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Using thermoanalytical data.
Part 5. Effect of experimental constraints and data processing on the accuracy of kinetic parameters determined by dynamic thermal analysis

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Abstract

The accuracy of the kinetic parameters determined by TG or DTA/DSC is evaluated through the calculation of simulated $\{W, Tp\}$ curves. The already proposed method of simultaneous refining of thermal and kinetic parameters is much more accurate than commonly used methods. The reaction enthalpy, thermal capacity and heat transfer, are discussed with respect to parameter accuracy, as well as to noise and discrete sampling and to temperature inaccuracy. The errors are evaluated and some suggestions are derived to improve the reliability of experiments.

INTRODUCTION

Many authors [1–5] have recently underlined the problems connected with the reliability of solid state decomposition kinetic parameters, determined through thermoanalytical techniques. With no attention paid to the whole heat transfer taking place during the experiments, some other authors found a way to fit experimental data through a quite arbitrary complication of the chemical model, for example, by introducing a dependence of kinetic parameters on the degree of conversion [6] or by assuming a multiple step reaction instead of a single one [7]. The limitations of fitting data with a complex kinetic law, including nucleation as well as diffusion and phase boundary reactions with several geometries, have also been discussed [8].

It is surprising that just a few other authors until now have considered that kinetic measurements are mainly affected by the heat transfer taking place into a TG [9], DTA [10], or DSC [11] apparatus. Just when that

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contribution has been considered, a refinement of the chemical model should be tried.

Moreover we have suggested a method to evaluate true (not necessarily real) kinetic parameters by refining them together with thermal ones [13, 15], referred to here as simultaneous refinement, and we have underlined the high predictive power of the so determined Z, E, N appearing in the general kinetic expression

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

where the symbols have already been defined [13].

The predictive power of the parameters so determined has been shown to be higher than that of the corresponding ones determined by the simple regression [12] of the logarithmic form of the above relationship (in the assumption that the program temperature is always equal to the sample temperature), hereby referred to as common regression.

As observed, a more complicate expression, where the term W^N is replaced by another taking into account different mechanicsms (diffusion, nucleation, phase boundaries, geometries), could be just the way to add flexibility to the function to be fitted with experimental data. This latter approach probably leads to the erroneous assignment of a reaction mechanism, on the basis of data being perturbed by heat transfer in the instrument, much more than by the chosen mechanism.

When thermal parameters are considered in the simultaneous refinement (they cannot be neglected to describe the sample behaviour under heating) the flexibility is sufficient so attempts to introduce other parameters (such as exponents of an Avrami-like expression) could lead to ill conditioned systems and consequently to misunderstandings when evaluating the results.

In this paper we have examined the influence of the experimental constraints, as well as influence of the numerical processing of data, on the determination of the kinetic parameters through the proposed simultaneous refinement.

By using simulated (calculated) curves, the accuracy of this method has been compared with that of the common regression, in several conditions, while the accuracy of the method itself has been checked with respect to the noise added to the signal, to the sampling effect (discrete $\{W, T\mathrm{p}\}$ curves) and to the temperature in accuracy.

EXPERIMENTAL

The simulations were preformed using the parameters already found for the first (dehydration) step of $CaC_2O_4 \cdot H_2O$ [13]. Calculations were performed using the same programs and equipment as described previously [13–15].

RESULTS

The $\{W, Tp\}$ curves, i.e. reagent fraction versus programmer (read) temperature, were simulated by using all the parameters described in Table 1 in turn as reference parameters.

As a preliminary test the kinetic parameters obtained by simultaneous refinement were compared with those obtained by common regression, to evaluate the inaccuracies induced by numerical processing (Table 2), and by the operative conditions (Table 3).

Dealing with both simultaneous refinement and common regression, the influence of the reaction heat, i.e. of the enthalpy, has been considered, as an evaluation of the thermal effect contribution (Table 4), as well as the influence of the total heat capacity and of the heat transfer coefficient, as whole delay factors (Table 5).

After that checks were made on the contribution of processing parameters, as noise (Table 6) and discrete representation of curves (Table 7), and on the contribution of temperature inaccuracy (Table 8).

TABLE 1

Reference parameters used to build $\{W, Tp\}$ curves

CTo/mcal °C^{-1}	0.4019	Holder thermal capacity
k/mcal °C^{-1} s^{-1}	0.3673	Heat transfer coefficient
m/mg	10.0	Reactant mass
Bp/°C min^{-1}	20.0	Programmer heating rate
$C1$/cal g^{-1} °C^{-1}	0.25	Specific heat of reactant
$C2$/cal g^{-1} °C^{-1}	0.25	Specific heat of product[a]
H/cal g^{-1}	86.0	Reaction enthalpy
$A1$/s mg^{-1}	0.79	$(CTO/m + C2)/k$
$A2$/s mg^{-1}	0.0	$(C1 - C2)/k$
$A3$/°C s mg^{-1}	234.14	H/k
Z/s^{-1}	1.870×10^8	Pre-exponential factor[b]
E/kJ mol^{-1}	86.47	Activation energy[b]
N	0.6193	Reaction order[b]
NT	200	Number of points in curve[c]
No	0	Random noise

[a] Calculated with respect to the mass of reactant.

[b] Apparent values.

[c] Temperature range 80–230°C.

TABLE 2

Kinetic parameters determined from simulated curves: (a) by simultaneous refinement of the curve simulated with reference parameters; (b) by simultaneous refinement of the curve simulated with CTo = $C1$ = $C2$ = H = 0, m = Bp = 0.1; (c) by common regression of the curve such as b (standard deviations in parentheses)

Method	$Z \times 10^{-8}/\mathrm{s}^{-1}$	$E/\mathrm{kJ\ mol}^{-1}$	N	$A1/\mathrm{s\ mg}^{-1}$	$A2/\mathrm{s\ mg}^{-1}$	$A3/{}^{\circ}\mathrm{C\ s\ mg}^{-1}$
(a)	2.204	86.8	0.627	0.85	0.21	258
	(0.065)	(0.1)	(0.005)	(0.07)	(0.04)	(1)
(b)	2.511	87.3	0.624			32584
	(0.045)	(0.1)	(0.001)			(3579)
(c)	2.157	86.9	0.621			
	(0.020)	(0.1)	(0.001)			

DISCUSSION

From row (a) of Table 2 the accuracy of the simultaneous refinement can be estimated: the refined values match the reference ones (used to simulate the curve) within an approximate range of 3% for Z, E and N (about five times the standard deviations) and of 10% for $A1$ and $A3$. The estimate of thermal parameters are found to be the most critical, particularly when considering $A2$ or when all temperature perturbations are eliminated as in row (b), even though the estimate of kinetic parameters is always

TABLE 3

Kinetic parameters determined by simultaneous refinement versus common regression (lines where $A1$–$A3$ are not displayed); masses m in mg and programmer heating rate Bp in °C min^{-1} are varied

	$Z \times 10^{-8}/\mathrm{s}^{-1}$	$E/\mathrm{kJ\ mol}^{-1}$	N	$A1/\mathrm{s\ mg}^{-1}$	$A2/\mathrm{s\ mg}^{-1}$	$A3/{}^{\circ}\mathrm{C\ s\ mg}^{-1}$
$m = 1$	1.818	86.2	0.615	5.33		240
	0.971	84.5	0.602			
$m = 10$	2.204	86.8	0.627	0.85	0.21	258
	0.014	71.1	0.541			
$m = 100$	1.197	83.7	0.568	1.20		302
	1.6×10^{-4}	56.1	0.510			
$B\mathrm{p} = 1$	2.298	87.0	0.621	4.34		279
	0.939	84.5	0.602			
$B\mathrm{p} = 10$	2.300	87.1	0.624	0.90	0.04	250
	0.069	76.3	0.577			
$B\mathrm{p} = 100$	1.416	84.4	0.584	1.07	0.10	301
	1.5×10^{-4}	55.8	0.504			

TABLE 4

Kinetic parameters determined by simultaneous refinement versus common regression (lines where $A1$–$A3$ are not displayed); reaction enthalpy H is varied

H/cal g^{-1}	$Z \times 10^{-8}$/s^{-1}	E/kJ mol^{-1}	N	$A1$/s mg^{-1}	$A2$/s mg^{-1}	$A3$/°C s mg^{-1}
−50	2.230	87.1	0.623	0.98	−0.16	−136
	887.3	107.3	0.697			
0	2.053	86.9	0.618	0.65		0[a]
	2.364	87.9	0.619			
+50	1.769	85.9	0.624	0.95	0.42	154
	0.081	76.9	0.568			
+100	2.215	86.8	0.628	0.81	0.28	301
	0.008	69.3	0.534			

[a] The convergence is very slow: iterations are oscillating.

satisfactory. The common regression also leads to good results when temperature perturbations are absent as in row (c).

The uncertainty ranges found must be viewed as tolerances of the data processing process: they are low enough to be widely accepted, especially when compared with the spread of literature data [12].

TABLE 5

Kinetic parameters determined by simultaneous refinement versus common regression (lines where $A1$–$A3$ are not displayed); sample holder thermal capacity CTo in mcal °C^{-1} and transfer coefficient k in mcal °C^{-1} s^{-1} are varied

	$Z \times 10^{-8}$/s^{-1}	E/kJ mol^{-1}	N	$A1$/s mg^{-1}	$A2$/s mg^{-1}	$A3$/°C s mg^{-1}
CTo = 0.0	2.271	87.0	0.627	0.73	0.16	256
	0.013	70.8	0.533			
CTo = 0.8	2.086	86.6	0.622	1.04	0.22	260
	0.016	71.6	0.551			
CTo = 1.6	1.976	86.4	0.624	1.24	0.32	262
	0.017	71.9	0.555			
CTo = 3.2	1.589	85.4	0.625	2.59	0.75	276
	0.031	74.7	0.583			
$k = 0.1$	1.528	85.0	0.594	4.03	0.26	1064
	9.5×10^{-5}	55.9	0.506			
$k = 1.0$	2.015	86.5	0.621	0.45	0.14	94
	0.190	79.3	0.572			
$k = 10$	2.646	88.2	0.626	0.0	0.31	20
	1.528	85.9	0.613			

TABLE 6

Kinetic parameters deremined by simultaneous refinement. The random noise 0.00001 to 0.01 is applied to the $\{W, Tp\}$ curve, i.e. from 0.001 to 1% of the full scale, 0–1, of W

No	$Z \times 10^{-8}$	E/kJ mol^{-1}	N	$A1$/s mg^{-1}	$A2$/s mg^{-1}	$A3$/°C s mg^{-1}
10^{-5}	3.153	88.5	0.659	0.39		243
10^{-4}	3.189	88.5	0.672	0.28		242
10^{-3}	2.208	87.6	0.676			212
10^{-2}						

As expected, the accuracy of the method decreases when mass or heating rate increase, as shown in Table 3, or when a considerable heat of reaction is involved, as shown in Table 4. However the simultaneous refinement always gives much more reliable results than those obtained from common regression. It seems that the absolute increase of reaction enthalpy leads to a slight overestimate of kinetic parameters, due to thermal perturbation.

Table 5 shows that the accuracy increases with the whole thermal capacity up to a given value (around the sample thermal capacity), and decreases when this value is passed: this behaviour accounts for a filtering effect on sample temperature variation, becoming just a temperature shift

TABLE 7

Kinetic parameters determined by simultaneous refinement; the temperature range 80–230°C, where simulation is performed, is divided into NT steps

NT	$Z \times 10^{-8}$ s^{-1}	E/kJ mol^{-1}	N	$A1$/s mg^{-1}	$A2$/s mg^{-1}	$A3$/°C s mg^{-1}
100	3.696	89.0	0.639	0.73	−0.30	248
200	2.204	86.8	0.627	0.85	0.21	258
400	1.674	85.8	0.620	0.90	0.42	260

TABLE 8

Kinetic parameters determined by simultaneous refinements; the temperature scale is shifted by T_{pff} when refining is done

T_{pff}	$Z \times 10^{-8}$ s^{-1}	E/kJ mol^{-1}	N	$A1$/s mg^{-1}	$A2$/s mg^{-1}	$A3$/°C s mg^{-1}
−20	0.525	77.9	0.627	0.72	0.40	254
−10	1.076	82.3	0.627	0.78	0.30	256
0	2.204	86.8	0.627	0.85	0.21	258
+10	4.516	91.5	0.626	0.92	0.11	259
+20	9.260	96.2	0.625	0.99	0.01	261

when too high. However accuracy also increases with k, due to the fact that high k values account for a sample temperature which is always equal to that of the programmer. It must be noted that when the thermal effect is smoothed by high k values ($k = 10$), as well as by zero reaction enthalpy as in Table 4, the simultaneous refinement shows a low convergence and final results oscillate between two sets of values: this is the only case where a common regression should be preferred.

From Table 6 sensitivity to the noise can be observed: when noise equals 1% of the full scale range the data processing fails, due to the the difficulty of making finite derivatives. The smoothing of data becomes essential: the use of common regressions (one for each experimental curve) as smoothed functions gave good results [13]. A noise of less than 0.01% should be ensured to enable data to be processed.

The sampling of the curve at 0.75, i.e. (230 − 80)°C/200°C, seems to be a good compromise between accuracy and speed of operations, as shown in Table 7. More rapid processes would anyway require a shorter sampling interval.

Table 8 shows how critical the temperature inaccuracy could be: an accurate calibration should be made to avoid large errors.

To give an estimate of the reaction temperature range displacement, the temperatures corresponding to $W = 0.75$, 0.50, 0.25 are reported in Table 9, as calculated by simulation with reference parameters, changing some or one of them.

As reported in the two last rows of Table 9, the temperature range is the same both when all sources of thermal effects are cleared and when the heat transfer coefficient is high enough to allow the sample temperature to always be equal to the programmer temperature. A low value of the k coefficient, on the contrary, shifts the reaction range towards higher temperatures: it should be maintained as high as possible in modern instruments, for example by browning the surface of the sample holder; some limitation to its increase could be encountered when dealing with DTA apparatus, where just the temperature difference between sample and reference (or programmer through calibration) is the recorded signal.

The increase of holder thermal capacity becomes just a displacement of the termperature scale: this value should be kept as high as possible because of its filtering effect on temperature variations. An accurate calibration should be made to relate program temperatures and samples temperatures.

Heating rates influence the reaction range much more than sample. In fact, on a thermal basis, masses are only involved in thermal capacity, whilst heating rates act as amplifiers of both thermal capacity delay and reaction enthalpy perturbation. Disregarding other phenomena, such as gas evolution, better results could be achieved when working at low heating rates and high masses. When a temperature calibration (with an inert thermal capacity equal to that of the sample mass) has been performed, the use of

TABLE 9

Temperatures in °C corresponding to $W = 0.75$, 0.50, 0.25 when varying simulation parameters

Simulation parameter	W		
	0.75	0.50	0.25
$m = 5$	160	176	187
$m = 10$	163	180	193
$m = 20$	169	189	204
$B\mathrm{p} = 10$	145	164	175
$B\mathrm{p} = 20$	163	180	193
$B\mathrm{p} = 40$	181	201	216
CTo = 0.2	163	180	193
CTo = 0.402	163	180	193
CTo = 3.2	166	183	196
$k = 0.09$	180	204	222
$k = 0.3673$	163	180	193
$k = 1.48$	158	173	184
$k = 50$	156	170	180
$H = \mathrm{CTo} = C1 = C2 = 0$	156	170	180

high masses both filters off the temperature variations, between programmer and sample, and reduces the instrumental noise contribution to the full scale signal.

CONCLUSIONS

The present paper completes a series of five fully describing an original approach to the determination of kinetic parameters, from TG, DTA and DSC curves, for single step reactions. After a revision of the inability of many literature data to rebuild experimental curves [12], a model has been implemented to simulate TG curves taking into account thermal coefficients as well as kinetic ones [13]. Through this model an iterative procedure has been proposed for simultaneous refinement of both thermal and kinetic parameters: both mass and heating rate are used for calculation, whilst mass was never considered before, and reaction enthalpy can also be evaluated from TG curves alone. A linear combination of all kinetic and thermal parameters has been tested to assist the iterative procedure in calculating true kinetic parameters [14]: the approach was not very useful. The model was extended to DTA and DSC curves [15], introducing the program (DTA) or estimated (real DSC) temperature differences as additional information to calculate a pseudo TG curve, from which the kinetic parameters could be obtained using the simultaneous refinement. Finally the accuracy of the method has been discussed (present paper) with respect to operating conditions, including numerical processing.

The possibility of extending the model to complex kinetic expression, by reducing the signal to noise ratio to avoid numerical indetermination, or to multiple step reactions, through deconvolution of curves are presently under examination.

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