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KINETIC ANALYSIS OF SIMULATED DTA RESPONSES

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ABSTRACT

The classical and Boersma DTA signals produced by melting, by endothermic and by exothermic first-order reactions have been simulated using a simple model of a DTA instrument. The simulations have been related to reality by comparison with experimental results. The simulated DTA curves have been subjected to non-isothermal kinetic analysis using the Borchardt and Daniels method and the kinetic parameters derived have been compared with the input values. The consequences of the approximations used are discussed.

INTRODUCTION

There have been numerous discussions concerning the expected shapes of DTA curves derived from various models of DTA instruments [1–4]. The models used have been of varying degrees of sophistication and some of the more sophisticated models have permitted examination of the effects on the DTA curve of changes in physical properties of the sample relative to the reference [5].

Considerable attention has also been paid to the extraction of kinetic information from DTA responses arising from chemical reactions in the sample [6–10]. Kinetic analyses, especially those done by purchasers of commercial software, are often uncritically based on the assumption that the experimental DTA curve is an acceptable starting point for analysis. There have been several warnings [7,10] about blindly following such procedures.

In this discussion we start with a very simple model of a chemical reaction in an idealised DTA instrument and simulate the DTA responses for both endothermic and exothermic reactions. Most discussions of DTA deal explicitly or implicitly with endothermic processes and imply that the

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treatment for exothermic processes is identical. It is important to confirm this as there is considerable interest in the use of DTA for the study of strongly exothermic processes such as the decomposition of explosives and the ignition of pyrotechnic compositions [11–15]. The procedure required to extract the kinetic and thermochemical parameters used in the simulation from the resulting DTA curves is then investigated. This procedure also involves a simulated calibration of the DTA instrument with a reference substance. Having shown some of the problems involved in this analysis in the idealised DTA instrument, we comment on the problems encountered in more realistic instruments.

THE CHEMICAL REACTION

Following most treatments, the reaction is assumed to be an irreversible first-order ($n = 1$) process, $d\alpha/dt = k(1-\alpha)^n$ (where α is the fractional extent of reaction), although this is not a very realistic model for reactions involving solid samples. There is no fundamental reason why a more complex model, e.g. $d\alpha/dt = k\alpha^m(1-\alpha)^n$, should not be used, provided, of course, that some suitable starting process is included.

The rate coefficient, k, is assumed to show normal obedience to the Arrhenius equation, so that

$$d\alpha/dt = A\,\exp(-E/RT)(1-\alpha) \tag{1}$$

where A is the pre-exponential factor and E is the activation energy. This assumption has also been questioned for reactions involving solids. The heat of reaction, $Q = qm_s$, and the heat capacity of the sample, $C_s = c_s m_s$, refer to the mass m_s of the sample, where q and c_s are values per unit mass, and Q is taken as being positive for endothermic processes.

THE DTA INSTRUMENT

The model used to represent a DTA instrument is shown in Fig. 1. Unlike real instruments, provision has been made for monitoring both the classical DTA signal, $\Delta T_C = T_{sc} - T_s - T_r$, and the Boersma DTA signal, $\Delta T_B = T_{sc} - T_{rc}$ [3,4]. It is assumed, simplistically of course, that: (i) the temperature sensors measure the temperatures as specified without interfering with the system; (ii) there are no temperature gradients in the sample or in the reference during the programmed heating or even during the course of reaction in the sample; (iii) the temperature of the heat source (furnace), T_h, rises at a set constant rate, ϕ, so that $T_h = T_0 + \phi t$ where T_0 is the uniform temperature of all parts of the instrument at time $t = 0$; (iv) energy transport is confined to conduction governed by Newton's Law; (v) the heat capaci-

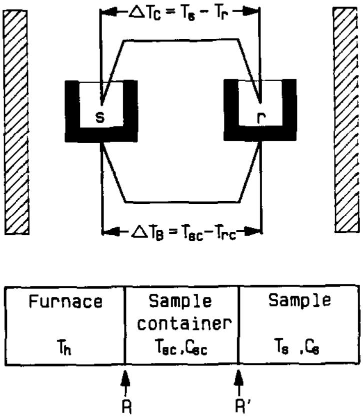

Fig. 1. Model of an idealised DTA instrument: s = sample; r = reference; sc = sample container; rc = reference container. ΔT_C = classical DTA signal; ΔT_B = Boersma DTA signal. R' = thermal resistance between container and contents; R = thermal resistance between container and surroundings.

ties, $C_s = C_r$ and $C_{sc} = C_{rc}$, and all are independent of temperature; (vi) the system can be described by two thermal resistance terms: R' for heat transfer from sample or reference material to the corresponding container, and R for heat transfer from the containers to the surroundings (furnace): R and R' are assumed to be independent of temperature.

MATHEMATICAL DESCRIPTION OF THE MODEL DTA

The energy balance equations [2–4] are as follows.

For the sample, energy changes are produced by reaction (heat of reaction, Q, taken as positive for endothermic reactions), and by heating of the sample by the sample container, which, in turn, is heated by the furnace.

$$C_s(\mathrm{d}T_s/\mathrm{d}t) = -Q(\mathrm{d}\alpha/\mathrm{d}t) - (T_s - T_{sc})/R' \tag{2}$$

$$C_{sc}(\mathrm{d}T_{sc}/\mathrm{d}t) = (T_s - T_{sc})/R' - (T_{sc} - T_h)/R \tag{3}$$

Similarly for the reference side

$$C_r(\mathrm{d}T_r/\mathrm{d}t) = -(T_r - T_{rc})/R' \tag{4}$$

$$C_{rc}(\mathrm{d}T_{rc}/\mathrm{d}t) = (T_r - T_{rc})/R' - (T_{rc} - T_h)/R \tag{5}$$

In the simplest case, with $C_s = C_r = C_1$ and $C_{sc} = C_{rc} = C_2$

$$C_1[\mathrm{d}(T_s - T_r)/\mathrm{d}t] = -Q(\mathrm{d}\alpha/\mathrm{d}t) - [(T_s - T_r) - (T_{sc} - T_{rc})]/R' \tag{6}$$

$$C_2[\mathrm{d}(T_{sc} - T_{rc})/\mathrm{d}t] = [(T_s - T_r) - (T_{sc} - T_{rc})]/R' - (T_{sc} - T_{rc})/R \tag{7}$$

From eqns. (6) and (7)

$$C_1[\mathrm{d}(T_s - T_r)/\mathrm{d}t] = -Q(\mathrm{d}\alpha/\mathrm{d}t) - C_2[\mathrm{d}(T_{sc} - T_{rc})/\mathrm{d}t] - (T_{sc} - T_{rc})/R \tag{8}$$

and integrating with respect to time between 0 and t

$$C_1(T_s - T_r) = -Q\alpha - C_2(T_{sc} - T_{rc}) - (1/R)\int_0^t (T_{sc} - T_{rc})\,\mathrm{d}t \tag{9}$$

where $\int_0^t (T_{sc} - T_{rc})\,\mathrm{d}t$ would be the partial area, $s_{B,t}$, under the curve of the Boersma DTA signal, $\Delta T_B = T_{sc} - T_{rc}$. After a suitably long time, $T_s \approx T_r$ and $T_{sc} \approx T_{rc}$ and $\alpha = 1$, so

$$-Q = (1/R)\int_0^{\infty} \Delta T_B\,\mathrm{d}t = S_B/R \tag{10}$$

where S_B is the total area under the curve of the Boersma DTA signal. At any intermediate time, t, however

$$\alpha_t = \left[C_1\Delta T_C + C_2\Delta T_B + (s_{B,t}/R)\right]/(S_B/R) \tag{11}$$

so, unless C_1 and C_2 are small

$$\alpha_t \neq (s_{B,t}/S_B) \tag{12}$$

and unless these heat capacity values are available *and* the DTA signal in both classical and Boersma configurations is measured, an accurate value of α cannot be calculated.

NUMERICAL SIMULATION OF THE DTA RESPONSE

The finite difference method is applied to eqn. (1) $(\mathrm{d}\alpha/\mathrm{d}t) = A\exp(-E/RT)(1-\alpha)$, so that in a small time interval, Δt, an amount of reaction, $\Delta\alpha$, will occur. $\Delta\alpha$ is determined by the two factors: the (average) temperature of the *sample* during the interval and the kinetic model term, $(1-\alpha)$, i.e.

$$\Delta\alpha = A\exp(-E/RT_s)(1-\alpha)\Delta t \tag{13}$$

Instead of the average temperature, we have used the temperature at the start of the interval, Δt. It is assumed that initially all parts of the instrument are at a uniform temperature, T_0.

The furnace temperature, T_h, increases according to the set, constant, heating rate, ϕ. So $\Delta T_h = \phi\Delta t$ and $T_h = T_0 + \Sigma\,\Delta T_h$. The sample and reference containers are then heated according to the temperature gradients between the furnace and the containers, the thermal resistance, R, and the corresponding heat capacities, C_{sc} and C_{rc}, while the heating of the sample and reference materials is governed by the temperature gradients between the containers and the materials, the thermal resistance, R', and the heat capacities, C_s and C_r

$$\Delta T_{sc} = \Delta t\left[(T_s - T_{sc})/R' - (T_{sc} - T_h)/R\right]/C_{sc} \tag{14}$$

$$\Delta T_{rc} = \Delta t\left[(T_r - T_{rc})/R' - (T_{rc} - T_h)/R\right]/C_{rc} \tag{15}$$

and

$$\Delta T_s = [-Q\Delta\alpha - \Delta t(T_s - T_{sc})/R']/C_s \tag{16}$$

$$\Delta T_r = [-\Delta t(T_r - T_{rc})/R']/C_r \tag{17}$$

By keeping track of T_s, T_r, T_{sc} and T_{rc}, it is possible to calculate the classical DTA signal, $T_s - T_r$, or the Boersma DTA signal, $T_{sc} - T_{rc}$, at any time, or referred to any of the above temperatures or the furnace temperature, T_h.

Simulated DTA responses were output to files using programs in GWBASIC and a MICROSOFT BASIC compiler. Double precision variables were used where necessary and time intervals used for calculations were as small as 0.2 ms. Significant errors, particularly in area measurements, were introduced by decreasing the resolution. The output files were examined further in spreadsheet form, using LOTUS 123.

SIMULATION OF INSTRUMENT CALIBRATION

To calibrate the idealised DTA instrument, i.e. to determine the value of R in the expression $Q = S/R$, it was necessary to simulate the melting of a standard, e.g. indium metal, under the same idealised conditions.

The sample and reference were again regarded as being identical except that the sample melted at T_m. When $T_s < T_m$, $\Delta T_C = 0$ and α = fraction melted = 0. When $T_r > T_m$, $T_s = T_m$ until $\alpha = 1$ (melting complete).

The equations used in the simulation were those used before, except that

$$\Delta\alpha = \Delta t(T_m - T_{sc})/(R'Q) \tag{18}$$

and the sample container was heated, as before, by the furnace.

THE THERMAL RESISTANCES, *R* AND *R'*

To obtain realistic simulated DTA curves, it was necessary to use realistic values of R and R'.

Normally a value of R would be obtained by calibration of an actual DTA instrument

$$Q_{\text{calibrant}} = S/R \tag{19}$$

For a heat-flux DSC instrument, the actual value of R is often less accessible.

An experimental heat-flux DSC curve for the melting of 6.6 mg of indium metal, heated at 20 K min^{-1} in a silica-glass crucible (94.9 mg) in a Stanton–Redcroft DSC 1500, is shown in Fig. 2, solid line.

Several melting curves were simulated with the parameters listed in Table 1 and various combinations of R and R' (assuming $R > R'$) and these

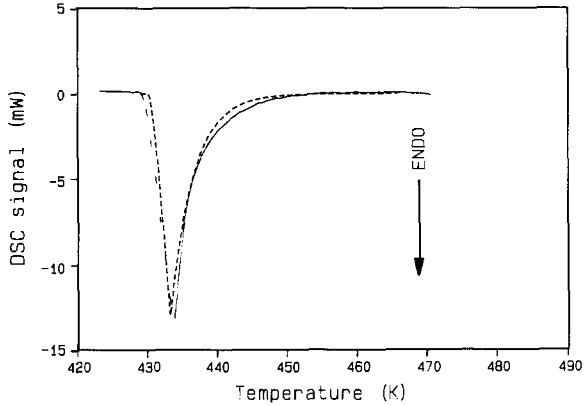

Fig. 2. Experimental heat-flux DSC curve (solid line) for the melting of 6.6 mg of indium heated at 20 K min^{-1} in a silica-glass crucible (94.9 mg), compared with a simulated curve (dashed line) for $R = 116$ K s J^{-1} and $R' = 50$ K s J^{-1}.

curves were compared with Fig. 2, solid line. Satisfactory agreement was achieved with $R = 116$ and $R' = 50$, as shown in Fig. 2, dashed line.

Once a value of R has been guessed for the experimental curve, the appropriate value of R' may be obtained from the relationships below

$$C_{sc}[d(T_{sc} - T_{rc})/dt] = (T_{sc} - T_{rc})/R' - (T_s - T_r)/R' - (T_{sc} - T_{rc})/R \quad (20)$$

So

$$C_{sc}[d(T_{sc} - T_{rc})/dt] + (T_{sc} - T_{rc})/R = [(T_{sc} - T_{rc}) - (T_s - T_r)]/R' \quad (21)$$

TABLE 1

Melting of indium

Indium
Mass = 6.60 mg
Atomic mass = 114.8 g mol^{-1}
$\Delta H_{fusion} = 28.5$ J g^{-1}
Heat capacity = 0.2343 J K^{-1} g^{-1}
$Q/C = 121.6$ K
$T_m = 429.6$ K
$Q = 28.5 \times 6.60 \times 10^{-3} = 0.1881$ J
$C_s = 0.2343 \times 6.60 \times 10^{-3} = 1.55 \times 10^{-3}$ J K^{-1}

Silica-glass crucible
Mass = 94.9 mg
Heat capacity = 0.753 J K^{-1} g^{-1}

Platinum sensor
Mass = 91.96 mg
Heat capacity = 0.150 J K^{-1} g^{-1}

$C_{sc} = C_{rc} = 0.0715 + 0.0138 = 0.085$ J K^{-1}

Before melting, $(T_s - T_r)$ is very small. When $T_r = T_m$, let $t = 0$, then at any later stage during melting, $T_s = T_m$ and $T_r \approx T_m + \phi t$, so

$$C_{sc}[d(T_{sc} - T_{rc})/dt] + (T_{sc} - T_{rc})/R = [(T_{sc} - T_{rc}) - (T_m - T_m - \phi t)]/R'$$
$$= [(T_{sc} - T_{rc}) + \phi t]/R' \qquad (22)$$

and the heat-flux signal is converted to the Boersma DTA signal by multiplying by R. Thus a plot of the left-hand side of eqn. (22) against the quantity in square brackets, should (and does) give a straight line of slope $= 1/R'$.

SIMULATION OF CHEMICAL REACTION

Several authors [16,17] have described the effects of varying parameters such as E, A and the heating rate, ϕ, on the shape of DTA curves. In general terms, increasing the value of E and/or decreasing the value of A, shifts the temperature range over which the reaction rate is measurable to higher values. We have not varied these parameters in this study, except (see below) where they may influence kinetic analyses.

ENDOTHERMIC DECOMPOSITION

The parameters, chosen rather arbitrarily, for our simulation are given in Table 2. The resulting DTA signals (classical and Boersma) are shown in Fig. 3. Division of the classical signal by $R + R'$ and the Boersma signal by R gives a single heat-flux DSC signal.

TABLE 2

Reaction parameters

Reaction order $n = 1$
Activation energy $E = 100000$ J mol^{-1}
Pre-exponential factor $A = 1 \times 10^7$ s^{-1}
$Q/C_s = 5000$ K
$Q = 25$ J
$R = 116$ K s J^{-1}
$R' = 50$ K s J^{-1}
$C_s = C_r = 0.005$ J K^{-1}
$C_{sc} = C_{rc} = 0.085$ J K^{-1}
Heating rate $\phi = 20/60$ K s^{-1}

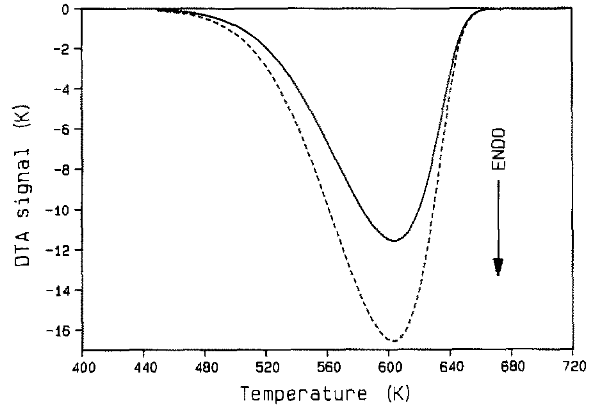

Fig. 3. Simulated DTA signals for an endothermic reaction with the input parameters given in Table 2: ———, Boersma DTA; — — —, classical DTA. (The abscissa is the reference container temperature.)

EXOTHERMIC REACTION

The DTA signals corresponding to Fig. 3, with the sign of *Q* reversed for exothermic reaction, are shown in Fig. 4. It is immediately evident that the two sets of curves are not mirror images and this is confirmed by the altered shape of the (α, t) curve for exothermic reaction, Fig. 5, curve a, compared to endothermic reaction, curve b.

This set of parameters is close to the limits beyond which thermal runaway [15] is likely to occur under the conditions represented. Runaway can be caused by increasing *A* and/or decreasing *E*, or increasing the thermal resistances *R* and/or *R'*.

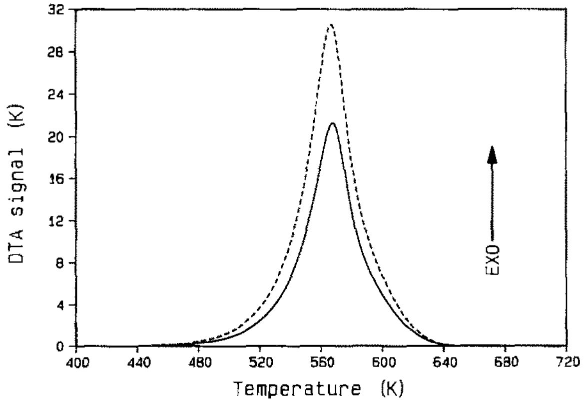

Fig. 4. Simulated DTA signals for the exothermic reaction corresponding to Fig. 3 and Table 2, with the sign of *Q* reversed: ———, Boersma DTA; — — —, classical DTA. (The abscissa is the reference container temperature.)

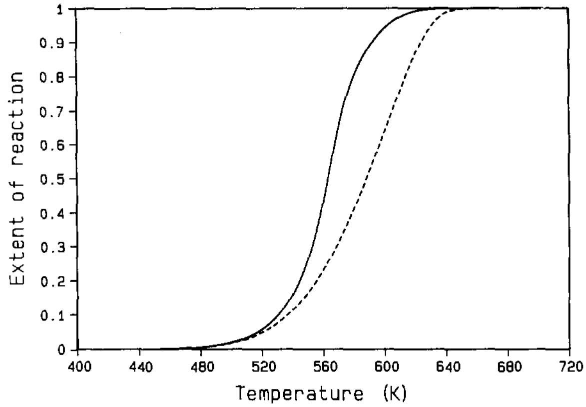

Fig. 5. Extent of reaction, α, vs. reference container temperature: ———, exothermic reaction (Fig. 4); — — —, endothermic reaction (Fig. 3).

EXTRACTION OF KINETIC INFORMATION FROM DTA CURVES

Any kinetic analysis requires sets of values of the fractional extent of reaction, α, at some time, t, at which the *sample* temperature was T_s. Calculation of α at time t, even in the idealised DTA instrument, strictly requires more than the determination of the partial area under the DTA curve up to that time. As discussed above, for the idealised Boersma DTA

$$\alpha_t = (RC_1\Delta T_C + RC_2\Delta T_B + s_{B,t})/S_B \tag{23}$$

so that both the classical and Boersma signals are required, but normally only ΔT_B is available. In most experimental situations, $C_1(=C_s=C_r) < C_2(=C_{sc}=C_{rc})$ while $\Delta T_C > \Delta T_B$. If R is small, both DTA signals are small, so that the correction terms are small and $\alpha_t \approx s_{B,t}/S_B$.

The areas s or s_B and S or S_B are obtained by integration of the DTA signal as a function of time. If they are obtained by integration of the DTA signal as a function of the programmed temperature and corrected by scaling by the heating rate, ϕ, further errors may be introduced through deviations from true linearity of the programmed heating.

THE TEMPERATURE, T

The DTA signals, ΔT_C or ΔT_B, could be displayed as a function of t, or of the programmed temperature (T_r or T_{rc}), or, conceivably, as a function of T_s or T_{sc} which distorts the time base required for area determination (see above). The temperature which determines the rate of reaction is, obviously the actual sample temperature, T_s, and, unless this is known, any kinetic analysis must be in error, e.g. in Boersma DTA (heat-flux DSC) it is assumed that $T_{sc} \approx T_s$, while in some software packages the reference temperature, T_r or T_{rc}, is used on the assumption that $T_r + \Delta T_C \approx T_r$ (or $T_{rc} + \Delta T_B \approx T_{rc}$). In the extreme case, it is possible that the furnace temperature, T_h, could be used as the abscissa.

THE KINETIC ANALYSIS

Numerous methods have been proposed for kinetic analysis [6,10]. These are usually divided into differential or integral methods, depending upon whether they use measurements of $(\mathrm{d}\alpha/\mathrm{d}t)$ or not. Differential methods applied to DTA curves generally assume that the DTA signal, ΔT_C or ΔT_B, is proportional to $\mathrm{d}\alpha/\mathrm{d}t$, as well as the general assumption, discussed above, that $\alpha = s/S$.

As the assumptions made in the systems simulated above are similar to the assumptions made by Borchardt and Daniels [6], the BD method was used to analyse the simulated DTA curves. The BD method is a specific case of a more general analysis considered by Sharp [7] and others, and it is used in several commercially available software packages. The method involves calculating first-order rate coefficients

$$k = (\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha) \tag{24}$$

on the assumption that the available DTA signal, ΔT_C or ΔT_B, is a measure of $\mathrm{d}\alpha/\mathrm{d}t$, and that $(1-\alpha)$ is proportional to $(S-s)$, or $(S_B - s_b)$. So

$$k = F_C \Delta T_C/(S-s) \tag{25}$$

or

$$k = F_B \Delta T_B/(S_B - s_B) \tag{26}$$

where F_C and F_B are appropriate scale factors. The slope of an Arrhenius plot of ln k against $1/T$ should then yield the activation energy, E. The intercept contains the scale factor, F_C or F_B, in addition to the pre-exponential factor, A.

The procedure can be made general by assuming an order of reaction, n, and plotting $\ln(\Delta T) + n \ln(S-s)$ against $1/T$ for various values of n. Alternatively, instead of assuming $g(\alpha) = (1-\alpha)^n$, any of the other functions $g(\alpha)$ used in solid-state reactions [18] could be tested for suitability.

We have not complicated matters further by considering those methods of kinetic analysis based on comparison of features, such as peak maximum temperatures, of several DTA curves recorded at different heating rates.

When the BD method was applied to the endothermic reaction shown in Fig. 3, the kinetic parameters listed in Table 3 were obtained. The corrections to α were small and even use of the incorrect temperatures did not introduce significant errors in the parameters. Note that the maximum

TABLE 3

Kinetic analysis (Borchardt and Daniels) of the endothermic reaction (Table 2). Input: $E = 100000$ kJ mol^{-1}; $A = 1\times10^7$ s^{-1}; $\phi = 20/60$ K s^{-1}; $R = 116$ K s J^{-1}; $R' = 50$ K s J^{-1}; $Q = 25.00$ J; ln $A = 16.12$

T scale used	E (kJ mol^{-1})	Intercept	ln A	r^2
Sample	100.61 ± 0.05	24.08 ± 0.02	16.11 ± 0.02	0.99984
Sample container	97.95 ± 0.05	23.40 ± 0.02	15.43 ± 0.02	0.99986
Furnace	93.36 ± 0.14	22.06 ± 0.07	14.09 ± 0.07	0.99876

Area (DSC) = 24.99 J

True α = 0.501
Fractional area = 0.462
Correction = 0.039
Corrected α = 0.501

TABLE 4

Kinetic analysis of the exothermic reaction. Input: $E = 100.000$ kJ mol^{-1}; $A = 1.000\times10^7$ s^{-1}; $\phi = 20/60$ K s^{-1}; $R = 116$ K s J^{-1}; $R' = 50$ K s J^{-1}; $Q = -25.00$ J; ln $A = 16.12$

T scale used	E (kJ mol^{-1})	Intercept	ln A	r^2
Sample	100.8 ± 0.1	24.11 ± 0.06	16.14 ± 0.06	0.99938
Sample container	102.6 ± 0.2	24.58 ± 0.10	16.61 ± 0.10	0.99837
Furnace	107.8 ± 0.6	25.80 ± 0.29	17.83 ± 0.29	0.98466

Area = 24.99 J

True α = 0.5000
Fractional area = 0.427
Correction = 0.073
Corrected α = 0.500

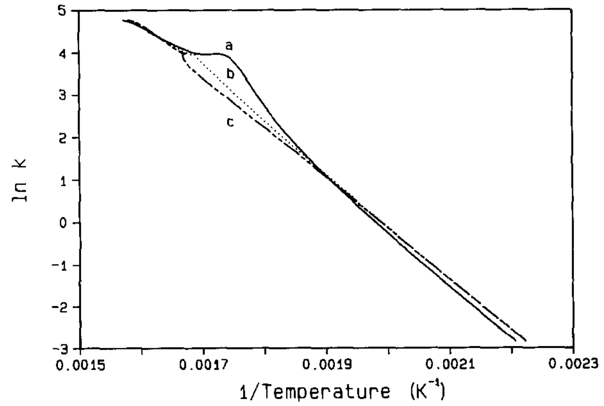

Fig. 6. Arrhenius plots for the exothermic reaction of Fig. 4, using the Borchardt and Daniels method ($n = 1$): a, furnace temperature, T_h; b, sample container temperature, T_{sc}; and c, sample temperature, T_s.

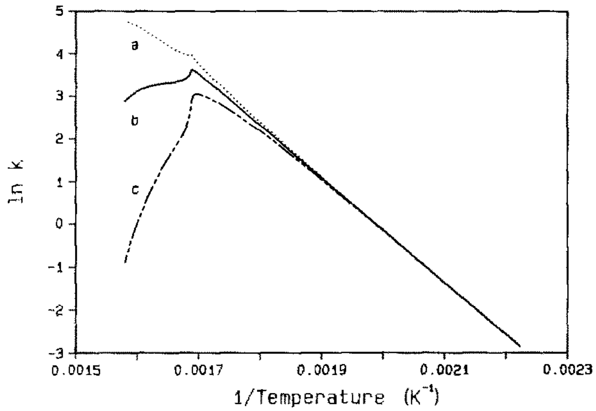

Fig. 7. Arrhenius plots for the exothermic reaction of Fig. 6, using different orders of reaction, n: a, $n=1$; b, $n=2/3$; c, $n=0$. (The abscissa refers to the sample container temperature).

values of the DTA signals were about −15 K (classical) and −10 K (Boersma) or −86 mW (DSC).

Kinetic analysis of the analogous exothermic reaction, Fig. 4, gave the values of E and the intercepts listed in Table 4. The errors in the calculated value of E are larger than for the endothermic reaction (Table 3). The absolute values of the maximum DTA and DSC signals were significantly greater than those for the endothermic reaction (30 K (classical) and 21 K (Boersma) or 180 mW (DSC)).

The Arrhenius plots using the furnace temperature, the sample container temperature and the sample temperature are shown in Fig. 6.

The sensitivity of the analysis to the kinetic model selected was tested by drawing Arrhenius plots (using the sample container temperature) for the contracting volume model ($n=\frac{2}{3}$) (Fig. 7, curve b), and the zero-order model ($n=0$) (Fig. 7, curve c). The deviations from the expected plot shown, curve a, are not large especially, as expected, at low T and low α.

CONCLUSIONS

The theoretical basis of DTA has been extensively discussed over many years. Much attention has been directed to the effects of the physical properties of the sample, relative to those of the reference, on the shape of the DTA curve. Calorimetric aspects of DTA have generally received more attention than kinetic aspects, although kinetic analysis of DTA curves is a fairly routine procedure.

In this study, it has been shown that even before details of the fine structure of the DTA system, such as temperature gradients within the sample and reference materials, and the variation of thermal properties with temperature, are considered, there are potential problems in extracting kinetic information from DTA or heat-flux DSC curves.

If such problems exist in the most idealised of instruments, they will certainly be more severe in real instruments and need to be considered even ahead of the added complexities of real reactions such as the effects of particle size, sample disposition and influences of the prevailing gaseous atmosphere [10].

The simulations and discussion above confirm [2] that there is generally little problem in obtaining values of the heats, Q, of endothermic processes from measurements of the total area under a DTA (classical or Boersma) curve.

For exothermic processes, the DTA signal is distorted, at least to a small extent, by the fact that the DTA instrument (or heat-flux DSC) is a temperature-measuring device, in contrast to power-compensated DSC which measures energy [2].

When the energy produced by reaction in the sample during a given time interval is less than that available from the furnace to the reference during the same time interval, the furnace supplies the energy required by the sample for the balance of the temperature rise and $\Delta T = 0$. The energy release by the sample does not therefore show up as a temperature difference, because the full quota of energy cannot be transferred from the furnace, T_h, to the sample, if $T_s > T_h$. T thus remains zero in spite of the occurrence of a small amount of reaction, and the total area under the DTA curve will be an underestimate of Q, especially when the reaction is slow and/or Q is not a large exothermic value.

From the above it can be seen that if the total area of an exothermic DTA peak is not a true reflection of Q, then the usual assumption in kinetic analysis that $\alpha = \text{partial area} = s/S$ is not valid for exothermic reactions, except perhaps where reaction is rapid and Q is large. Under these conditions, though, the more complex factors of real DTA systems, such as temperature gradients within the sample, the responses of temperature-measuring systems and the cooling possible in an instrument, introduce their own distortions.

Many kinetic analyses of DTA curves not only ignore the possibility of errors in the determination of α, but also incorporate an inexact temperature in the Arrhenius equation. The use of the Arrhenius equation is an assumption which has itself often been challenged [10,19]. In the idealised systems considered above, the only temperature which actually governs the rate of reaction in the sample is, obviously, the actual sample temperature, T_s. In a Boersma DTA, the closest available quantity to T_s is T_{sc}. Use of T_{sc} in the analysis thus inevitably introduces some error. If, instead of using T_s or T_{sc} in a kinetic analysis, T_r or T_{rc} were to be used, on the assumption that ΔT_C or ΔT_B were small, a further error is introduced.

It is worth noting that areas s, s_B, S and S_B must be determined on a time base (or in terms of the programmed temperature, T_r or T_{rc}, and the heating rate, ϕ, but obviously not in terms of T_s or T_{sc}).

In spite of the above reservations, typical procedures for extraction of kinetic information from DTA curves, exemplified by the Borchardt and Daniels (BD) method [6], are not very sensitive to small errors in α and in temperatures used in Arrhenius-type plots.

In real instruments, provided that the heat capacity and thermal resistance terms have reasonably low values, DTA signals are not large, except for very rapid reactions with large Q values, and values of activation energies, E, recovered from realistic simulations are within a few per cent of the input values. It is more difficult to recover the A values on account of the instrumental scale factors. Values of E are not very sensitive to the kinetic model assumed and, where the Arrhenius plot deviates from linearity, the early stages of the DTA curve, i.e. low T and low α, should, in most cases, be given the most weight in determining the slope. In general, the assumption that $\alpha = s/S$ introduces errors, which may be small, but should at least be considered .

For accurate kinetic measurements in a Boersma DTA, it is necessary, both for the calculation of α and for the Arrhenius plot, to have access to the actual sample and reference temperatures, T_s and T_r.

It is useful, for any real instrument, to have some idea of both the thermal resistances R and R', even if these are composite quantities and are temperature dependent. For heat-flux DSC instruments, the simulation of a curve to match an experimental curve, as described above, can lead to the required information.

The actual value of R' determines the difference between the classical and Boersma DTA signals and hence provides a way of correcting from T_{sc} to T_s for kinetic analysis.

In a further paper [14], we will describe the simulation of the DTA response to very rapid exothermic processes using a two-dimensional finite-element model.

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REFERENCES

1 A.D. Cunningham and F.W. Wilburn, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol 1, Academic Press, London, 1970, p. 32.

2 A.P. Gray, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Plenum, New York, 1968, p. 209.
3 S.C. Mraw, Rev. Sci. Instrum., 53 (1982) 228.
4 Y. Saito, K. Saito and T. Atake, Thermochim. Acta, 99 (1986) 299.
5 R. Melling, F.W. Wilburn and R.M. McIntosh, Anal. Chem., 41 (1969) 1275.
6 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
7 J.H. Sharp in RC Mackenzie (Ed.), Differential Thermal Analysis, Vol 2, Academic Press, London, 1972, p. 47.
8 W.W. Wendlandt, Thermal Analysis, Wiley, New York, 3rd edn, 1986.
9 M.E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London, 1988, Chap. 13.
10 P.D. Garn, Thermoanalytical Methods of Investigation, Academic Press, New York, 1965, Ch. 6; Crit. Rev. Anal. Chem., 3 (1972) 65.
11 P.G. Laye and E.L. Charsley, Thermochim. Acta, 120 (1987) 325.
12 A.J. Beardell and A.D. Kirshenbaum, Thermochim. Acta, 8 (1974) 35.
13 M.E. Brown, Thermochim. Acta, 148 (1989) 521.
14 M.W. Beck and M.E. Brown, to be published.
15 T. Boddington, P. Gray and S.R. Kay, Proc. Roy. Soc. Lond. A, 425 (1989) 269.
16 J.P. Elder, J. Therm. Anal., 30 (1985) 657.
17 J. Zsako, in Z.D. Zivkovic (Ed.), Thermal Analysis, Univ. Beograd, Yugoslavia, 1984, p. 167.
18 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
19 M. Arnold, G.E. Veress, J. Paulik and F. Paulik, Thermochim. Acta, 52 (1982) 67; Anal. Chim. Acta, 124 (1981) 341.