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Using thermoanalytical data. Part 6. Heat transfer contribution in TG/DTA/DSC data processing: non-isothermal kinetics — do they become "applied science" by exiting the "dichotomy"?

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Abstract

After a brief overview of the state of the art of kinetic study of solid state reactions, a new promising approach is described. Whilst details of such an approach have been previously reported, the model and its performances are presented here as an overall picture, including the evaluation of the heat transfer perturbations induced in both TG and DTA/DSC. A summary of the results obtained with $CaC_2O_4 \cdot H_2O$ is also reported, and a strategy is suggested, which should be used when facing the problem of such a kinetic evaluation or, in general, when processing data according to an assumed model.

INTRODUCTION

The description of a heterogeneous reaction becomes difficult if a single chemical equation is used to represent the complex system where several homogeneous reactions take place simultaneously and transport through interfaces takes place.

When dealing with a solid state reaction of the type

solid reactant → solid product + gas

where the gas could be given off or could be replaced by other solid phases, in order to describe phase transitions, the reaction rate is generally assumed to have the form

$$d\alpha/dt = K(T)f(\alpha) \qquad (1)$$

where α ($\alpha = 0 \ldots 1$) is the extent of reaction, $f(\alpha)$ represents a function

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

EXHIBIT 1

Considerations on solid kinetics

Statements	References
cn1 Almost all thermoanalytical techniques such as TG, DTA, DSC, TMA and EGA are suitable for kinetic analysis.	1
cn2 The assumption of a one-step process could be a necessary oversimplification.	2
cn3 The influence of the pressure of the gaseous product is limited to reversible reactions (organic/polymer and some inorganic materials).	3, 4
cn4 The Arrhenius form of $K(T)$ in eqn. (1) has no theoretical basis when solid state reactions are considered.	4–6

depending on mechanism, t is the time and $K(T)$ is a coefficient depending on the absolute temperature T of the sample.

A knowledge of $K(T)$ and $f(\alpha)$ in eqn. (1), i.e. knowledge of a model representing the "rate-determining step", should be of great interest when dealing with "theoretical aspects of molecular modelling reactions" or may be vital when used as an empirical approach to the solution of practical "problems such as failure and service life prediction, oxidative stability, thermal breakdown, quality assurance and control, and optimization of conditions during industrial syntheses and fabrication", as Flynn [1] has highlighted.

In the recent past, many authors have reviewed heterogeneous kinetics, the class that solid state reactions belong to, discussing with criticism both the chosen models and the processing of data obtained through different techniques. Their main considerations are summarized in Exhibit 1.

In spite of these considerations, a way to approach the kinetics of solids must be found in order to provide answers to both theoretical and practical needs. Therefore at constant pressure, the single-step assumption is generally used as well as the Arrhenius form of $K(T)$:

$$K(T) = Z\ \exp(-E/RT) \tag{2}$$

where R is the gas constant, and Z and E are the pre-exponential factor and activation energy respectively. Suitable forms for $f(\alpha)$ are eventually chosen according to a hypothesized mechanism [7,8]: for example

$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$ Johnson–Mehl–Avrami (JMA)

$f(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$ Šesták–Berggren (SB)

EXHIBIT 2

Observations on solid state kinetic data processing

Statements	References
ob1 The accuracy of temperature measurements is highly critical for obtaining a kinetic model.	1
ob2 The sample temperature is generally different from the observed one (heater) owing to heat transfer: this transfer should be considered when processing data.	1–3, 6, 8
ob3 Many kinetic models were proposed for $CaC_2O_4 \cdot H_2O$, but none included critical testing.	4
ob4 There is no basic difference between isothermal and non-isothermal behaviour, so the models obtained should fit both conditions.	4–6
ob5 The only way to accept kinetic models is to show that they are able to reconstruct experimental data and to predict behaviour under conditions different from those in which they were determined.	4–6, 8, 9
ob6 Models based on partial calculation of kinetic parameters, i.e. just E, or Z and E in eqn. (2), with no estimate of the form of $f(\alpha)$ are not useful because all parameters are necessary to reconstruct curves and to predict sample behaviour.	9
ob7 The so-called kinetic compensation effect (KCE) shows a fairly linear correlation between log Z and E, thus implying great difficulty in assigning a physical meaning to each value alone.	6, 9–11

Data are collected using several techniques, under isothermal and non-isothermal conditions. Finally such data are processed in several ways to obtain an estimate of Z and E in eqn. (2), and of the coefficients appearing in $f(\alpha)$. Mathematical methods of such data processing are evolving continuously; the decomposition of $CaC_2O_4 \cdot H_2O$ is often used as a test. However, in dealing with data processing, many observations emerge, as summarized in Exhibit 2.

Owing to considerations *cn2–cn4*, the approach to solid decompositions through eqns. (1) and (2) could seem invalid. However, when observations *ob1–ob7* are taken into account, a kinetic model, assumed on an empirical basis, turns out to be very useful. In particular, *ob5* can help the scientific community to resolve this apparent "dichotomy" [4], allowing solid state kinetics to become an "applied science" [5].

When dealing with such an applied science, the processing of thermoanalytical data to obtain kinetic parameters is the main task to be considered.

PROCESSING OF THERMOANALYTICAL DATA

As a general rule, eqns. (1) and (2) are combined to represent the reaction rate as a function of time and sample temperature:

$$\mathrm{d}\alpha/\mathrm{d}t = Z \exp(-E/RT) f(\alpha) \tag{3}$$

and the dependence of the observed (programmed) temperature T_p on time, controlled by the thermoanalytical equipment, identifies the operating conditions:

$$T_p = \theta(t) \tag{4}$$

Under isothermal conditions $\theta(t) = T_0$, while under the most common non-isothermal conditions linear heating $\theta(t) = T_0 + B_p t$ is used, where T_0 is a starting temperature.

Efforts are concentrated on finding a way to fit experimental data represented by α (indirectly measured from TG, DTA, DSC, etc.) vs. T_p, i.e.

$$\alpha = \alpha(T_p) \tag{5}$$

with several manipulations of eqn. (3), for instance by transforming the equation in a linear relationship through logarithms. To simplify the mathematical approach, the assumption

$$T = T_p \tag{6}$$

is often used, instead of a more general assumption

$$T = \beta(T_p) \tag{7}$$

where the heat transfer function $\beta(T_p)$ accounts for the difference between the sample temperature and the observed one (programmed or measured close to the sample). Such an assumption requires that heating rates (B_p) and sample masses are kept sufficiently low [1,3,8].

The known methods for the processing of thermoanalytical data to obtain kinetic parameters, referred to here as PTDK, can be grouped into two main classes [1,6]:

(1) PTDK1, where several chosen α_i ($i = 1 \ldots n$) are detected on various thermoanalytical curves, obtained at various B_{pj} ($j = 1 \ldots m$), and the measured $(\mathrm{d}\alpha/\mathrm{d}t)_{ij}$ vs. T_{ij} data are processed by eqn. (3), the whole mathematical system being simplified by assuming that each $f(\alpha_i)$ is constant for all the corresponding j values.

(2) PTDK2, where, most commonly on a single thermoanalytical curve, the α_i ($i = 1 \ldots n$) and/or the corresponding $(\mathrm{d}\alpha/\mathrm{d}t)_i$ values, numerically computed or calculated by the instrument itself, are collected for each T_i and used to calculate the parameters via eqn. (3).

The class PTDK2 should be rigorously divided into two subclasses: PTDK2-D, using the derivatives as described above, and PTDK2-I, using several integrations of eqn. (3). The PDTK-I methods were used extensively in the past to overcome numerical differentiation, possible only when many data can be collected by a computer at high sampling frequencies.

THE STATE OF THE ART OF PTDK METHODS

The history of PTDK methods is long and can be followed in the literature cited here and in the respective references.

A leitmotiv seems to be present: when the number of experimental data increases, eqns. (3) and (4) often fail in representing data sets, i.e. relationship (5), with the assumption of eqn. (6). This also happens when a relatively simple system such as the thermal decomposition of $CaC_2O_4 \cdot H_2O$ [12] is considered:

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

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

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

An interesting review of the thermal decomposition of oxalates has been published by Dollimore [13], in which the chemical and structural aspects are widely discussed with reference to the kinetic behaviour. The author also pointed out that $CaC_2O_4 \cdot H_2O$ is generally used as a "model material" to test kinetic approaches.

To obtain a better fit of data under the assumption expressed by eqn. (6), the function obtained from eqn. (5), combined with eqns. (3) and (4), must become sufficiently flexible to include all the available data points. From a mathematical point of view, this goal can always be attained with an increase in the number of parameters appearing in the function, as is generally obtained in a polynomial expansion. Some examples [14–34] of the considerable interest in PTDK methods are summarized below.

In a long series of studies, including those in refs. 14–18, Urbanovici and Segal assumed a non-constancy of all the kinetic parameters; i.e. $Z = Z(\alpha)$ and $E = E(\alpha)$ in eqn. (3) as well as $n = n(\alpha)$, $m = m(\alpha)$, $p = p(\alpha)$ for an SB form of $f(\alpha)$ [18]. They therefore assigned a non-classical meaning to these kinetic parameters, becoming dependent on heating rates when other conditions are maintained constant. A PDTK method, based on integration over narrow ranges of variables, allowed the calculation of a series of kinetic parameters. Whilst the approach could be useful to fit obtained data (examples for calcium oxalate and potassium permanganate are reported), it is questionable whether it can also predict the sample behaviour as required by observation *ob5*. Moreover they have recently questioned [19] the validity of the common form $f(\alpha) = (1-\alpha)^n$, i.e. an SB with $m = p = 0$. The conclusion that this form could not be valid is questionable. In fact they take the derivative of eqn. (1) to obtain $d^2\alpha/dt^2$, by assuming T is constant and then, after taking the derivative, they introduce the time dependence expressed by eqn. (4): a correct derivative of eqn. (1) should be made by considering that $K(T)$ is also time dependent.

To improve the identification of suitable forms of $f(\alpha)$, Malek et al. [20] discussed the validity of several $f(\alpha)$ in terms of two boundary conditions of an integrated form of eqn. (1), after division of both members by $f(\alpha)$. The common form, $f(\alpha) = (1-\alpha)^n$, corresponding to the RO (reaction order) model, does not seem to fulfil the second boundary condition, i.e. $\alpha \rightarrow 1$ when $n < 1$. Without questioning the validity of such a common form, a restriction on its use when $\alpha < 1$ can be derived.

Malek and Criado [21] also proposed a PDTK method based on the analysis of the shape of thermoanalytical curves. Although limited to an estimate of the reaction mechanism, the approach seems to be promising. However some points should be considered. The invariance of the distances between singular points (max/min and inflections), with respect to kinetic parameters, is not demonstrated analytically and could just be the result of the numerical calculation with the parameters used. However, an experimental application is not reported and an accurate identification of singular points on a real curve could be a hard task, owing to noise; sophisticated smoothing would probably have to be performed.

After having followed a PTDK2-I approach, Reich et al. [22] used a PTDK2-D method by calculating the derivatives through a convolutional filter. Unfortunately they tested the method on simulated (calculated) curves with no noise: thus the smoothing power and distortion cannot be estimated. The isothermal hydrolysis of 2,7-dicyanonaphthalene was modelled by Reich and Stivala as two consecutive first-order reactions [23]. Although the model is quite specific and difficult to extend to a general picture, an iterative procedure allowed them to refine some EGA literature data [24].

A two-step model, i.e. nucleation and reaction at the cylinder interface with appropriate forms of $f(\alpha)$, has allowed TG data obtained during the dehydration of calcium oxalate to be fitted [25]. Whilst the two steps were identified from isothermal experiments, the kinetic parameters Z and E were satisfactorily obtained only from non-isothermal runs.

Although $f(\alpha) = (1-\alpha)^n$ is commonly used in empirical approaches, i.e. an SB form where $m = p = 0$, Cusido et al. demonstrated [26] that a JMA form is preferable when dealing with crystallizations. In fact, such an $f(\alpha)$

was identical to an overall expression obtained from a theoretical treatment of the crystallization process with an adjustment of some coefficients.

Equation (3) was modified by Hurst [27], according to the suggestions of Criado et al. [28], to include a pressure-dependent term. With such a modification, the mathematical problem of PDTK was overcome by a predictor-corrector method [29]. For carbonate decomposition in a CO_2 atmosphere, curves described by relationship (5) were simulated with different parameters in eqn. (3) up to convergence with experimental data.

When fitting experimental data with calculated TG curves, Wong et al. [30] stressed that differences between T values are more meaningful than differences between α values. A non-linear least-squares PTDK2-D approach allowed them to calculate the Z and E parameters of eqn. (3), where $f(\alpha) = 1$ for a zero-order acid-catalysed iodination of acetone. Even though the differences $T - T_{\text{calc}}$ were minimized by starting from estimated values of the parameters, a comparison with literature data on E was preferred to a check of the ability of the calculated values to reproduce experimental points.

The reproduction of experimental points seems to be quite good in the DSC data reported by Neag et al. [31] for the degradation of 2,2′-azobis(isobutyronitrile). Using both PTDK2-I and PTDK2-D methods, they obtained the kinetic parameters from several curves, each one being processed separately. Although they stated that there were no significant differences (Student t statistical test was used) between various sets of parameters, only one curve was reconstructed using its own parameters, i.e. obtained from the same curve. A comparison of all available experimental data with curves calculated using average parameters would probably have shown a worse agreement.

The comparison becomes difficult when a DTA peak must be isolated from a base line including mixed processes. Whilst the first peak was quite correctly isolated for the curing reaction of epoxy resins [32], the second was "deconvoluted" from a noisy base line. This approach could be acceptable with caution, always with some additional information: the knowledge of the chemical process, the physical base line drift, etc. However, the use of kinetic parameters, determined from a peak thus obtained, to predict isothermal behaviour seems unsound.

To simplify the mathematical aspects of PTDK, Ozawa [33] and Ortega et al. [34] proposed the use of equipment capable of working with a function, represented by eqn. (4), different from the linear heating commonly available. Ozawa proposed an inverse temperature linear decrease, $1/T = 1/T_0 - bt$, whilst Ortega described an instrument that can maintain, for instance, $d\alpha/dt$ = constant, by reverse control.

In spite of the observation *ob2*, concerning taking into account the heat transfer during measurements, the statement of eqn. (6) is quite generally accepted by workers involved with PTDK methods, as in the examples reported above. Urbanovici and Segal [16] highlighted the problem, leaving it as an "open question"; Alves [35] tried to estimate the temperature error $T_p - T$ in the readings. However, many workers in calorimetric fields i.e. using mainly DTA and/or DSC, have faced the problem of heat transfer, without linking it to some real evolution of PTDK methods. Some examples [36–39] are summarized below.

A computer simulation of DTA peaks [36] was used to compare them with DTG ones. However, the chosen abscissa was the sample temperature, not the programmed one, which is generally available in both techniques.

Using a model describing heat transfer in real DSC, the behaviour of a first-order phase transition (melting) was simulated by Van Miltenburg and Cuevas-Diarte [37]. The assumption that the sample reacts immediately the melting temperature is reached did not follow any PTDK method, although the indium fusion was well fitted. Similarly Bauerecker et al. [38] reported an analogous DSC model to correct the fusion temperature. They used the comparison between experimental and simulated peaks to estimate sample purity through the van 't Hoff law, but for PTDK.

A model for heat transfer in DTA equipment has been presented by Beck and Brown [39]. Whilst taking into account kinetic aspects, they used a previously established PTDK method [40], including the assumption expressed by eqn. (6), to study the effect of positioning the sample thermocouple on the kinetic parameters thus measured.

A PTDK METHOD THAT CONSIDERS HEAT TRANSFER

When dealing with practical problems [1], such as predicting the behaviour of ablative materials [41,42], the flexibility of the function, represented by eqn. (5) combined with eqns. (3) and (4), should not simply be increased, as reported above. Moreover it is not so easy to evaluate a priori conditions (masses and heating rates) where $T_p - T$ is sufficiently low. In such a way, experimental data may also be satisfactorily fitted by calculated curves. However, the heat transfer, destroying the assumption expressed by eqn. (6), should be considered in a suitable PTDK method, as stated in observation *ob2*. In fact this represents an unquestionable physical effect, also adding the needed parameters (and thus increasing flexibility) to the function to be fitted.

In a series of papers [43–47], this approach was fully described, including computational details and definitions of parameters involved. Equations (3) and (4) were rewritten in the form

$$-(\mathrm{d}W/\mathrm{d}t) = Z\exp(-E/RT)W^N \tag{3a}$$

$$T_p = T_0 + B_p t \tag{4a}$$

TABLE 1

Maximum temperature differences (°C, exp. – calc.) at $W = 0.5$ for the three thermal decomposition steps of $CaC_2O_4 \cdot H_2O$ at several masses (10–20 mg) and heating rates (2.5–20°C min^{-1})

	A[a]	B[b]	C[c]	D[d]
Step 1	9	−35	−31	−115
Step 2	−8	23	−40	< 200
Step 3	12	59	< 200	> 200

[a] Data from BF2 of ref. 43.

[b] Data from ref. 48 calculated in ref. 43.

[c] Data from ref. 49 calculated in ref. 43.

[d] Data from ref. 50 calculated in ref. 43.

where $W = 1 - \alpha$ represents the fraction of reagent, measured both by TG [43,44] or by DTA/DSC [46], and where the common simplified SB form was chosen for $f(\alpha)$, i.e. $f(\alpha) = (1 - \alpha)^n$ or $f(W) = W^N$ (n replaced by N).

Using a PTDK2-D method with the common assumption of eqn. (6), a procedure [43] was implemented to calculate the kinetic parameters Z, E, N in chosen ranges of W, i.e. excluding from the linear fitting of a logarithmic expression of eqn. (3a) those points where W is too close to zero or unity, thus reducing noise errors and complying with the above-discussed boundary condition [20]. Extending the common use of PTDK2 methods, the procedure was designed to work both with a single TG curve or with multiple TG curves, obtained with different masses and heating rates. Under the same assumption of eqn. (6), a procedure to calculate W vs. T_p curves, hereafter referred to as $\{W, T_p\}$, was also implemented, by numerical integration of a combination of eqns. (3a) and (4a) with $T = T_p$ and known Z, E, N. For the three steps of $CaC_2O_4 \cdot H_2O$ thermal decomposition, the ability of the kinetic parameters so determined to allow the reproduction of experimental $\{W, T_p\}$ curves was checked, as well as the same ability displayed by literature data [48–50] on the same kinetic parameters. Whilst the calculated parameters gave a fairly satisfactory reproduction, the literature data did not, thus supporting observation *ob3*. Table 1 shows a summary of the maximum temperature differences between the experimental and calculated T_p at $W = 0.5$.

This type of presentation is preferred to a statistical test because it is more impressive and meaningful when large differences are involved that are mainly due to model inaccuracy rather than to random errors [51].

The whole set of kinetic parameters, in accordance with observation *ob6*, allowing the reproduction of experimental curves in a wide range of experimental conditions, or displaying a given level of predictive power in agreement with observation *ob5*, were identified as true.

According to observation *ob2*, the heat transfer process was successively taken into account [44,46] and eqn. (7) was replaced by a thermal balance:

$$T_p - T = a_1 m_i B + a_2 m_i W B - a_3 m_i B_p (dW/dT_p) \tag{7a}$$

where B is the unknown sample heating rate dT/dt and m_i is the initial mass; the thermal coefficients a_1–a_3, normalized with respect to the overall heat transfer coefficient, contain the sample holder thermal capacity and the sample specific heat (a_1), the difference between the specific heat of the reagent and of the product (a_2) and the reaction enthalpy (a_3).

The thermal balance (eqn. (7a)) has the same form for both TG [44] and DTA or, replacing $T_p - T$ with heat flux Q, for DSC [46].

Procedures were implemented for simulating the sample behaviour, i.e. for calculating $\{W, T_p\}$ curves, as well as for obtaining kinetic parameters from a single or from multiple experimental/simulated $\{W, T_p\}$ curves [44]. The simulation was performed through the simultaneous solution of eqns. (3a), (4a) and (7a) by finite elements, whilst an iterative process, referred to as simultaneous refinement, was used to calculate Z, E, N and the a_1–a_3 parameters from $\{W, T_p\}$ curves in the $0 < W < 1$ range. The simulation procedure was then completed with the calculation of DTA/DSC curves [46] and another iterative process was used to calculate the base line under the peak, as well as the $\{W, T_p\}$ curve from the DTA/DSC curves themselves.

With such an approach, the reaction enthalpy can also be evaluated from TG, through the thermal coefficient a_3, and a $\{W, T_p\}$ suitable for kinetic analysis can be obtained from DTA/DSC. The physical model is in fact the same in all cases and the total information should always be presented even if hidden.

Moreover the sample mass itself appears as an operational datum, as well as the heating rate, which is also involved in the calculation of the kinetic parameters from a single curve or from several ones. The method could be classed as PTDK2-D, even though iterative (integral) calculations could also allow it to be included in PTDK2-I, whilst the extension to multiple curves accounts for a PTDK1 classification.

The accuracies of the iterative processes were first checked by recalculating from simulated $\{W, T_p\}$ curves the parameters used to make the simulations themselves. The method was then applied to $CaC_2O_4 \cdot H_2O$ thermal decomposition, examined by TG and DTA. The poor agreement between TG and DTA data for step 2 and step 1, when considering $\{W, T_p\}$ from DTA, has been discussed [46] according to consideration *cn2*. However, a complete picture of the thermal behaviour has been obtained and summarized in Table 2.

The kinetic parameters listed in Table 2 can be considered as true owing to their high predictive power displayed in conditions different from those in which they were obtained, as per observation *ob5*. Isothermal measure-

TABLE 2

True kinetic parameters Z, E, N and enthalpies H (referred to initial mass) for the three steps of $CaC_2O_4 \cdot H_2O$ thermal decomposition

	Z (s^{-1})	E (kJ mol^{-1})	N	H (cal g^{-1})
Step 1	1.87×10^8	86.5	0.619	86
Step 2	3.04×10^{14}	246.7	0.696	70
Step 3	2.60×10^8	212.9	0.443	140

ments can be performed choosing low temperatures so as to obtain slow reaction rates, thus making the assumption of eqn. (6) valid. The half-life times $t_{0.5}$ were calculated from eqn. (3a) using the values in Table 2, and compared with those found [44,46], as reported in Table 3.

The agreement between calculated and found values accounts for observation *ob4*. When considering the calculated ranges for $t_{0.5}$, where the assigned temperature is varied only a few degrees, i.e. ±2 or ±5°C, the observation *ob1* finds strong numerical support.

Through a series of simulations in a wide range of operative conditions [45], correlations between kinetic parameters, calculated with the general assumption of eqn. (6), were examined with the aim of finding a possible linear relationship to replace the iterative process [44]. A relationship exists, but the coefficients are not independent of operating conditions, thus suggesting that the iterative procedure remains the best approach. However a high correlation was observed between log(Z) and E, thus the KCE, reported in observation *ob7*, should be regarded as a mathematical consequence of the model assumed in eqn. (3).

Using simulations, the accuracy of the PTDK method was finally tested [47] with respect to noise, sampling interval, temperature inaccuracy and with respect to perturbations induced by thermal coefficients. The PTDK method of simultaneous refinement turns out to be much more accurate

TABLE 3

Half-life times $t_{0.5}$ (s) for the three thermal decomposition steps of $CaC_2O_4 \cdot H_2O$: calculated vs. isothermically found values

	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

than other methods, assuming eqn. (6). While the former is not, the latter are very sensitive to masses and heating rates: for step 1 of $CaC_2O_4 \cdot H_2O$ decomposition with the instrument parameters used, values such as 10 mg and 10°C min^{-1} are not "low enough". Temperature inaccuracies were also shown to affect strongly the kinetic parameter calculation, thus supporting, once more, observation *ob1*. The method performs satisfactorily, even from a numerical point of view: noise up to 0.1% can be tolerated, and a smoothing procedure helps in reducing it when higher.

From experimental data, and also from simulated data when the reaction enthalpy is high [44,46], the attempt to obtain Z, E, N and a_1–a_3 often fails (especially when processing few curves) owing to ill-conditioned numerical systems. It should be remembered that Varhegyi came to a similar conclusion about the limited information content of a single curve [51] just on the basis of a survey by "the human eye". In such cases, a solution can be found if the thermal parameters to be refined are reduced to a_1 and a_3 or only to a_3. This means that the whole function is sufficiently flexible and an attempt to introduce other parameters, such as other expressions of $f(W)$, to modify eqn. (3a) would lead to serious numerical problems.

CONCLUSIONS

Like all known PTDK method, the reported simultaneous refinement, though designed only for TG and DTA/DSC among the techniques summarized under consideration *cn1*, still remains subject to the theoretical limitations expressed by considerations *cn2–cn4*. However this method seems to be able to take into account all the observations *ob1–ob7*.

By considering the differences between observed temperatures and sample temperatures, the suggestion derived from observation *ob2* is followed. The main feature of the method is the high predictive power, required by observation *ob5*, displayed by the so-called true kinetic parameters, and also when comparing isothermal and non-isothermal measurements, in agreement with observation *ob4*. The method of course allows the calculation of all the parameters needed to characterize the sample behaviour, required by observation *ob6*. Through simulations, observations *ob1* and *ob7* can be easily explained by the adopted model, and an application of the method to experimental data has allowed a critical review of $CaC_2O_4 \cdot H_2O$ thermal decomposition, required by observation *ob3*.

The simultaneous refinement can work by using as many data as are available, i.e. both on a single thermoanalytical curve or on any number of these. In principle, isothermal curves could also be mixed with non-isothermal ones to calculate more accurate parameters. In any case, special attention must be paid when mixing data from different equipment: the thermal parameters are generally different, owing to differences in the overall heat transfer coefficient or in the thermal capacity of the holder, so that simultaneous refinement would fail, as would any other method [52,53].

Though the predictive power of the determined true kinetic parameters can be very high, their physical meaning is questionable, both remembering considerations *cn2–cn4* or looking at KCE. This statement also becomes evident when comparing the reconstructive ability (limited to the considered data) shown by the two sets of parameters [43,44] determined for the dehydration of calcium oxalate. As a consequence, the identification of a mechanism through $f(W)$ or $f(\alpha)$ could also be a hard task: the processing of very many data curves with very low noise could lead, in principle, to obtaining numerical systems allowing the determination of more than 3–5 parameters (Z, E, n, m, p, a_1–a_3, ...) from such S-like curves as $\{W, T_p\}$.

Some points of a strategy that should be common to all PTDK methods (and also to all mathematical methods used in other fields) can be summarized as general suggestions.

1. A mathematical model describing the considered phenomenon must first be defined, and a simulation procedure must be implemented, i.e. a procedure allowing the expected experimental data to be constructed (calculated) from assigned, and exactly known, parameters.
2. The method proposed to calculate parameters from experimental data, generally including approximations, must be checked for simulated experimental data: if the method fails in recalculating simulation values, then it must be rejected.
3. When the method has passed the test on simulated data, it must finally be applied to real experimental data to test the validity of the assumed model: the parameters obtained should be true, i.e. able to allow a satisfactory reconstruction of experimental data through simulation; some statistical tests, such as the chi-square or Student test, depending on the assumed error distribution, could be helpful, although not always convenient.
4. If the parameters are not true, the chosen model must be revised and the whole process repeated from the start.
5. The accuracy of the measured true parameters should be evaluated by simulating perturbations such as noise, sampling frequency etc.
6. The physical meaning of the true parameters should be assigned with care, limited by the theoretical background available for the chosen model; however, they can always help researchers in characterizing compounds. For instance true kinetic parameters were used to quantify thermal stabilities through calculated temperatures at 10% reaction [54], instead of from graphically evaluated starting temperatures [55].

The design of the described method and the definition of a common strategy were possible using data collected and processed by a computer.

An acronym could be used to identify such an approach, similar to those in various fields of chemistry, i.e. CAC (Computer Aided Chemistry), analogous to CAD (Computer Aided Design), CAE (Computer Aided Engineering), etc. When using such useful tools, however, it must be remembered that the chemical sense should never be lacking: "the computer has no physical or chemical soul" [5].

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