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Using thermoanalytical data.
Part 4. Processing of DTA/DSC curves to calculate reaction enthalpy and kinetic parameters. An application to calcium oxalate [1]

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Abstract

With regard to single step reactions, a new approach to the processing of DTA/DSC curves is presented, taking into account the heat transfer into the instrument. It is an extension of a previous physical model, that allowed the calculation of true kinetic parameters from TG curves. The peak area can be properly calculated as well as the degree of reaction, this also being suitable for kinetic parameters calculation. Through numerical simulations, other methods for DTA/DSC curve processing are discussed with respect to that proposed. By TG and DTA, the true kinetic parameters have been finally determined for the second and third steps of the thermal decomposition of $CaC_2O_4 \cdot H_2O$, to complete previously reported data for the first dehydration step. The agreement of the results with isothermal experiments seems to indicate a way to escape from the dichotomy between isothermal and non-isothermal kinetics. Several other approaches to non isothermal kinetics are reviewed and discussed. The software developed is also briefly described.

INTRODUCTION

Extraction of kinetic parameters from thermoanalytic curves has recently provided research with a new stimulus. The greater or lesser reliability of kinetic parameters obtained from dynamic as opposed to isothermal measurements has been debated [1], and new instruments have been proposed to maintain a constant assigned value of the derivative of selected quantities [2].

We have investigated the perturbations induced in dynamic TG measurements by heat transfer phenomena [3–5]. In many operating conditions,

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such phenomena destroy the assumption that the sample heating rate is constant and equal to that of the programmed temperature of the heater. Because many literature data fail in re-building experimental curves [3], we have defined as true kinetic parameters those displaying a good predictive power or, in other words, able to satisfactorily predict the behaviour of a material in a wide range of heating conditions [4].

It is mandatory to provide true data for models used to predict the behaviour of ablative materials [6,7], when their working conditions are not easily reproducible in a laboratory instrument. The concept of "true" is not concerned with the physicochemical meaning of the parameters, nor with a reaction mechanism [8].

This paper extends the previous model [4] to the processing of DTA/DSC curves by taking the temperature differences (DTA) between sample and programmer into account. In a theoretical DSC equipment those differences are zero, whereas many real DSC equipments substantially have a DTA architecture. As far as the measurement of reaction enthalpy is concerned, the model has only been discussed with respect to the methods proposed by Brennan et al. [9] and Henderson et al. [10]. With several variations, other known approaches [11–15] are in fact based on equivalent models. Tests to evaluate the accuracy of these three methods have been performed by using simulated curves.

Moreover, by using both TG and DTA curves, calculation of kinetic and thermal parameters, previously determined for step 1 [4], has been extended to the second and third steps of $CaC_2O_4 \cdot H_2O$ thermal decomposition. Reaction enthalpies have also been calculated.

The true kinetic parameters obtained were used to predict sample behaviour when decomposition takes place in isothermal conditions. Several calculated half-lives were compared with experimental observations to check the predictive power of the proposed approach.

The architecture of the developed software system was finally summarized.

EXPERIMENTAL

TG and DTA were carried out using Perkin-Elmer TGS-2 and DTA 1700 instruments, connected to a Data Station 3700, equipped as previously reported [3]. During all measurements a flow of N_2 at 50 ml min^{-1} was maintained. Calculations were implemented in MS-QUICKBASIC 4.0 on a PC 386, with a mathematical coprocessor, operating in MS-DOS 3.3. Simulations were performed in the PC environment. For processing experimental curves, data transfer from Data Station to PC and smoothing were carried out as previously described [4] and hereafter summarized under "Programs overview". Calcium oxalate monohydrate was an analytical grade product (from Carlo Erba RPE).

MODEL AND SYMBOLS

General description

For a single reaction step

solid reagent → solid product + evolved gas

taking place when reagent is heated, as in TG, the thermal balance (where time t has been replaced by temperature T_p as independent variable [4]) provides the relationship

$$T_p - T = a_1 m_i B + a_2 m_i W B - a_3 m_i B_p (\mathrm{d}W/\mathrm{d}T_p) \tag{1}$$

where T_p is the programmer temperature, i.e. experimental abscissa and T the sample temperature; $B_p = \mathrm{d}T_p/\mathrm{d}t$ is the constant controlled heating rate and $B = \mathrm{d}T/\mathrm{d}t$ the sample heating rate; $W = (m - m_f)/(m_i - m_f)$ is the measured fraction of reagents ($W = 1 - \alpha$, when α is the conversion degree); m_i is the initial mass, m_f the final mass and m the actual mass; $a_1 = (C_{t0}/m_i + C2)/k$; $a_2 = (C1 - C2)/k$; $a_3 = H/k$; $C1$ is the specific heat of reactant, $C2$ the specific heat of product (referred to initial mass m_i), H the reaction enthalpy, k the heat transfer coefficient and C_{t0} the sample holder thermal capacity. The a_1–a_3 mixed thermal coefficients were defined previously as experimentally accessible quantities [4].

That balance can be numerically integrated [4] together with the kinetic law

$$-(\mathrm{d}W/\mathrm{d}T)B = Z\,\exp(-E/(RT))F(W) \tag{2}$$

or, using time t from start as variable

$$-\mathrm{d}W/\mathrm{d}t = Z\,\exp(-E/(RT))F(W) \tag{3}$$

where R is the gas constant, $F(W) = W^N$ is assumed for dominant boundary phase reaction and Z, E, N are kinetic parameters, namely pre-exponential factor, activation energy and reaction order.

Equations (1) and (2) can be solved simultaneously through finite elements analysis [4]. In this way a TG simulation can be performed with assigned values of all the above parameters.

By contrast an approximation to the first term of a polynomial expansion [4] allows the calculation of Z, E, N and a_1, a_2, a_3 from W versus T_p curve/curves, hereafter referred to as $\{W, T_p\}$, through an iterative procedure. This approach was used to calculate parameters from $\{W, T_p\}$ curves, obtained by TG or through the DTA/DSC processing described below under the "Peak area calculations" section. When the calculation is applied to simulated curves, the term back-calculation of parameters is used.

When isothermal conditions are assumed, $B_p = 0$, so eqn. (1) should be rewritten, by replacing $B_p(\mathrm{d}W/\mathrm{d}T_p)$ with $\mathrm{d}W/\mathrm{d}t$, as obtained from the physical balance [4]. To observe the phenomenon, i.e. to obtain long times, the reaction temperature must be lower than temperatures reached in dynamic conditions. This implies that $B \approx 0$ and $\mathrm{d}W/\mathrm{d}t \approx 0$ become good assumptions. As a consequence, eqn. (3) can be integrated alone between $W = 1$ and $W = 0.5$ to obtain the half life $t_{0.5}$.

DTA / DSC simulation

Through the difference between heats flowing towards the sample and towards the reference, both expressed with relationships similar to eqn. (1) with $a_2 = a_3 = 0$ on the reference side, thermal balances can be derived for DTA or theoretical DSC equipments

$$T_r - T = d_1 m_i B + d_2 m_i W B - d_3 m_i B_r (\mathrm{d}W/\mathrm{d}T_r) \tag{4}$$

$$Q = s_1 m_i B + s_2 m_i W B - s_3 m_i B_r (\mathrm{d}W/\mathrm{d}T_r) \tag{5}$$

where the suffix r accounts for reference, whilst $a_2 = a_3 = 0$ on the reference side implies $B_p = B_r$ and $\mathrm{d}T_p = \mathrm{d}T_r$; Q represents the difference between two heat flows ($\mathrm{d}q/\mathrm{d}t$), the first from heater to reference, the other from heater to sample.

On changing r to p, eqn. (4) is found to be formally identical to eqn. (1). Coefficients d_1, d_2 and d_3 have the same meaning as a_1, a_2 and a_3, if k is assumed to be the same for both reference and sample. Coefficient $d_1 = [C_{t0}/m_i - (C_{t0r}/m_i)(B_r/B) + C2]/k$ will be similar to a_1, if C_{t0r} is assumed to be low enough with respect to $m_i C2$, or if $B_r/B \approx 1$.

With the same assumptions about s_1, eqn. (5) is also found to be formally identical to eqn. (4), and so to eqn. (1), whilst k disappears from the s_1, s_2, s_3 definition ($s_i = a_i k$): k can be saved in calculations just as a scale factor for measuring Q. Moreover theoretical DSC requires that $T = T_r$ and $B = B_r$.

More complex models [12,15] do not give real improvements, owing to the large number of parameters describing the curves and consequently to the excessive flexibility of the function to be fitted: even with no noise added, six parameters (Z, E, N and a_1, a_2, a_3) often proved to be more than enough during refinement of simulated curves [4].

Compared with the previous version of the TG simulation procedure, in this work the recording of $T_p - T$ versus T_p, referred to as $\{T_p - T, T_p\}$, has been added for DTA, using the same heating cycle. The simulation of a purely DSC curve Q versus T_p, referred to as $\{Q, T_p\}$, has also been added through a different heating cycle, where $T = T_p$ was maintained.

To allow a quick reference to other reported data, calculations were performed using the following units: T, T_p in K (displayed as °C), B, B_p in °C min^{-1}; m, m_i, m_f in mg; a_1, a_2 in s mg^{-1}; a_3 in °C s mg^{-1}; $C1$, $C2$ in cal g^{-1} °C^{-1}; H in cal g^{-1}; k in mcal s^{-1} °C^{-1}; C_{t0} in cal °C^{-1}; Z in s^{-1}; E in kJ mol^{-1} and N real number.

Peak area calculation, proposed model referred to as U

Numerical integration of eqn. (1), as well as of (4) or (5), between $T_p = T_{p0}$ together with $W = 1$, i.e. from peak start, and the current values T_{pc} and W_c leads to

$$\begin{aligned} a_3 m_i (W_c - 1) &= (1/B_p)\mathrm{SUM}(T_p - T, T_p, T_{pc}) \\ &\quad - \mathrm{SUM}\left[(a_1 m_i + a_2 m_i W)(\mathrm{d}T/\mathrm{d}T_p), T_p, T_{pc}\right] \end{aligned} \tag{6}$$

with the function SUM defined as the discrete sum corresponding to the integral

$$\int_{x_0}^{x_c} y(x)\,\mathrm{d}x = \mathrm{SUM}(y, x, x_c) \tag{7}$$

When $T_{pc} = T_{pf}$ and $W_c = 0$, i.e. when the numerical integration is performed until peak end, the leftmost term in eqn. (6) turns out to be proportional to the reaction enthalpy, whilst the right side is just the area included between peak and baseline. The baseline physically represents the variation in thermal capacity of the reacting mixture.

The function $T_p - T$, appearing as argument of SUM in eqn. (6), is known: it is simply the DTA signal $\{T_p - T, T_p\}$, or, changing units to Q, the DSC signal $\{Q, T_p\}$.

On dealing with the other functions in the argument of SUM, definition of the mixed thermal coefficients leads to

$$a_1 m_i + a_2 m_i W = \left[C_{t0} + C1 m_i W + C2 m_i (1 - W)\right]/k \tag{8}$$

where in eqns. (4) and (5) C_{t0} becomes approximately $(C_{t0} - C_{t0r})$.

The quantities $(C_{t0} + C1 m_i)/k$ and $(C_{t0} + C2 m_i)/k$ can be directly evaluated from DTA/DSC curves in ranges where $T_{p1} < T_p < T_{p0}$, or $W = 1$, and $T_{pf} < T_p < T_{p2}$, or $W = 0$, respectively, as they represent the thermal capacities of the reactant and of the product, corrected for a baseline shift due to C_{t0}. From the above quantities $a_1 m_i$ and $a_2 m_i$ can be easily calculated as fixed values or as straight lines in a limited range, when a specific heat variation versus temperature (baseline drift) is observed.

Whilst $\mathrm{d}T/\mathrm{d}T_p = 1$ in pure DSC, when dealing with DTA this value, the last one in eqn. (6) in the argument of SUM, must be calculated at each T_p. The instrument-supplied value of the DTA ordinate is simply the needed $Y = T_p - T$ value: so at the nth point, using finite elements

$$\begin{aligned} (\mathrm{d}T/\mathrm{d}T_p)_{(n)} &= \left(T_{(n)} - T_{(n-1)}\right)/\left(T_{p(n)} - T_{p(n-1)}\right) \\ &= \left(Y_{(n-1)} - Y_{(n)}\right)/\left(T_{p(n)} - T_{p(n-1)}\right) + 1 \end{aligned} \tag{9}$$

where $T_{p(n)} - T_{p(n-1)}$ is the constant sampling interval of abscissas.

Finally only the $\{W, T_p\}$ remains unknown. It can be iteratively calculated through eqn. (6), allowing a new $\{W_c, T_p\}$ to be determined from a previous $\{W, T_p\}$.

The iterative process proposed in this work can be summarized as: (i) interactive selection of ranges $T_{p1}, \ldots, T_{p2}$ and $T_{p0}, \ldots, T_{pf}$; (ii) linear fitting of $a_1 m_i$ and $a_2 m_i$ in ranges $T_{p1}, \ldots, T_{p0}$ and $T_{pf} \ldots T_{p2}$ respectively; (iii) guesting of an initial $\{W, T_p\}$ as straight line from 1 to 0 into the peak range $T_{p0}, \ldots, T_{pf}$; (iv) calculation of a new $\{W_c, T_p\}$ by eqn. (6); (v) replacement of the used $\{W, T_p\}$ by the new $\{W_c, T_p\}$; (vi) repetition of steps (iv) and (v) until, at the end of step (iv), $\{W_c, T_p\} = \{W, T_p\}$, according to a predefined tolerance; (vii) final calculation of the peak area as leftmost term of eqn. (6). The peak area is thus measured and a $\{W, T_p\}$, value closely representing the phenomenon, is also obtained.

Peak area calculation according to Brennan et al. [9], referred to as B

Brennan et al. [9] proposed a method for measuring the area of a DSC peak, involving a similar iterative calculation of the baseline under the peak. With the symbols defined above, they assumed $B = B_p$ and consequently $dT/dT_p = 1$ in the whole range. This means that, at every iteration step, they use the simplified relationship, obtained from eqn. (6)

$$a_3 m_i (W_c - 1) = (1/B_p)\mathrm{SUM}(T_p - T, T_p, T_{pc}) \\ - \mathrm{SUM}\left[(a_1 m_i + a_2 m_i W), T_p, T_{pc}\right] \qquad (10)$$

Whilst eqn. (10) is only valid for pure DSC, the authors presented a method where conceptually $a_1 m_i$ and $a_2 m_i$ were assumed to be constant in the peak range.

Peak area calculation according to Henderson et al. [10], referred to as H

Henderson et al. [10] have re-elaborated Brennan's method, using the $\{W, T_p\}$ curves, obtained from TG, into eqn. (10). In such a way they overcame the need for an iterative process. To do so, the thermal geometry, i.e. C_{t0} and k, of the TG instrument must be equal to that of the DTA/DSC instrument. However this condition is difficult to obtain experimentally, bearing in mind the different meanings C_{t0} and k have in eqns. (1) and (4). For simulations only this condition can be realized, as in this work. Henderson et al. introduced the calculation of specific heats, $a_1 m_i$ and $a_2 m_i$ within the above description, as dependent on temperatures: straight lines or higher order polynomials were suggested.

Investigated reactions

The investigated reactions are summarized as

$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O(g)$ step 1

$CaC_2O_4 \rightarrow CaCO_3 + CO(g)$ step 2

$CaCO_3 \rightarrow CaO + CO_2(g)$ step 3

Reactions are simply referred to in the text as steps 1, 2 or 3.

SIMULATION RESULT

Table 1 summarizes the results of an initial set of simulations using the values determined [4] for step 1, reported under the sim column. Specific heats $C1$ and $C2$ were rounded to 0.25, with respect to found values, whilst a_1 and a_3 were recalculated to be consistent with $C_{t0} = 0$ and $k = 0.35$, assigned to equipment parameters and close to previously found values. Except for values assigned for simulation (sim), found data are reported with as many significant digits as compatible with the standard deviations found.

The $\{W, T_p\}$, i.e. simulated TGs, the $\{T_p - T, T_p\}$, i.e. simulated DTAs, and the $\{Q, T_p\}$, i.e. simulated pure DSCs, were calculated at two different heating rates.

By processing the $\{W, T_p\}$ from TG, the parameters listed under column p-TG were back-calculated.

TABLE 1

Simulation of step 1: 10 mg, 10°C min^{-1} and 40°C min^{-1}; used values (sim) are shown with values obtained by back-calculation from $\{W, T_p\}$ obtained by TG (p-), DTA (d-) and DSC (s-) curves. The highest and lowest values are reported for enthalpy

	sim	p-TG	d-TG			s-TG(B)
			U	B	H	
Z	1.878×10^8	2.84×10^8	8.5×10^8	2.0×10^5	[a]	8.3×10^7
E	86.5	87.8	91.4	66	[a]	84.3
N	0.619	0.624	0.599	0.29	[a]	0.575
a_1	0.71	0.89	1.52	41	[a]	
a_2	0.00	−0.12	−0.78	40	[a]	
a_3	245.7	273.8	293	-1.0×10^3	[a]	
H	86.00		84.7	84.6	84.7	84.5
			85.9	85.9	85.9	85.6
k	0.35					
$C1$	0.25					
$C2$	0.25					

[a] Method does not include a $\{W, T_p\}$ calculation.

TABLE 2

Enthalpy calculation for steps 1–3 of calcium oxalate decomposition, from DTA by U method; highest and lowest found values

	m_i, B_p			Mean
	20, 20	10, 20	20, 10	
Step 1	89.1	85.6	89.3	86
	88.6	81.4	84.0	
Step 2	61.6	72.8	79.9	70
	59.6	68.4	79.3	
Step 3	147.6	153.4	144.2	14
	135.6	142.5	135.5	

The $\{W, T_p\}$ were also calculated from $\{T_p - T, T_p\}$, together with enthalpies, according to the proposed U method and the B method. Since the H method requires knowledge of the corresponding TG curve, the enthalpies only were calculated by using the simulated $\{W, T_p\}$ as TG, thus implying the needed condition about thermal geometry of TG and DTA. The back-calculated values are listed under columns d-TG(X), where X = U, B or H.

The $\{Q, T_p\}$ were processed according to the B method only and the back-calculated values are listed under column s-TG(B). In theoretical DSC, the U method is equivalent to the B one, whilst the H method only allows an enthalpy calculation, once more equivalent to B when the needed condition is respected.

CALCIUM OXALATE RESULTS

The enthalpy values of steps 1, 2 and 3 were calculated according to the U method from DTA curves recorded at three different operating conditions. Values are listed in Table 2, with intervals coming from repeated interactive choices of peak range and external ranges. The chosen weighted means are also reported.

Figures 1–3 show examples of DTA processing according to the U method. The parameters of steps 2 and 3 were calculated using a series of experimental TG curves at different masses and heating rates: 10 and 20 mg; 2.5, 10, 20, 40°C min^{-1} each. For steps 1–3, the extractions of $\{W, T_p\}$ curves were taken from experimental DTA curves and the corresponding parameters were calculated.

In Table 3 the values found by processing both TG and DTA curves are reported, where $a_2 = 0$ was assumed to avoid “ill-conditioned” systems (see also ref. 4). Found data are reported with as many significant digits as compatible with standard deviations found.

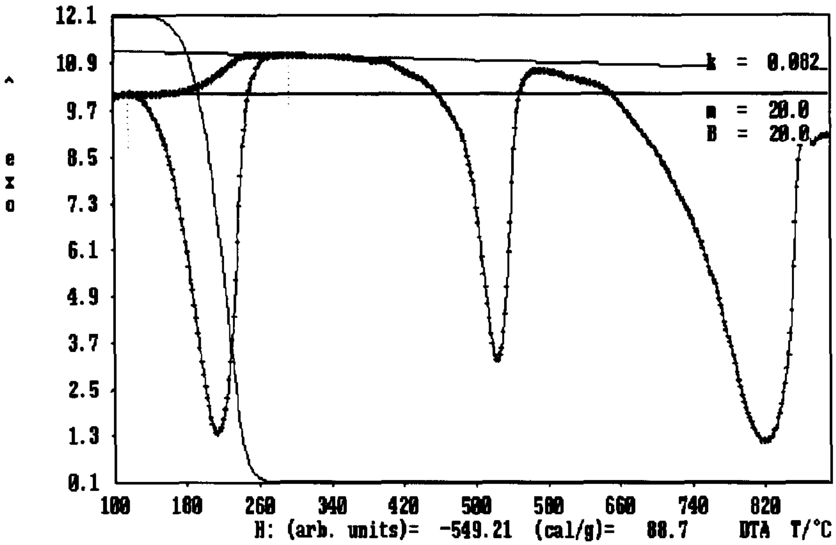


Fig. 1. Calculation of peak area and $\{W, T_p\}$ function of step 1 from DTA: 20 mg, 20°C $\min^{-1}$.

To rebuild both experimental TG and DTA curves, the kinetic parameters reported under column TG of Table 3 were chosen, as the more accurate, and $a_2 = 0$ was maintained. Dealing with values of a_1, a_3 for TG, those found for step 3 were also used to calculate those needed for step 2, by changing reaction enthalpy (affecting a_3). This is because the negative

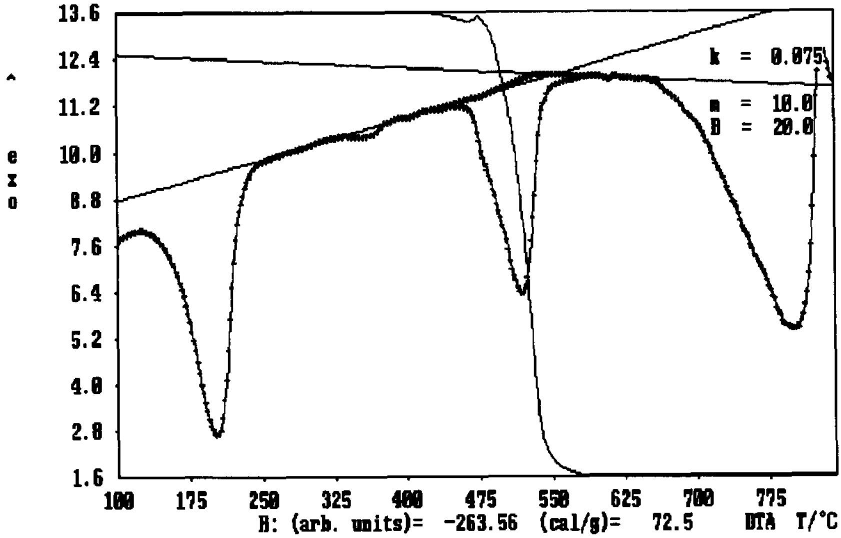


Fig. 2. Calculation of peak area and $\{W, T_p\}$ function of step 2 from DTA: 10 mg, 20°C $\min^{-1}$.

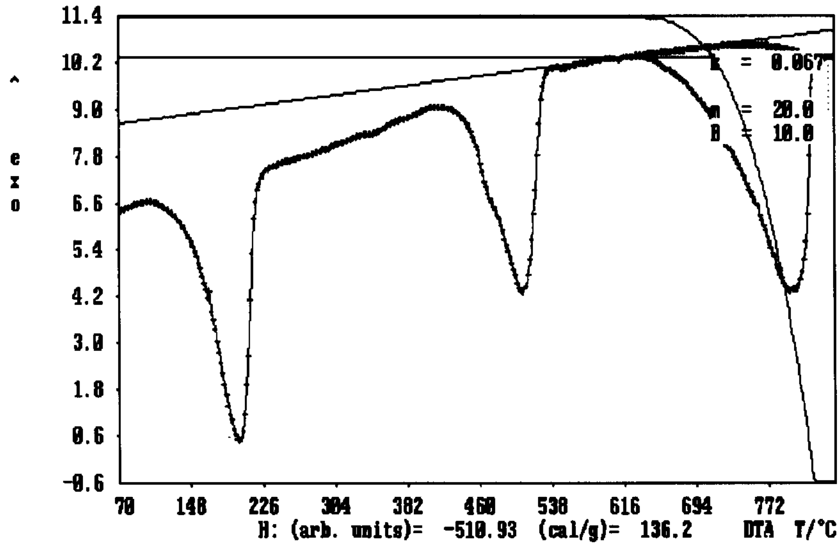


Fig. 3. Calculation of peak area and $\{W, T_p\}$ function of step 3 from DTA: 20 mg, 10°C $\min^{-1}$.

TABLE 3

Kinetic and thermal parameters of calcium oxalate obtained from TG and DTA curves

	TG [a]	DTA (U)	DTA (B)
Step 1			
Z	1.87×10^8	3.0×10^5	1
E	86.5	67	25
N	0.619	0.88	0.24
a_1	0.79	5.8	5
a_3	234	-2.5×10^2	-1.0×10^3
Step 2			
Z	3.04×10^{14}	5.0×10^7	2.0×10^2
E	246.7	152	74
N	0.696	0.65	0.50
a_1	1.75	1.8	12
a_3	−48	-3.5×10^2	-2.0×10^3
Step 3			
Z	2.60×10^8	8.0×10^7	3.0×10^5
E	212.9	212	161
N	0.443	0.3	0.40
a_1	0.54	6	1.7
a_3	466	-3.0×10^2	4

[a] Values for step 1 are from ref. 4.

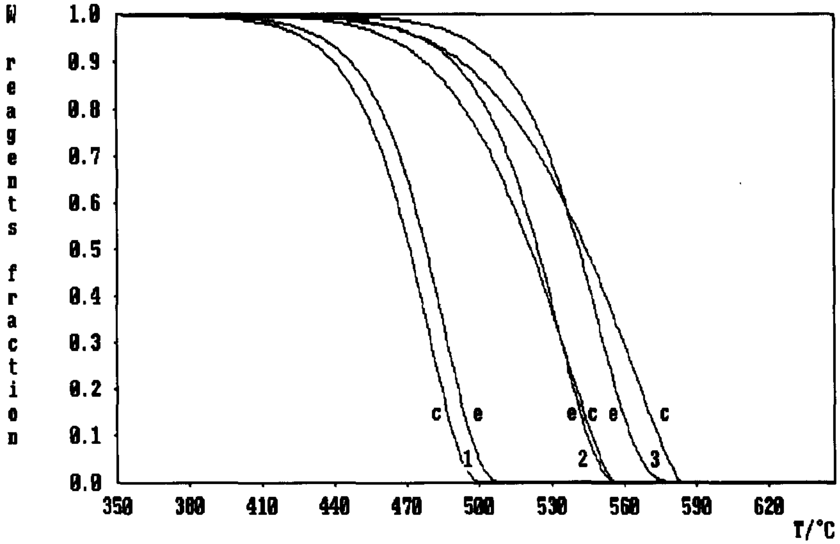


Fig. 4. Experimental (e) and calculated (c) {W, T_p} curves from TG for step 2; 10 mg at 2.5°C min^{-1} (1), 20 mg at 20°C min^{-1} (2), 20 mg at 40°C min^{-1} (3).

a_3 of step 2 does not match the found (from DTA) positive enthalpy. For DTA, this being different equipment, a_1, a_3 were calculated by their definition, using $k = 0.1$ (from calibrations), $C_{t0} = 0$, $C1 = C2 = 0.25$ and H set to found enthalpies.

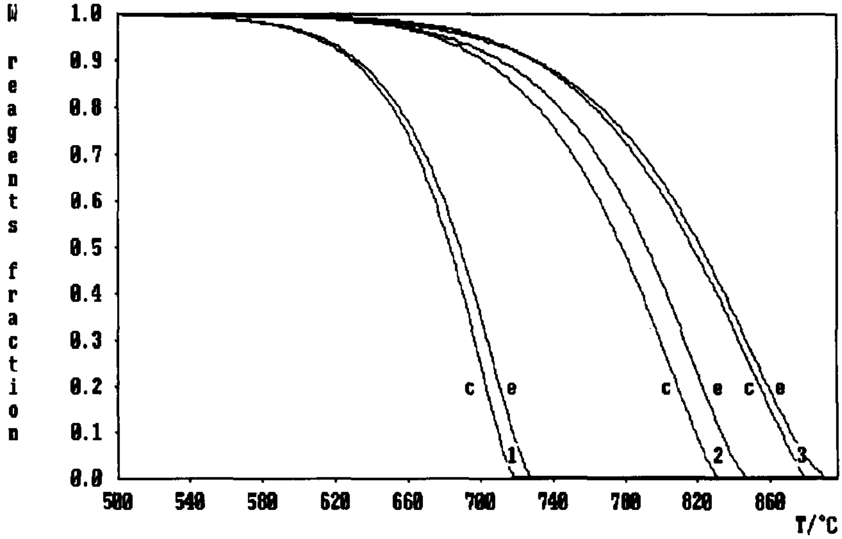


Fig. 5. Experimental (e) and calculated (c) {W, T_p} curves from TG for step 3; 10 mg at 2.5°C min^{-1} (1), 20 mg at 20°C min^{-1} (2), 20 mg at 40°C min^{-1} (3).

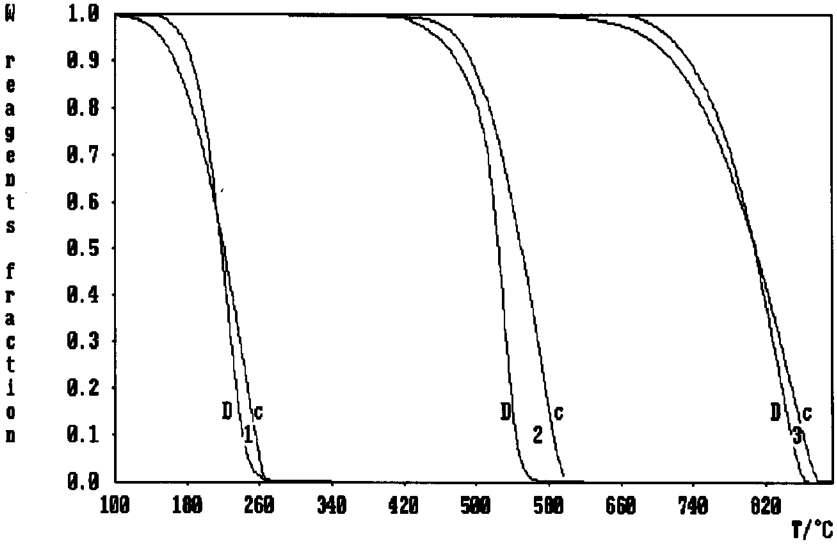


Fig. 6. Experimental (D) and calculated (c) $\{W, T_p\}$ curves from DTA for steps (1), (2), (3); 20 mg at 10°C min^{-1}.

Whilst the comparison between calculated and smoothed experimental curves has been previously reported for TG of step 1, figs. 4 and 5 show the same for TG of steps 2 and 3. Moreover Fig. 6 shows a similar comparison for DTA of steps 1–3.

Using the same kinetic parameters, the half-life times $t_{0.5}$ were also calculated for selected temperatures, as well as for temperature ranges centred on the selected values. In Table 4 these values are compared with results obtained in isothermal conditions.

TABLE 4

Half-life times $t_{0.5}$ (s) for steps 1–3 of calcium oxalate; calculated and isothermically found values are compared

	Temp (°C)	$t_{0.5}$ (calc)	$t_{0.5}$ calc. range		$t_{0.5}$ (found)
			±2°C	±5°C	
Step 1	120	1010	892–1167	731–1433	1130–1160
	140	280	250–320	209–385	270–290
Step 2	430	4442	3911–4973	3273–5965	4360–4500
	440	2457	2171–2742	1826–3273	2280–2580
Step 3	620	6265	5916–6727	5377–7412	6200–6500
	640	3345	3166–3579	2889–3928	3710–3960

DISCUSSION

The proposed U method seems to work better than the other two. From Table 1, the accuracy of kinetic parameters, from $\{W, T_p\}$ curves obtained by TG, is quite high. The results are in very good agreement with the source values used in simulations. The $\{W, T_p\}$ curves, obtained from the corresponding simulated DTAs with U processing, also lead to satisfactory, even though somewhat less accurate, results: extraction of $\{W, T_p\}$ from simulated DTA causes a predictable information loss. As done when processing experimental results, TG should be preferred, when available, to calculate kinetic parameters.

The B method provides quite as good results as H for enthalpy, calculated from both DTA and DSC, but fails in the calculation of a $\{W, T_p\}$ curve, suitable for kinetic parameter determination. The H method also gives a good enthalpy value, but requires the same thermal geometry in the TG and DTA/DSC apparatus, as during simulations, and therefore should only be used with equipment capable of carrying out DTA/DSC and TG simultaneously.

When processing experimental DTA data, the U method gives the enthalpies listed in Table 2. On real curves the method, like all others, is very sensitive to the interactive choice of the range where the peak is integrated and where the interpolation of the specific heats is performed. Several operators, by making diverse selections, can obtain enthalpy values varying by up to 5–10%.

For step 3 the kinetic parameters, obtained by DTA, are quite acceptable, as observed when comparing columns TG and DTA(U) of Table 3. Steps 2 and 3 do not show the same agreement. Step 2 is surely "contaminated" by a disproportionation reaction of carbon monoxide [16,17], as can also be observed from the enthalpy values, strongly dependent on operating conditions (Table 2). The exothermic side reaction

$$2CO \rightarrow CO_2 + C$$

markedly changes the DTA response and leads to the appearance of a negative a_3 coefficient in calculation of the parameters from TG curves as well (Table 3). For step 1 the DTA results are so different from those obtained by TG, which have a good predictive power [4], as to suggest water recondensation in the DTA cell or a solid solution equilibrium strongly influencing the thermal response [18]. Thus neither steps 2 or 3, in a DTA equipment, can be modelled as single step reactions, whereas in TG the directly recorded $\{W, T_p\}$ function should be less sensitive to gas-phase reactions: the evolved gas is also more easily transported far from the sample, since the crucible is different.

The calculated kinetic parameters for steps 2 and 3 complete previous data [4] on step 1. These values, listed under column TG of Table 3, have a satisfactorily good ability in rebuilding experimental $\{W, T_p\}$ curves, obtained both from TG (Figs. 4,5) and from DTA (Fig. 6), in several conditions. This is not a poor result if one considers that many literature data do not work as satisfactorily [3].

Moreover these parameters show a high predictive power, i.e. they are able to predict the sample behaviour in conditions different from those used to calculate the parameters themselves. Comparison of the calculated $t_{0.5}$ half-lives with those observed in isothermal conditions (Table 4) gives an evaluation of the high predictive power. However, to compare dynamic and isothermal results, an accurate calibration of temperature scale should be performed: dependence of $t_{0.5}$ on temperature is very critical and even inaccuracies of a few degrees can lead to large differences between calculated and observed values, as reported in Table 4 for ±2 and ±5°C.

CONCLUSION

Our proposed method for processing DTA/DSC and TG curves offers the following advantages compared with others: (i) it allows simultaneous processing of several curves, taking into account both mass and heating rate; when applied to DTA curves it uses all information in the experimental data, i.e. temperature differences, allowing peak baseline identification through the calculation of a $\{W, T_p\}$ curve very close to the real one; (ii) it provides values of kinetic parameters with high predictive power, allowing a comparison between dynamic and isothermal measurements; (iii) the kinetic parameters obtained must be accepted as empirical values (different Z, E, N values may equally represent data in limited ranges of operative conditions [5], and physicochemical meanings should not be assigned to them, except with great care and after a discriminating analysis between alternative models; (iv) the proposed model can be extended to other expressions of the $F(W)$ appearing in eqn. (2), but we do not believe that the result of introducing more parameters can be any better; when just simulated curves are processed, it is still difficult to recalculate back Z, E, N and all coefficients a_1, a_2, a_3 without finding "ill-conditioned" systems (when this is so, only a_1, a_3, can be calculated).

Many authors have recently faced the problem of improving the flexibility of the functions representing the thermoanalytical curves (generally TG) because of the difficulty of satisfactorily fitting the experimental data. Some are still involved in elaborating integral methods [19] of fitting just eqn. (2) with a general expression of the term $F(W)$, so sacrificing in principle many data available in a computer controlled instrument (few points are considered). Attention has also to be paid in integrating DTA peaks [20], especially when they are sampled using large (5–10°C) temperature steps and when a subsequent smoothing is performed to "enhance" resolution (0.05°C), with no baseline identification through the variation in mixture heat capacity.

The heat transfer process is often underestimated. A two step model, i.e. nucleation and reaction at the interface, has also allowed fitting of the dehydration of calcium oxalate [21], but a comparison with isothermal data was not attempted. The quality of the fitting has been artificially improved by the graphic representation chosen, i.e. calculated degrees of conversion versus experimental ones: especially when heating rates and/or degrees of reaction are low, small differences in the degree of conversion can also correspond to high differences in temperature. The same reaction has been fitted [22] by arbitrarily assuming dependence of activation energy on conversion degree and heating rate. A model of the dependency of thermal decomposition of calcium carbonate on the partial pressure of CO_2 has been introduced [23], with questionable reliability of the results obtained due to the fact that this dependency alone is assumed to be responsible for sample behaviour.

A few authors have considered the existence of phenomena of thermal exchange, but the contribution of the reaction kinetics has not been approached in a general way. A method of calculating the enthalpy of indium fusion has been proposed [13], using a real model of DSC which is DTA-like. This model has been used exclusively to fit a first-order phase transition, where the sample reacts instantaneously when it reaches the transition temperature: the response delay, providing an experimental peak rather than a line, has been considered as a result of the heat transfer, without taking into account the reaction kinetics. An attempt to model the DTA behaviour rigourously [15] included many instrumental parameters difficult to fix in real experiments, but did not take into account the specific heat variations during reaction. Complex DSC curves have also been "deconvolved" [24] into single peaks using a model that, assuming the temperature read to be equal to that of the sample, can be accepted only with theoretical DSC architectures and when baseline subtraction takes the specific heat changes into account.

PROGRAMS OVERVIEW

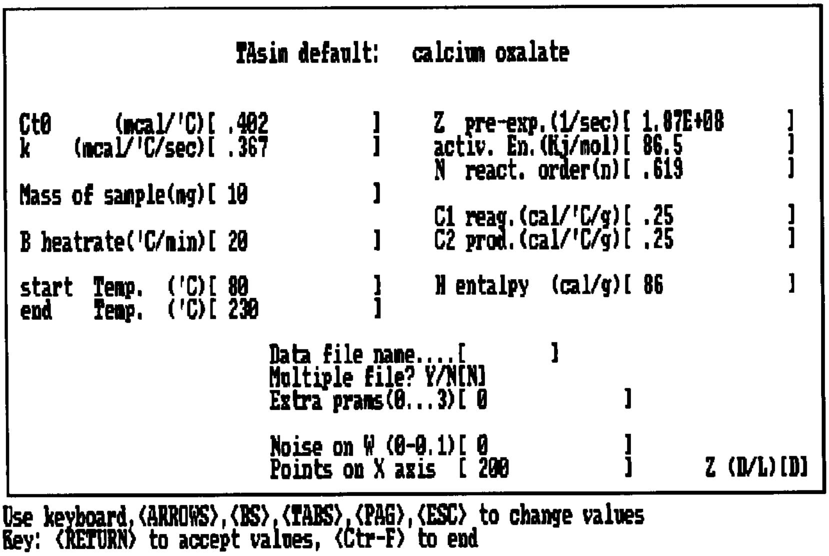
Three procedures were developed, each including several modules. In an interactive environment, data are entered through input "masks". The operator moves the cursor through selected fields and changes their values.

TG-TADSOFT

This procedure has been specifically designed for the equipment used, i.e. the 3700 Perkin Elmer data station operating in PETOS.D. TADSOFT is the software module allowing user procedure implementation in BASIC to process acquired data.

This procedure performs the following functions: (i) $\{W, T_p\}$ curve extraction from TG data, interactively choosing the temperature range where the selected reaction step takes place; (ii) calculation of pseudo-kinetic parameters Z, E, N from these curves, using a linear regression of the logarithmic form of the kinetic equation, with the common assumption $T = T_p$ [3]; (iii) extraction of DTA curves and print out of their values, i.e. of $(T_p - T)$ versus T_p.

The $\{W, T_p\}$ curves are loaded on the MS-DOS environment by using the Z, E, N pseudo-parameters to rebuild each curve, selecting no contribution of thermal parameters: since each curve has its own parameters, the rebuilding is highly accurate [3] and a satisfactory smoothing is performed through a function derived from the kinetic expression itself; the noise sensitivity of the successive differential processing is thus reduced by processing such smoothed experimental curves [4]. DTA curves, on the contrary, do not require smoothing because of their integral processing and are loaded by manual input of the printed pairs of values. Other ways of smoothing TG data will be tested later, such as spline functions used in XPS [25], to check their noise sensitivity and eventual improvement of processing. However the rebuilding and predictive power of the parameters obtained now accounts for good performance of the smoothing chosen.



```
                 TAsim default:   calcium oxalate

Ct0      (mcal/'C)[ .402         ]   Z  pre-exp.(1/sec)[ 1.07E+08      ]
k    (mcal/'C/sec)[ .367         ]   activ. En.(Kj/mol)[ 86.5          ]
                                     N  react. order(n)[ .619          ]
Mass of sample(mg)[ 10           ]
                                     C1 reag.(cal/'C/g)[ .25           ]
B heatrate('C/min)[ 20           ]   C2 prod.(cal/'C/g)[ .25           ]

start  Temp.  ('C)[ 80           ]   H entalpy  (cal/g)[ 86            ]
end    Temp.  ('C)[ 230          ]

                        Data file name....[       ]
                        Multiple file? Y/N[N]
                        Extra prams(0...3)[ 0          ]

                        Noise on W (0-0.1)[ 0          ]
                        Points on X axis  [ 200        ]      Z (D/L)[D]
Use keyboard,<ARROWS>,<BS>,<TABS>,<PAG>,<ESC> to change values
Key: <RETURN> to accept values, <Ctr-F> to end
```

Fig. 7. Input mask of TG-SIM.

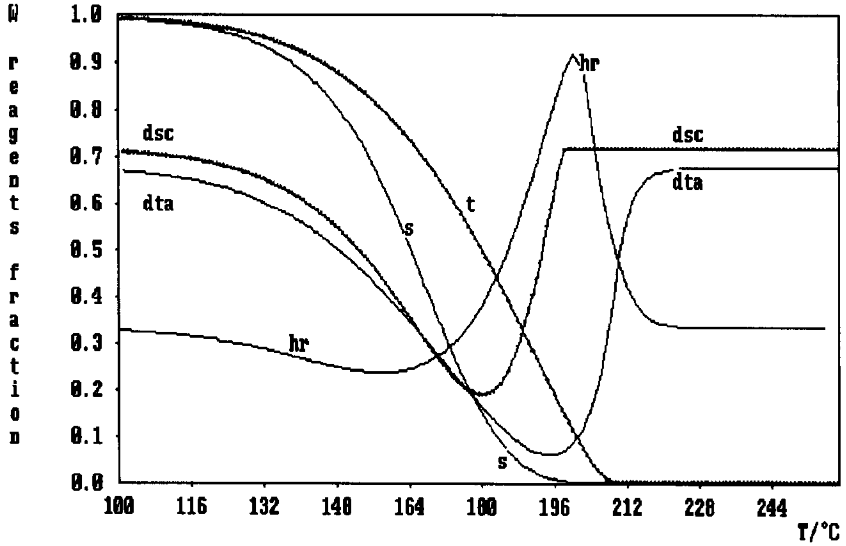


Fig. 8. Simulation: {W, T_p} displayed as (t), {W, T} as (s), {dT/dt, T} as (hr), {$T_p - T$, T_p} as (dta), {Q, T_p} as (dsc).

TG-SIM

Operating in a DS–DOS environment, this procedure allows the following.

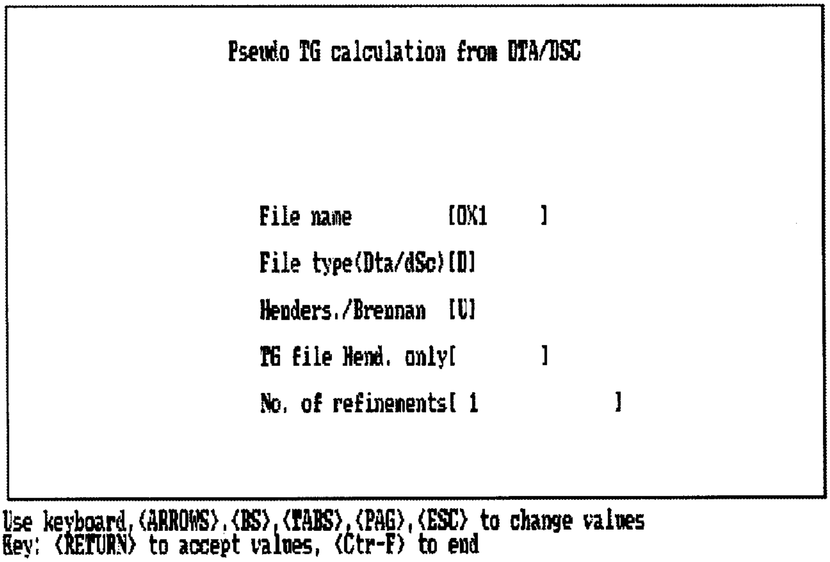
Simulation, i.e. rebuilding of {W, T_p} curves, as well as the {$T_p - T$, T_p} and {Q, T_p} curves, from the whole set of parameters displayed in the input mask, shown in Fig. 7. As reported, heat transfer into a DTA/DSC apparatus can be described in the same way as into a TG.

Simultaneous refining of both kinetic (Z, E, N) and/or thermal (a_1, a_2, a_3) parameters (according to extra prams assigned in input mask), using just one or more than one {W, T_p} curves (multiple data files in input mask), obtained from TG and/or from DTA/DSC at different masses or heating rates.

Figure 8 shows an example where the displayed curves are simulated using the kinetic parameters of step 1 with 10 mg, 20°C min^{-1} (C_{t0} = 0.402, k = 0.367). The last row on the screen summarizes the operator commands allowed, including refinement or back-calculation, calculation of the variance–covariance matrix of the regression and saving of simulated curves (TG, DTA or DSC).

DT-PROC

Running under MS–DOS, this procedure allows calculation of the area of DTA/DSC peaks, as well as extraction of the corresponding {W, T_p} curves (for processing by TG–SIM). Through the input mask, displayed in Fig. 9,



```
                Pseudo TG calculation from DTA/DSC



                   File name          [OX1     ]
                   File type(Dta/dSc)[D]
                   Henders./Brennan  [U]
                   TG file Hend. only[         ]
                   No. of refinements[ 1          ]

Use keyboard,<ARROWS>,<BS>,<TABS>,<PAG>,<ESC> to change values
Key: <RETURN> to accept values, <Ctr-F> to end
```

Fig. 9. Input mask of DT-PROC.

the operator choses the type of processing (H, B, U). The procedure allows interactive selection of peak range and external ranges through displayed markers, iterative calculation of peak area and of $\{W, T_p\}$ (see bottom line in Figs. 1–3), and saving of $\{W, T_p\}$ for processing by TG–SIM.

The number of iterations required can be chosen by the operator or, as an alternative procedure, the process can be repeated until the same area (within a tolerance) is obtained.

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