflection point is associated with the minus sign on the right-hand-side of eqns. (72) and (69).

Using eqns. (69) and (72) to substitute terms in eqn. (65), the shape index becomes

$$\phi = \left| \frac{(3 - \gamma)[\delta - (3 - \gamma)]}{(3 + \gamma)[\delta - (3 + \gamma)]} \left[\frac{n\delta - (n - 1)(3 - \gamma)}{n\delta - (n - 1)(3 + \gamma)} \right]^{1/(n-1)} \left[\frac{T_2}{T_1} \right]^4 \right|;$$

$$n > 0, \; n \neq 0.5 \text{ and } n \neq 1 \tag{73}$$

For a temperature ratio very close to unity [16], the shape index of the DSC curve is primarily a function of the reaction order.

The transformation kinetics at the inflection points is analytically related to the heating rate. From eqns. (47), (69) and (72), one finds the relation

$$\ln[\alpha/T_i^2] = \ln(\{[(4n - 2)/(3 \pm \gamma)] + 1 - n\}[C_0^{n-1}AR/E])$$
$$- (E/R)(1/T_i); \qquad n > 0 \text{ and } n \neq 0.5 \tag{74}$$

where the minus sign solution applies to the first inflection point. The graph $\ln[\alpha/T_i^2]$ versus $1/T_i$ is a straight line for chemical transformations in DSC; the relation holds for both inflection points.

Discussion

(a) For data analysis, eqns. (73) and (74) can be simplified using polynomial correlations to fit the corresponding n-functions

$$\phi[T_1/T_2]^4 = -0.1228 + 0.259n - 0.0787n^2; \qquad 0.5 \leqslant n \leqslant 2.5 \tag{75}$$

$$\ln\left[\alpha/T_1^2\right] = \ln\left[(1.427 + 1.142n)C_0^{n-1}AR/E\right] - (E/R)(1/T_1);$$

$$0.1 \leqslant n \leqslant 3 \qquad\qquad (76a)$$

$$\ln\left[\alpha/T_2^2\right] = \ln\left[(0.380 - 0.157 \ln(n))C_0^{n-1}AR/E\right] - (E/R)(1/T_2);$$

$$0.1 \leqslant n \leqslant 3 \qquad\qquad (76b)$$

where the temperature at the first inflection point is always considered to be smaller than the temperature at the second inflection point.

(b) The procedure to derive apparent kinetic parameters from relations at the inflection points implies data solely pertaining to only one DSC curve. The reaction order, activation energy and pre-exponential factor of a chemical transformation can be deduced from the system of eqns. (75), (76a), and (76b).

Curve-bounded area

At any temperature (Fig. 7), the area bounded by the DSC curve is estimated through the integral of the pure transformation signal, eqn. (50), as follows

$$s = (\Delta H_R)m_0 C_0^{n-1}A \int_{T_0}^{T} \exp(-E/RT)(1-f)^n \, dT \qquad\qquad (77)$$

where s is the partial area (W K) before a given temperature. At the maximum/minimum of the curve, it can be shown that eqn. (77) has a particular solution

$$s_m = \alpha(\Delta H_R)m_0\left[1 - n^{1/(1-n)}\right]; \qquad n \geqslant 0 \text{ and } n \neq 1 \qquad (78)$$

where s_m is the area before the peak (W K). To reach this result, one substitutes the binomial term in eqn. (77), i.e., $(1-f)_m^n$, with its value calculated from eqn. (58), and performs the mathematics with the following assumptions: $2RT_m/E \ll 1$, respectively $\exp(-E/RT_0) \simeq 0$, and

$$C_0^{n-1}A\left(RT_m^2/E\right)\exp(-E/RT_m) = \alpha; \qquad n > 0 \text{ and } n \neq 1 \qquad (59a)$$

Note that, for a vanishing order of reaction, eqn. (78) takes the form

$$s_m = \alpha(\Delta H_R)m_0; \qquad n = 0 \qquad\qquad (78a)$$

The integral of eqn. (49) over the entire DSC curve is the expression of the total heat involved during the reaction

$$s_t = \alpha(\Delta H_R)m_0; \qquad n \geqslant 0 \qquad\qquad (79)$$

where s_t is the peak area (W K) in Fig. 7. For zero-order reactions, the area before peak and the peak area are identical (Fig. 8). Combining eqns. (78) and (79) gives the area after peak (W K)

$$s_t - s_m = \alpha(\Delta H_R)m_0 n^{1/(1-n)}; \qquad n \geqslant 0 \text{ and } n \neq 1 \qquad (79a)$$

The asymmetry index is the ratio of the area before peak to the area after peak of the DSC curve. Its value is derived by manipulating eqns. (78) and (79a)

$$\phi^\star = n^{1/(n-1)} - 1; \qquad n > 0 \text{ and } n \neq 1 \tag{80}$$

where $\phi^\star$, the asymmetry index (dimensionless), is a function of the reaction order.

Substituting eqns. (46) and (79) into eqn. (49) yields the expression

$$dC/dT = -(\pm b)(C_0/s_t) \tag{81}$$

whose integral form is shown to be

$$C = C_0(1 - s/s_t) \tag{82}$$

where s is the partial area before a given temperature (Fig. 7). Rearranging eqns. (1), (81), (82) and (45) results in the relation

$$(\pm b) = \left[(A/\alpha)(s_t/C_0)^{1-n}\right](s_t - s)^n \exp(-E/RT); \qquad n \geqslant 0 \tag{83}$$

This is the Borchardt and Daniels equation [15], which relates the apparent kinetic parameters with the deflection of the DSC curve at any temperature. At the peak of a zero-order reaction curve, eqn. (83) has a particular solution, eqn. (55).

Discussion

(a) The two distinctive areas bounded by the DSC curve, area before peak and peak (total) area, allow the calculation of the apparent reaction order and heat of reaction from eqns. (78) and (79). The asymmetry index, eqn. (80), is probably the simplest and most powerful result of the modeling of the DSC data. The larger the asymmetry index, the smaller the reaction order; DSC curves originating with less than second-order chemical transformations have larger areas before peak. Analytically related to the asymmetry index, the shape index (eqn. (75)) decreases as the reaction order becomes smaller.

(b) Assuming absolute values for the parameters determined on the DSC curve (that is, signal deflection, partial area, and peak area), the logarithmic form of eqn. (83) can be used to determine the apparent reaction order, activation energy and pre-exponential factor

$$\ln b = \ln\left[(A/\alpha)(s_t/C_0)^{1-n}\right] + n \ln(s_t - s) - (E/R)(1/T); \qquad n \geqslant 0 \tag{84}$$

where partial area and peak area have the dimension (W K), that is, the DSC curve is a plot whose abscissa represents temperature. The procedure applies non-linear regression analysis (of data solely pertaining to one DSC curve) to determine the coefficients in eqn. (84).
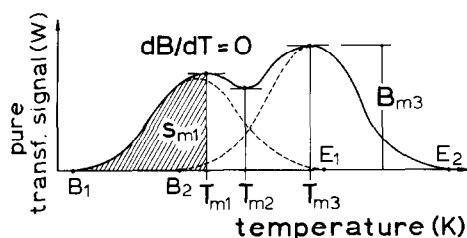
Fig. 9. DSC curve of two chemical transformations (exotherm). Mechanistically coupled reactions yield complicated mathematics.

Multiple chemical reactions

When a physical transformation is in progress, no other physical changes can start; the sample material remains at a constant temperature until the ongoing transformation is complete. In contrast, chemical reactions take place simultaneously at different rates and with different heats of reaction. The latter result in a much more complicated DSC curve.

Even for simple cases, the DSC curve of a system undergoing multiple chemical reactions requires complicated mathematics. In this section, we present the analytical model of: (a) two irreversible, first-order, parallel reactions, and (b) two irreversible, first-order, consecutive reactions.

A DSC transformation that involves two extents of reaction can display a series of patterns: two distinct maxima/minima separated by one minimum/maximum; one distinct maximum and one distinct minimum; and only one distinct maximum/minimum, preceded or followed by a less distinct one. This behavior depends on the amount of species as well as the magnitude of the reaction rates and exothermic/endothermic effects. Figure 9 illustrates a DSC curve with two distinct maxima separated by one minimum, where both reactions are exothermic.

In modeling multiple reaction systems, it is more convenient to work in terms of the extent of the reaction [21]

$$\zeta = (m_j - m_{j0})/\nu_j \tag{85}$$

where ζ has the dimension (kg-mol), m_j is the amount of species j (kg-mol) at a given time, m_{j0} is the initial amount of species j (kg-mol), and ν_j is the generalized stoichiometric coefficient (dimensionless), positive for a product species and negative for a reactant species. Substituting the extent of reaction for the fraction conversion, eqn. (49) is redefined

$$\pm b = -\nu_j \alpha \, \Delta H_R (d\zeta/dT) \tag{86}$$

where the $\pm$ sign designates the exothermic/endothermic effects.

Assumptions

(a) The transformations involved are two homogeneous chemical reactions of first-order. The system is characterized by two extents of reaction,

and its DSC signal is the result of both processes

$$B = (\pm b_1) + (\pm b_2) \tag{87}$$

where B is the deflection of the DSC curve (W), and subscripts 1 and 2 refer to each reaction.

(b) When only two first-order reactions are present in the system, eqns. (86) and (87) can be combined to give

$$B = \alpha(\Delta H_{R1})(d\zeta_1/dT) + \alpha(\Delta H_{R2})(d\zeta_2/dT); \qquad \nu_j = -1 \tag{88}$$

where the extent of reaction is expressed as for a reactant species. From an analytical viewpoint, the features that identify the DSC curve of a multiple-reaction transformation are the number of distinct maxima and minima, their position and their magnitude. For a system of two extents of reaction, the DSC curve can display from one to three places where the first derivative vanishes. The subsequent modeling is based entirely on the mathematics of the DSC curve at the positions where the relation $dB/dT = 0$ is true (Fig. 9).

First-order parallel reactions

Consider species C which undergoes two first-order parallel reactions

$$\begin{array}{l} C \rightarrow \text{products of reaction 1} \\ C \rightarrow \text{products of reaction 2} \end{array} \tag{89}$$

The progress of reaction can be described by the following system of differential equations

$$\begin{array}{l} \alpha(d\zeta_1/dT) = k_1(m_0 - \zeta_1 - \zeta_2) \\ \alpha(d\zeta_2/dT) = k_2(m_0 - \zeta_1 - \zeta_2) \end{array} \tag{90}$$

where k is the apparent constant of reaction (s^{-1}) assumed to follow an Arrhenius behavior

$$k = A \exp(-E/RT) \tag{91}$$

To uncouple eqns. (90), divide the first by the second, integrate and substitute the result back into the system of eqns. (90)

$$(d\zeta_1/dT) = (A_1/\alpha)m_0 \exp(-E_1/RT)$$
$$\qquad - [(A_1/\alpha) \exp(-E_1/RT) + (A_2/\alpha) \exp(-E_2/RT)]\zeta_1$$
$$(d\zeta_2/dT) = (A_2/\alpha)m_0 \exp(-E_2/RT) \tag{92}$$
$$\qquad - [(A_1/\alpha) \exp(-E_1/RT) + (A_2/\alpha) \exp(-E_2/RT)]\zeta_2$$

Equations (92) are substituted into eqn. (88) and, from the condition $dB/dT = 0$, it can be shown that the following relation is valid

$$\frac{-(\beta_2/T_{mi}^2) \exp(\beta_3/T_{mi}) + (\beta_8/\alpha) \exp(\beta_9/T_{mi}) + (\beta_{11}/\alpha)}{(\beta_1/T_{mi}^2) \exp(\beta_4/T_{mi}) - (\beta_7/\alpha) \exp(\beta_{10}/T_{mi}) - (\beta_{11}/\alpha)} = \frac{\beta_5 - S_{mi}/\alpha}{\beta_6 - S_{mi}/\alpha};$$
$$n = 1 \tag{93}$$

where T_{mi} is the temperature at a given maximum/minimum (K), S_{mi} is the area under the DSC curve up to a given maximum/minimum (W K), and β_1–β_6 are constants which embody the kinetic parameters of the two reactions (see list of symbols). The other constants, β_7–β_{11}, are directly related to the first group (see list of symbols).

Equation (93) for first-order parallel reactions correlates the heating rate, the temperature at the maximum/minimum and the area before the maximum/minimum with the apparent kinetic parameters of the two reactions. Equation (93) is verified at any maximum/minimum; attention has to be given to the exothermic/endothermic sign of the term S_{mi}.

First-order consecutive reactions

Consider a species C which undergoes two first-order consecutive reactions

$$C \rightarrow C^\star \tag{94}$$

$C^\star \rightarrow$ products of reaction

The following system of differential equations describes the progress of the reactions

$$\alpha(d\zeta_1/dT) = k_1(m_{01} - \zeta_1)$$
$$\alpha(d\zeta_2/dT) = k_2(m_{02} - \zeta_2) - k_1(m_{01} - \zeta_1) \tag{95}$$

where the apparent constant of reaction is given by eqn. (91).

Equations (95) are substituted into eqn. (88) and, from the condition $dB/dT = 0$, an intermediate relation is derived that will require explicit solutions to a couple of 'particular expressions', before the mathematics can proceed. These particular expressions are

$$(m_{01} - \zeta_1) \simeq m_{01} \exp\left[-(A_1/\alpha)(RT^2/E_1) \exp(-E_1/RT)\right] \tag{96}$$

$$(\Delta H_{R2})(m_{02} - \zeta_2) = (1/k_2)\left[B - k_1[(\Delta H_{R1}) - (\Delta H_{R2})](m_{01} - \zeta_1)\right] \tag{97}$$

where the assumption was made that the extent of the first reaction is independent of the subsequent reaction. B is the deflection of the DSC curve. After mathematical manipulations, one finds the relation

$$\frac{-(\beta_4/T_{mi}^2) \exp(\beta_{17}/T_{mi}) + (\beta_{15}/\alpha) \exp(\beta_3/T_{mi})}{(\beta_1/T_{mi}^2) \exp(\beta_4/T_{mi}) - (\beta_7/\alpha) \exp(\beta_{10}/T_{mi}) + (\beta_{13}/\alpha)}$$
$$= \frac{\exp\left[-\beta_{16}(T_{mi}^2/\alpha) \exp(-\beta_3/T_{mi})\right]}{\beta_{12}B_{mi} - \beta_{14} \exp\left\{-[(\beta_3/T_{mi}) + \beta_{16}(T_{mi}^2/\alpha) \exp(-\beta_3/T_{mi})]\right\}};$$
$$n = 1 \text{ and } (\Delta H_{R1}) \neq (\Delta H_{R2}) \tag{98}$$

where B_{mi} is the deflection of the DSC curve at a given maximum/minimum (W), and the constants embody the kinetic parameters of the two reactions (see list of symbols).

Equation (98) for first-order consecutive reactions correlates the heating rate, the temperature at the maximum/minimum and the deflection at the maximum/minimum with the apparent kinetic parameters of the two reactions. Equation (98) is verified at any maximum/minimum; attention has to be given to the exothermic/endothermic sign of the term B_{mi}. As expected (see reactions (94)), eqn. (98) does not encompass the quantity m_{02}, the initial amount of the intermediate chemical species.

General-order reactions

Assume Fig. 9 is the DSC curve of a system of two mechanistically uncoupled reactions. In addition, consider that the deflection of the DSC curve verifies the conditions

$$B \simeq (\pm b_1); \qquad T \leqslant T_{m1}$$
$$B \simeq (\pm b_2); \qquad T \geqslant T_{m3} \qquad (99)$$

where T_{m1} and T_{m3} are the peak temperatures (K) defined in Fig. 9. Under these circumstances, the apparent kinetic parameters of the first reaction are determined from the relations at the inflection point and the area before the peak, eqns. (76a) and (78). Similarly, the kinetic parameters of the second reaction result from the expressions at the inflection point and the area after the peak, eqns. (76b) and (79b).

The procedure can be extended to systems of three mechanistically uncoupled reactions, where similar conditions, eqns. (99), are verified for the first and the third reactions. With known kinetic parameters, their DSC curves can be calculated (eqns. (49) and (47)) and subtracted from the DSC curve of the multiple reaction system. The result will be the DSC curve of the second reaction.

The DSC curve of mechanistically coupled reactions yields analytically complicated mathematics, as the examples of first-order, parallel or consecutive reactions show. In these cases, the apparent kinetic parameters are contained in the coefficients of eqns. (93) and (98). Using non-linear regression analysis on a set of experimental data (α, T_{mi}, S_{mi} at $m_0 = $ const.), the following parameters describing first-order parallel reactions can be determined from the values of $\beta_1-\beta_6$ in eqn. (93): A_1, E_1, (ΔH_{R1}), A_2, E_2, and (ΔH_{R2}). Similarly, experimental data (α, T_{mi}, B_{mi} at $m_{01} = $ const.) in eqn. (98) allow the calculation of the kinetic parameters of first-order consecutive reactions. Note that the correlating quantity for first-order parallel reactions is area before the maximum/minimum, whereas first-order consecutive reactions encompass the deflection at the maximum/minimum.

Nonetheless, mechanistically uncoupled reactions that do not verify eqns. (99) as well as mechanistically coupled reactions that do not follow eqns. (93) and (98), require further research before analytical solutions for their DSC curves can be derived.

CONCLUSIONS

As a means of studying chemical reaction kinetics, differential scanning calorimetry offers the advantages of a fast and precise technique. Nevertheless, the limitations inherently connected with DSC as well as the assumptions made in modeling DSC data can not be ignored. For instance, single physical or chemical transformations can be mathematically described with precision, whereas multiple transformations in DSC amount to analytically complicated solutions that may require supplemental information from other techniques or may even question the use of DSC. The present study, probably the first to develop a unified mathematical approach to physical and chemical DSC transformations, is intended to form the basis for further research. The potential of this particular technique is far from being exhausted.

(a) The DSC record, that is, the raw signal output, generally requires a baseline correction to identify the signal of the pure transformation, the DSC curve. For this reason, as well as for the purpose of defining the features of the DSC curve (onset and end temperatures, maximum or minimum, inflection points, partial or total curve area, etc.), the DSC technique (starting with data acquisition) implies extensive numerical analysis of data: curve fitting and smoothing, differentiation and integration as well as trial-and-error manipulations.

(b) The final analytical solutions to the transition baseline of chemical and physical transformations (eqns. (18) and (32)) exemplify the differences among these processes. There are particular assumptions under which the pseudo-baseline to a single physical transformation is the line connecting the onset and final points (Fig. 4). Similarly, the circumstances are unique when considering the transition baseline of a single chemical transformation as an extension of the pre-transition baseline (Fig. 3).

Equations (18) and (32) define the transition baseline of multiple chemical and physical transformations. Intermediary maxima/minima can not be used to 'draw' the transition baseline. For instance, in Figs. 5 and 9, it is incorrect to consider the curve minimum as the end point (respectively, the onset point) of any of the transformations involved. The only exception is line B_2F_2 in Fig. 5, that is, the pseudo-baseline of the second physical transformation.

(c) Simplifying solutions or high accuracy in modeling DSC data require a series of physical assumptions: 'empty' reference pan, negligible heat-transfer resistance, and extrapolation to 'zero heating-rate'. They have been incorporated into the equations describing DSC records of chemical and physical transformations. The validity of these assumptions needs the awareness of both the designer and operator of scanning differential calorimeters.

(d) Analytical (mathematical) assumptions are an important element in the modeling of DSC. It is difficult to assess their impact on the final

solutions. For instance, using eqn. (77) to derive eqn. (79) yields a result that cannot be analytically reconciled

$$s_t = \alpha(\Delta H_R)m_0\left\{1 - \left[1 + (n-1)(\theta_t/\theta_m)\right]^{1/(1-n)}\right\}; \qquad n > 0 \text{ and } n \neq 1$$

(100)

where θ is the temperature integral at the end (t), and respectively at the peak (m) of the DSC curve. Equations (79) and (100) are identical only for the vanishing square-bracketed term in eqn. (100), which analytically cannot be shown. This originates with the assumptions embedded in the model.

Future work in modeling differential scanning calorimetry needs to validate the analytical results of this study as well as their associated degree of accuracy by contrasting the mathematics with known, well characterized, physical and chemical transformations. In this manner, not only some solutions will prove more useful and accurate than others, but new approaches to multiple transformations in DSC could be developed.

LIST OF SYMBOLS

(area BEF)	Area under the transformation curve (W s) in Fig. 4
A	Apparent pre-exponential factor (kg-mol m^{-3}s^{-1})/(kg-mol m^{-3})^n
b	Pure transformation signal (W); deflection of the DSC curve when a single reaction occurs (W)
B	Deflection of the DSC curve when multiple reactions occur (W)
B	Beginning or onset point of a physical/chemical transformation
c	Heat capacity (J kg-mol^{-1} K^{-1})
C	Chemical species C (reactant); concentration (kg-mol m^{-3})
C	Heat content (J K^{-1})
C$\star$	Intermediate chemical species C$\star$
E	Apparent activation energy (J kg-mol^{-1})
E	End point of a physical/chemical transformation
f	Fraction conversion of the reactant (dimensionless)
F	Final point of a physical transformation
k	Apparent constant of reaction (kg-mol m^{-3} s^{-1})/(kg-mol m^{-3})^n
m	Amount of reactant (kg-mol)
m_0	Initial amount of sample material (kg-mol)
n	Apparent order of reaction (dimensionless)
q	Difference in heat flows to the sample and reference materials (W)
q_r	Heat flow to the reference material (W)
q_s	Heat flow to the sample material (W)
R	Gas constant, 8314 J kg-mol^{-1} K^{-1}

R_0	Heat transfer resistance (K W^{-1})
s	Integral value of DSC curve when a single reaction occurs (W K)
S	Integral value of DSC curve when multiple reactions occur (W K)
t	Time (s); zero time is fixed when the transition state of a physical transformation starts
T	Temperature (K); abscissa parameter of a DSC record
y	Ordinate signal (W) of a DSC record
y_1	Signal of DSC record during pre-transition (pre-transition base-line) (W)
y_2	Signal of DSC record during transition (W)
y_3	Signal of DSC record during post-transition (post-transition baseline) (W)
$y_3^\star$	Asymptotic value of y_3 (post-transition baseline in a physical transformation) (W)
y_{trans}	Transition baseline (W)
Y_0	Instrumental signal (W)

Greek letters

α	Heating rate (K s^{-1}); without a subscript refers to the heating rate instrumentally imposed
β	$= \arctan(\alpha/R_0)$, angle (deg.) defined in Fig. 4
β_1	$= A_1 E_1/R$
β_2	$= A_2 E_2/R$
β_3	$= E_1/R$
β_4	$= E_2/R$
β_5	$= m_0(\Delta H_{R1})$
β_6	$= m_0(\Delta H_{R2})$
β_7	$= (\beta_1/\beta_3)^2$
β_8	$= (\beta_2/\beta_4)^2$
β_9	$= \beta_3 - \beta_4$
β_{10}	$= \beta_4 - \beta_3$
β_{11}	$= \beta_1\beta_2/\beta_3\beta_4$
β_{12}	$= m_{01}^{-1}[(\Delta H_{R1}) - (\Delta H_{R2})]^{-1}$
β_{13}	$= \beta_{11}(\Delta H_{R2})/[(\Delta H_{R1}) - (\Delta H_{R2})]$
β_{14}	$= \beta_1/\beta_3$
β_{15}	$= \beta_2/\beta_4$
β_{16}	$= \beta_{14}/\beta_3$
β_{17}	$= \beta_3 + \beta_4$
(ΔH_R)	Apparent heat of transformation (J kg-mol^{-1})
δ	$= (4 - 2/n)$
γ	$= (1 + 4/n)^{1/2}$

ζ	Extent of reaction (kg-mol)
ν	Generalized stoichiometric coefficient (dimensionless)
ϕ	Shape index (dimensionless)
$\phi^\star$	Asymmetry index (dimensionless)
θ	$\simeq (RT^2/E)\exp[-E/(RT)]$, temperature integral

Subscripts

0	Initial; at zero time
1	Reaction 1; pre-transition state; first inflection point
2	Reaction 2; transition state; second inflection point
3	Post-transition state
B, E	Beginning or end point
i	Given maximum/minimum; given inflection point
j	Chemical species j
m	Maximum/minimum in a chemical transformation
max	End of transition state (curve maximum) in a physical transformation
r	Reference material
s	Sample material
source	Heating source
t	Total
trans	Transition baseline
transf	Physical transformation

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