Thermochimica Acta, 199 (1992) 77–83
Elsevier Science Publishers B.V., Amsterdam

Using thermoanalytical data. Part 3. Influence of calorimetric and instrumental parameters on estimating kinetic parameters by TG [1]

U. Biader Ceipidor [a], R. Bucci [b] and A.D. Magrí [b]

[a] *Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza (Italy)*
[b] *Dipartimento di Chimica, Università "La Sapienza", P. le A. Moro 5, 00185 Rome (Italy)*

(Received in final form 4 October 1991)

Abstract

The influence of calorimetric parameters on estimation of kinetic parameters by TG is considered. A numerical model is used to highlight the correlation displayed by the parameters themselves and the possibility of representing kinetic parameters as a linear combination of variables, describing heat transfer contributions, is examined. Simulations, using the previously determined kinetic parameters for calcium oxalate dehydration, show the limitations of such an approach, even though interesting observations are derived. The previously reported iterative method for kinetic parameters calculation therefore should not be replaced by a general linear combination.

INTRODUCTION

Fitting of experimental TG curves to chosen kinetic models is the general way of calculating kinetic parameters from so-called non-isothermal kinetics. The question whether they represent physical reality or not is open [1].

When dealing with weight–temperature (TG) curves, the influence of the evolved/absorbed reaction heat, as well as that of heat flow from heater to the sample, are always assumed to be low enough to be ignored. The kinetic parameters thus obtained strongly depend on operative conditions and may fail to describe TG curves satisfactorily, especially curves other than those from which they were derived [2].

An iterative procedure has been proposed to calculate true kinetic parameters [3], i.e. those able to describe sample behaviour in a wide range

---

Correspondence to: R. Bucci, Dipartimento di Chimica, Università "La Sapienza" P. le A. Moro 5, 00185 Roma, Italy.

[1] Presented at the 12th National Conference on Calorimetry and Thermal Analysis, Bari, Italy, 11–13 December 1990.

0040-6031/92/$05.00 © 1992 – Elsevier Science Publishers B.V. All rights reserved

of operative conditions. The possibility of using a more simple linear combination of all the parameters involved is considered in this work.

Kinetic parameters previously determined for $CaC_2O_4 \cdot H_2O$ dehydration with no heat transfer correction [2] are used to make numerical simulations when varying other parameters, such as mass, heating rate, specific heats, enthalpy, instrumental thermal capacity and heat transfer coefficient, to see whether a simple regression [2] could provide an alternative way to determine true kinetic parameters by a correction based on a general linear combination.

MODEL AND SYMBOLS

The numerical model for simulating a thermal decomposition, as well as the computing environment, have previously been described [3]. The procedure was based on the simultaneous solution of both relationships through finite elements analysis

$$-(\mathrm{d}W/\mathrm{d}t) = Z \exp[-E/(RT)]W^N \tag{1}$$

$$k(T_\mathrm{p} - T) = \{C_{\mathrm{t}0} + m_\mathrm{i}[C1W + C2(1 - W)]\}(\mathrm{d}T/\mathrm{d}t) - m_\mathrm{i}H(\mathrm{d}W/\mathrm{d}t) \tag{2}$$

where W is the reagent fraction ($W = 1 - \alpha$, α conversion degree), measured as $(m - m_\mathrm{f})/(m_\mathrm{i} - m_\mathrm{f})$; t is the time from the start; R is the gas constant; T is the sample temperature and T_p the operative temperature as read; m_i is the initial sample mass, m_f the final sample mass, m actual sample mass; H is the reaction enthalpy; $C_{\mathrm{t}0}$ and k are instrument parameters (holder thermal capacity and heat transfer coefficient respectively); $C1$ and $C2$ are specific heats of the sample before and after the reaction, both referred to initial mass m_i; Z, E, N are kinetic parameters of the assumed empiric law (1), already discussed [3].

The procedure output [3] is formatted to display all information on the screen: assigned parameters are shown in the graphic window; outside the window, the bottom line displays the kinetic parameters, back-calculated from W versus T_p, referred as $\{W, T_\mathrm{p}\}$, curves as described below. Curves W versus T_p, W versus T, $\mathrm{d}T/\mathrm{d}t$ versus T are displayed and marked with c, u and r respectively. The heating rate $\mathrm{d}T_\mathrm{p}/\mathrm{d}t$ is reported as B in °C min^{-1}, the mass m_i is reported as m in mg. Temperatures are reported in °C, H is in cal g^{-1}, $C1$ and $C2$ are in cal g^{-1} $°\mathrm{C}^{-1}$, Z is in s^{-1}, E is in kJ mol^{-1}, $C_{\mathrm{t}0}$ is in mcal $°\mathrm{C}^{-1}$, k is in mcal $°\mathrm{C}^{-1}$ s^{-1}.

The back-calculations of the kinetic parameters were executed using the common assumption $T = T_\mathrm{p}$, i.e. by linear fitting of simulated $\{W, T_\mathrm{p}\}$ curves, through the logarithmic form [2] of eqn. (1).

Linear dependence of the back-calculated kinetic parameters on other coefficients, appearing in eqn. (2), was empirically assumed and tested for validity. The following linear combinations where chosen:

$$\lg Z = z_0 + z_1 X1 + z_2 X2 + z_3 X3 + z_4 X4 \tag{3a}$$

$$E = e_0 + e_1 X1 + e_2 X2 + e_3 X3 + e_4 X4 \tag{3b}$$

$$N = n_0 + n_1 X1 + n_2 X2 + n_3 X3 + n_4 X4 \tag{3c}$$

where $X1$–$X4$ are composite variables defined as

$$X1 = C_{t0} B/k \quad X2 = (m_i B/k) C1 \quad X3 = (m_i B/k) C2 \quad X4 = (m_i B/k) H$$

The form of composite variables was chosen from eqn. (2): they represent separate contributions to temperature differences between sample and heater. While they include m_i (except $X1$) and B/k, $X1$ depends on instrument, $X2$ and $X3$ on sample specific heats, $X4$ on reaction enthalpy.

The z_0–z_4, e_0–e_4, n_0–n_4 coefficients were calculated through a linear best fit of lg Z, E, N values, back-calculated from simulated $\{W, T_p\}$ curves, where all parameters were known.

RESULTS

When dealing with simulated, i.e. the expected experimental, $\{W, T_p\}$ curves, the back-calculated kinetic parameters considerably differ from the values used to perform the simulations, as shown in Fig. 1. Just when thermal coefficients are low enough, the values are much the same, as shown in Fig. 2.

To empirically evaluate dependence of the kinetic parameters so determined on thermal coefficients, 120 simulations were performed, using kinetic parameters displayed in Figs. 1 and 2, i.e. those obtained in real conditions [2]. The thermal coefficients, as well as the masses and heating rates, were randomly varied in chosen ranges, the $\{W, T_p\}$ curves were simulated and the Z, E, N triplets were back-calculated from these curves. The Z, E, N values obtained in this way were used to fit the linear combinations (eqns. (3)).

TABLE 1

Coefficients of linear combination of composite variables with standard deviations in parentheses; last row displays RSD

a_i	lg Z ($a_i = z_i$)	E ($a_i = e_i$)	N ($a_i = n_i$)
a_0	12.13 (0.05)	116.4 (0.3)	0.591 (0.002)
$a_1 \times 10^4$	5.16 (4.48)	90.4 (32.5)	.0.394 (0.231)
$a_2 \times 10^3$	1.60 (0.17)	17.6 (1.2)	−0.076 (0.009)
$a_3 \times 10^4$	−5.58 (1.23)	−45.1 (8.9)	0.730 (0.064)
$a_4 \times 10^5$	−8.40 (0.30)	−65.0 (2.1)	0.032 (0.011)
RSD	0.37	2.6	0.019

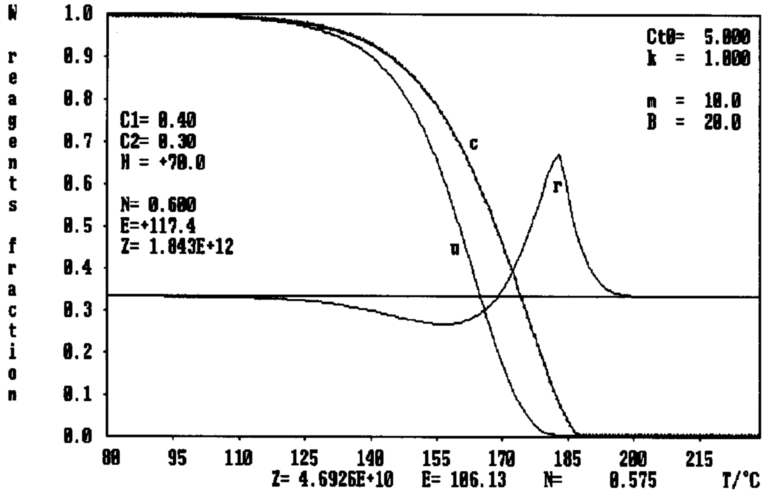

Fig. 1. Simulation of a TG curve influenced by heat transfer.

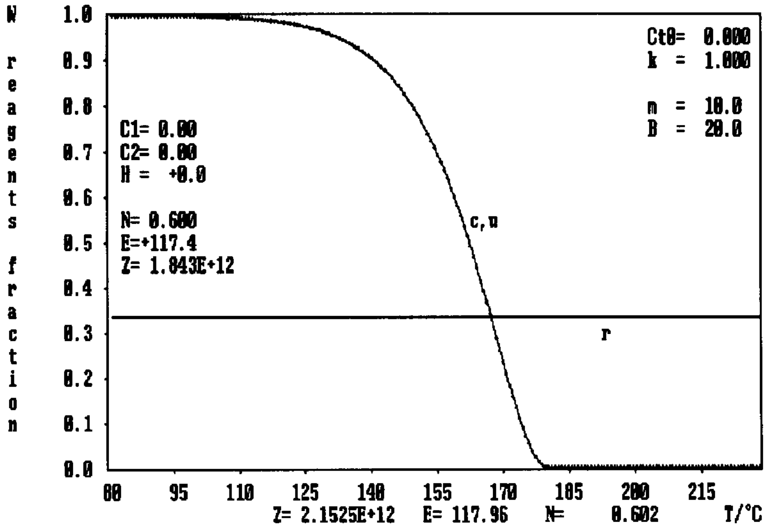

Fig. 2. Simulation of a TG curve not influenced by heat transfer.

TABLE 2

Correlation matrix of regression coefficients

	a_0	a_1	a_2	a_3	a_4
a_0	1.00				
a_1	−0.40	1.00			
a_2	−0.21	−0.12	1.00		
a_3	0.08	−0.23	−0.63	1.00	
a_4	−0.17	−0.08	−0.24	−0.09	1.00

TABLE 3

Correlation matrix of variables

	lg Z	E	N	$X1$	$X2$	$X3$	$X4$
lg Z	1.00						
E	0.98	1.00					
N	−0.22	−0.20	1.00				
$X1$	−0.15	−0.03	0.30	1.00			
$X2$	−0.15	0.03	0.08	0.41	1.00		
$X3$	−0.27	−0.13	0.57	0.45	0.73	1.00	
$X4$	−0.90	−0.83	0.23	0.27	0.44	0.39	1.00

The ranges into which the parameters were randomly varied are reported below, using the above defined units:
C_{t0} 0, ..., 9; k 0.2, ..., 2.0; m_i 0, ..., 50; B 2, ..., 20; $C1$ 0.2, ..., 1.1; $C2$ 0.2, ..., 1.1; H −20, ..., +70.

In Table 1, the coefficients found for the linear combinations (eqns.(3)) are reported with their standard deviations and the residual standard deviation (RSD) of the regression.

In Tables 2 and 3 the correlation matrices of coefficients and variables are reported. Each element of the matrices is $S_{ij}/(S_{ii}S_{jj})^{1/2}$, where S_{ij} represents the covariance of the ith with the jth element. Since the assumed linear combination (eqns. (3)) is the same for lg Z, E and N, the correlation matrix of the coefficients is unique. Coefficients z_0–z_4, e_0–e_4, n_0–n_4 are therefore assigned the general name a_0–a_4.

DISCUSSION

The standard deviations in Table 1 account for the considerations reported below.

A good reproducibility of values of a_0 (i.e. z_0, e_0, n_0) was found. In principle, true values can so be found by extrapolating the experimentally obtained kinetic parameters up to zero values of $X1$–$X4$.

The linear combinations fail to represent a complex model: a_1–a_4 values (i.e. z_1–z_4, e_1–e_4, n_1–n_4) show high relative standard deviations. Determinations of thermal coefficients through the calculation of $X1$–$X4$ values (by using a set of linear combinations (eqns. (3)), with known coefficients a_1–a_4, and extrapolated a_0 values) cannot be performed satisfactorily. The idea of calculating calorimetric parameters, included in $X1$–$X4$, from TG should be rejected.

Some interesting observations can be made from the correlation matrices of coefficients and variables (Tables 2 and 3), remembering that direct correlations between variables $X1$–$X4$ are meaningless because of the random generation of thermal coefficients, masses and heating rates.

The correlation between coefficients is mainly low, thus accounting for a satisfactory linear independence of the chosen variables. This observation is enhanced if it is considered that each correlation element in the matrix is in principle the angular coefficient of a straight-line fitting of the regression points in a normalized a_i–a_j plane of coefficients, while its squared value (lower than the element itself, this being less than unity) represents the fraction of variance of a_i explained by a_j.

The a_2 and a_3 are the only a_i values with a high enough negative correlation. This is due to the contribution of sample specific heat before ($C1$ appears in $X2$) and after ($C2$ appears in $X3$) the reaction, both describing the sample specific heat. When considering the whole thermal capacity, an increase of $X2$ should in fact correspond to a decrease of $X3$. Due to chosen simulation ranges, the same is displayed between $X2$ and $X1$, though to a lesser extent.

Both lg Z and E are strongly correlated as a consequence of eqn. (1), where they can be seen as arguments of an exponential: physically this means that many pairs of values could fit the same data.

By contrast lg Z and E are poorly correlated with $X1$, $X2$, $X3$, but strongly with $X4$, thus accounting for their main dependence on the enthalpy of reaction, in spite of other thermal parameters, such as C_{t0}, $C1$ and $C2$. The N value is strongly correlated with $X3$ and consequently seems mainly dependent on specific heat of product.

In principle these considerations are confined to the reaction examined, i.e. to chosen kinetic parameters describing the sample behaviour (used in simulations). Tests with other kinetic parameters account for similar results about the magnitude of standard deviations and correlations. However the coefficients are found to be different, depending on kinetic parameters chosen. To use this approach, the coefficients of eqns. (3) should thus be re-calculated for each sample and instrument, by redoing around 100 simulations, once the kinetic parameters have been roughly estimated.

CONCLUSION

The investigated approach could be used in principle to calculate kinetic parameters from TG, taking into account the perturbations induced by the heat transfer process. The calculations are tedious in any event and many simulations are required for each sample. However the reported correlation matrix of the variables could be used to understand the limitations of conventional TG data processing and for teaching purposes.

Only if the coefficients obtained had been independent of sample and instrument, would the method investigated in this work have offered an easy way to recalculate true kinetic parameters of samples from available data, i.e. from reported kinetic parameters. Unfortunately this independence cannot be assumed. For new experiments the iterative method [3] should be preferred owing to both its greater accuracy and to the fewer calculations required.

As already observed [3], the strong correlation between lg Z and E accounts for the equivalent ability of several pairs of such values (in general triplets Z, E, N) in re-building experimental curves [2], at least in a limited range of operative conditions. Since common methods often fail in rebuilding curves [2], the assignment of a physicochemical meaning to the kinetic parameters obtained should always be done very carefully.

However the influence of thermal coefficients must always be considered, when deriving kinetic parameters for modelling sample behaviour in extreme heating conditions [4,5] or when attempting to use experimental data to assign a kinetic model [6].

REFERENCES

1 J. Šesták, J. Therm. Anal., 33 (1988) 1263.
2 U. Biader Ceipidor, R. Bucci and A.D. Magrí, Thermochim. Acta, 158 (1990) 125.
3 U. Biader Ceipidor, R. Bucci and A.D. Magrí, Thermochim. Acta, 161 (1990) 37.
4 J.B. Henderson, J.A. Wiebelt and M.R. Tant, J. Compos. Mater., 19 (1985) 579.
5 J.B. Henderson and T.E. Wiecek, J. Compos. Mater., 21 (1987) 373.
6 El-H.M. Diefallah, S.N. Basahi, A.Y. Obajd and R.H. Abu-Eittah, Thermochim. Acta, 111 (1987) 49.