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DIFFERENTIAL SCANNING CALORIMETRIC MODEL FOR CORRECTIONS TO THE DSC RECORD *

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ABSTRACT

Based upon the signals of a DSC record, the equation of the transition baseline is analytically developed for a DuPont 990 thermal analyzer. The equation accounts for the effects on the transition baseline originating from (1) pretransition baseline, (2) heat-capacity change from that of the reactants to that of the products of reaction and (3) the fact that the sample material is subject, during the transition state, to a heating rate which differs from that of the reference material. If there is no change in heat capacities and either the heating rate or the heat transfer resistance are very small, then the transition baseline is merely an extension of the pretransition baseline. Any departure from these conditions makes the calculation of the transition baseline necessary, if correct kinetic parameters are to be expected from a DSC curve.

INTRODUCTION

Previously [1], we derived a set of equations to calculate apparent reaction-kinetic parameters from the DSC curve. In the context of the mathematical model used to generate this set of equations, the term "DSC curve" refers to the corrected record as compared to the DSC record obtained directly from the instrument. The present contribution deals specifically with the corrections of the DSC record required to deduce the real signal (i.e., the DSC curve) produced by the chemical/physical transformation in the sample material (i.e., reacting system).

The typical corrections of a DSC record are: non-linearity correction (which refers to the signal output from the thermocouple giving the temperature of the sample material), heating rate correction, thermal lag (thermal resistance) correction, and baseline (heat capacity differences) correction. Whereas the first two corrections are rather technical problems, which may or may not be important for a given instrument, the last two are analytical in

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nature and ought to be incorporated into every model used to evaluate DSC data. The non-linearity correction is usually done by running reference materials whose melting points are very well known [2]. Once the non-linearity correction is accomplished, the heating rate correction encompasses the direct checking of the instrument performance at different heating-rate settings [3]. As far as the corrections for thermal lag and baseline are concerned, they have been the subject of analytical models in the pertinent literature. Actually, the following work concentrates on a model which takes these two corrections into account for a DSC record obtained with a DuPont 990 thermal analyzer (E.I. DuPont de Nemours Co. (Inc.), Instrument Products Division, Wilmington, Delaware).

Selected references treating aspects related to those analyzed in this paper include: Heuvel and Lind [4], Brennan et al. [5,6], Richardson and Burrington [7], McNaughton and Mortimer [8], Holba et al. [9], and Gorbachev [10].

ASSUMPTIONS

The DuPont 990 thermal analyzer makes use of a constantan disc as the primary means of heat transfer to the sample and reference pans and as one element of the temperature-measuring thermocouples. Temperatures at the raised sample and reference platforms (upon which the sample and reference pans sit) are monitored by chromel–constantan thermocouples formed by the junction of the constantan disc with a chromel wire at each platform position. The difference output between those two thermocouples is monitored as difference in energy flow (W) on the ordinate of the DSC record. The sample platform has a chromel–alumel thermocouple, whose output is monitored as temperature (K) or time (s), on the abscissa of the DSC record, while the constantan disc is subject to a heating power so that the sample platform is changing its temperature linearly at a preset heating rate, α (K s^{-1}).

From the operating principle of the instrument, some assumptions are made. First, the constantan disc, as a heating source, is characterized by a uniform temperature, T_{source}. Second, the temperature of the sample platform does not necessarily represent the temperature inside the sample pan. With good contact between the sample pan and the sample platform and provided the platform and the pan are designed from very thin and highly thermally conductive materials, the temperature inside the sample pan is reasonably well represented by the abscissa of the DSC record.

Based upon these assumptions, the heat flows (W) between the heating source and both the sample material and reference material, at any moment, can be described by

$$q_s = (T_{\text{source}} - T_s)/R_0 \tag{1}$$

$$q_r = (T_{\text{source}} - T_r)/R_0 \tag{2}$$

where T_s and T_r are instantaneous temperatures of the sample and reference materials, respectively (K); and R_0 is the heat transfer resistance (K W^{-1}). Two assumptions have been incorporated: (1) the sample and reference materials are described by uniform temperatures (i.e., no thermal gradients inside the sample pans); and (2) the heat transfer resistance is the same for both platform–pan systems. The difference between the two heat flows is the actual signal monitored on the ordinate of the DSC record.

$$q \equiv q_s - q_r = (T_r - T_s)/R_0 \tag{3}$$

The differential form of this equation is used later on in the mathematical model

$$\frac{dq}{dT_s}\alpha_s = (\alpha_r - \alpha_s)/R_0 \tag{4}$$

where α_s and α_r are the instantaneous heating rates of sample and reference materials, respectively (K s^{-1}). The assumption was made that both sample and reference materials follow linear temperature changes, $T_s = T_0 + \alpha_s t$ and $T_r = T_0 + \alpha_r t$, where T_0 is the initial temperature (K) and t is time (s). Also, the heat transfer resistance, R_0, was assumed to be constant for a given heating rate, α, imposed by the instrument at the sample platform.

BASELINE EQUATION

At any time, the signal on the ordinate of the DSC record is the result of three effects: (1) an instrumental signal; (2) a signal due to the sensible-heat difference between sample and reference materials; and (3) a signal due to the chemical/physical transformation in the sample material (provided the reference material is inert)

$$y = Y_0 + (C_s\alpha_s - C_r\alpha_r) \pm b \tag{5}$$

where y is the DSC-ordinate signal (W); Y_0 is the instrumental signal (W); C_s and C_r are the mass of the sample and reference material, respectively, multiplied by heat capacity (J K^{-1}); and b is the pure transformation 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. The pure transformation signal is the deflection of the DSC curve from the baseline, as defined by Sandu et al. [1]. The ± sign depends on the conventional representation of the endothermic/exothermic effects on the DSC record. Eliminating α_r between eqns. (4) and (5), the DSC ordinate signal is expressed as

$$y = Y_0 + \alpha_s\left[C_s - C_r\left(1 + R_0\frac{dq}{dT_s}\right)\right] \pm b \tag{6}$$

Basically, the heat capacity of the sample material (i.e., reacting system) changes from that given by the mixture of the reactants, before the chemical/physical transformation, to that given by the mixture of the products of reaction, after the transformation. During the transformation, the heat capacity (J kg^{-1} K^{-1}) is that of a mixture of reactants and products of reaction corresponding to the instantaneous fraction conversion. At the same time, the pure transformation signal can be practically neglected before and after the transformation. As a result, eqn. (6), which holds at any moment of the DSC record, can be applied to three distinct states of a transformation: (1) pretransition; (2) transition; and (3) post-transition

$$y_1 = Y_0 + \alpha_s\left[C_{s1} - C_r\left(1 + R_0\frac{dq_1}{dT_s}\right)\right] \tag{7}$$

$$(y_2 \mp b) = Y_0 + \alpha_s\left[C_{s2} - C_r\left(1 + R_0\frac{dq_2}{dT_s}\right)\right] \tag{8}$$

$$y_3 = Y_0 + \alpha_s\left[C_{s3} - C_r\left(1 + R_0\frac{dq_3}{dT_s}\right)\right] \tag{9}$$

where the subscripts 1, 2 and 3 refer to pretransition, transition and post-transition states, respectively; and y_1, $(y_2 \mp b)$ and y_3 are the equations describing the baselines in the three states of the transformation.

From a heat balance point of view, the heat-flow difference between the sample and reference materials is equal to the sum of the last two terms in eqn. (5). In this case, the signal on the ordinate of the DSC record, for the three states of a transformation, can also be written as

$$y_1 = Y_0 + q_1 \tag{10}$$

$$y_2 = Y_0 + q_2 \tag{11}$$

$$y_3 = Y_0 + q_3 \tag{12}$$

At this stage of development, the intention is to convert eqn. (8), the equation of the transition baseline, to a more convenient form. First, the term C_{s2} in eqn. (8) can be evaluated from a relation of additivity, and it can be easily shown that

$$C_{s2} = (1 - f)C_{s1} + fC_{s3} \tag{13}$$

where f is the fraction conversion. Next, after mathematical manipulations involving eqns. (7)–(13), the final result is

$$(y_2 \mp b) = y_1 + f\left[(y_3 - y_1) + \alpha_s C_r R_0\frac{d(y_3 - y_1)}{dT_s}\right] - \alpha_s C_r R_0\frac{d(y_2 - y_1)}{dT_s} \tag{14}$$

The first term in eqn. (14) represents the pretransition baseline. The second term describes the heat-capacity change from that of the reactants to that of the products of reaction, and states that the post-transition baseline may not be an extension of the pretransition baseline. The third term is the result of the fact that the sample material is subject, during the transition state, to a heating rate which differs from that of the reference material. Equation (14) shows that the transition baseline is an extension of the pretransition line, only if two conditions are simultaneously fulfilled: (a) the pretransition and post-transition lines are identical (that is, no change in heat capacities); and (b) either the heating rate or the heat transfer resistance are sufficiently small making the third term in eqn. (14) negligible. In all situations, the transition baseline is going to deviate from the pretransition baseline corresponding to the magnitudes of the second and third terms.

DSC CURVE

In this section, practical procedures to find the transition baseline, which, generally, can be a fairly complicated "curve", are given. First, the instantaneous heating rate of the sample material, α_s, is assumed to be equal to the heating rate, α, applied at the sample platform by the instrument (this is the corrected heating rate). Second, the heat capacity of the reference material has to be known. Third, the heat transfer resistance (which may vary with heating rate) can be determined by measuring the slope of a sharp transformation (i.e., melting of high-purity indium) [3]. Finally, the temperature of sample material is assumed to be equal to the temperature monitored at the sample platform. Nonetheless, two problems connected with eqn. (14) require more attention: (a) the onset and final points of a transformation; and (b) the estimate of fraction conversion.

In eqn. (14), the functions describing the pretransition baseline (y_1) as well as the post-transition baseline (y_3) are estimated through a linear or second-order polynomial (in the case with wide temperature ranges) fit [4]. Heuvel and Lind [4] used a statistical approach to determine the onset temperature of the transformation. A linear equation is fitted to the estimated pretransition part of the baseline, and the standard deviation of the point extrapolated to the peak of the DSC record is calculated. The procedure is repeated, while the end of the pretransition baseline is shifted along the DSC record. 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. A similar procedure is used to find the equation of the post-transition baseline (y_3) and the final temperature of the transformation.

For the onset temperature, also, an analytical relation can be developed [10]. Starting from the equation describing the progress of reaction (see ref. 1)

$$\frac{\mathrm{d}f}{\mathrm{d}T} = C_0^{n-1} \frac{A}{\alpha} \exp\left(-\frac{E}{RT}\right)(1-f)^n \tag{15}$$

where C_0 is the initial concentration of the reactant (kg-mol m^{-3}); n is the apparent order of reaction; A is the apparent pre-exponential factor (kg-mol m^{-3} s^{-1})/(kg-mol m^{-3})^n; E is the apparent activation energy of reaction (J kg-mol^{-1}); and $R = 8314$ J kg-mol^{-1} K^{-1}, is the gas law constant. Close to the onset point, the fraction conversion may already have a value f_B (actually very close to zero), such that the term $(1 - f_B) \approx$ const. As a result, the integration of eqn. (15) produces a relation to calculate the onset temperature, T_B

$$f_B(1 - f_B)^{-n} = C_0^{n-1} \frac{A}{\alpha} \frac{RT_B^2 \exp(-E/RT_B)}{E + 2RT_B} \tag{16}$$

where an approximate solution to the temperature integral (see eqn. 11 in ref. 1) was used. A practical concept to estimate f_B would be based on the accuracy with which the equation of the pretransition baseline is determined. However, the apparent kinetic parameters n, A and E must be known in eqn. (16). This requires a trial-and-error procedure, using first the DSC record to determine the kinetic parameters. Similarly, close to the final point, the fraction conversion may have a value f_E (actually very close to unity), such that the term $(1 - f_E) \approx$ const. and, from eqn. (15), the relation for the final temperature, T_E, is

$$f_E(1 - f_E)^{-n} = C_0^{n-1} \frac{A}{\alpha} \frac{RT_E^2 \exp(-E/RT_E)}{E + 2RT_E} \tag{17}$$

where f_E is an estimate based on the accuracy of the equation of the post-transition baseline.

As far as the fraction conversion in eqn. (14) is concerned, the best way to estimate it is to couple eqns. (14) and (15) through a trial-and-error procedure, first using the DSC record to determine the kinetic parameters n, A and E. Once the transition baseline is computed, the actual DSC curve is obtained as $[y_2 - (y_2 \mp b)]$ vs. T, and the kinetic parameters of a transformation can then be readily calculated (see ref. 1).

CONCLUSIONS

A DSC record requires a series of corrections until the real signal produced by the chemical/physical transformation in the sample material is available. Because the mathematical model describing these corrections encompasses specific assumptions, it must be tested against some standard transformations to determine its usefulness.

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