Using thermoanalytical data.
Part 7. DSC/DTA/DTG peak shapes depending on operational settings, equipment features, sample kinetic and thermodynamic parameters

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Abstract

Through curves simulated (calculated) as previously reported, DSC/DTA/DTG peak shapes are discussed in terms of six parameters: height, position, left and right half width at half maximum, and also as left and right gaussian/lorentzian mixing ratio. By assigning several values to masses and heating rates (operational setting, OS), to transfer coefficients and thermal capacity (equipment features, EF), to Z, E, N (sample kinetic parameters, SK) and to ΔH, Δc_p (sample thermodynamic parameters, ST), peaks were simulated and the six parameters were calculated by a refinement procedure derived from X-ray photoelectron spectroscopy. The resulting peaks were hardly ever pure symmetric gaussian curves, as often assumed in so called "deconvolution" (peak sum resolution) procedures, where such an assumption may generate artifacts. A complete discussion of peak shapes versus OS, EF, SK and ST is reported. The extension of a previously described TG simulation procedure to DSC/DTA/DTG is also reported, together with a discussion of the already proposed method, for calculating true kinetic parameters, with respect to other approaches based on signal desmearing.

Keywords: Deconvolution; DSC; DTA; Kinetics; Peak shape

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1. Introduction

When dealing with a solid state reaction of the type

Solid reactant → Solid product + Gas

where the gas product could also disappear, to describe phase transitions, thermogravimetry (differential thermogravimetry) (TG (DTG)), differential thermal analysis (DTA) or differential scanning calorimetry (DSC) are widely used approaches to determine reaction enthalpy ΔH and/or kinetic parameters. Such kinetic parameters, i.e. Z (pre-exponential factor), E (activation energy) and N (pseudo reaction order), appear in a commonly used (reaction order) (RO) rate expression

$$-\mathrm{d}W/\mathrm{d}t = Z\mathrm{e}^{-E/RT}W^{N} \tag{1}$$

where W, ranging from 1 to 0, is the reagent fraction. As an alternative $\alpha = 1 - W$ is often used in the same expression as extent of reaction or degree of conversion.

An approach to solid state kinetics to obtain true kinetic parameters, i.e. those displaying a high predictive power with respect to unexplored experimental conditions, has been previously reported [1–5] and discussed with respect to other methods [6]. A TG/DTA/DSC or TA simulation procedure has also been described and implemented [3–5] to check such an approach to data processing, by using the same philosophy with which analytical methods are tested. When evaluating an analytical method, well known standards should be available with which to compare obtained results. Furthermore, simulated (or emulated, when a simple physical model is unavailable or too hard to implement) data become the unique available standard (pseudo-experimental signal) when evaluating complex data processing methods, without a priori knowledge of the physical parameters. As previously reported [1,2,4,5,7], a subsequent test on real signals is thereafter required to separately check the reliability of the chosen model, this question being separated from data processing performance, even though it is no less important.

Especially when faced with overlapped DTA/DSC peaks, a general method for isolating single reactions is based on peak sum resolution by assuming a purely gaussian shape [8–12] for each peak. Whilst deconvolution is sometimes used for such a procedure, this term should be reserved for inverse convolution problems, such as when desmearing [13] peaks convoluted by equipment transfer function. In this paper the shape of simulated peaks has been quantitatively determined to check whether or not this assumption is correct. To quantitatively express peak shapes, a previous [7] non linear least squares refinement with constraints (NLLSRC) has been used. When applied to X-ray photoelectron spectra, such a refinement could be of general use, describing each peak in a very flexible form, i.e. by H, height on y axis; P, position (maximum) on x axis; LHWHM, left half width at half maximum in x units; LGL, left gaussian/lorentzian mixing ratio; RHWHM, right half width at half maximum in x units; RGL, right gaussian/lorentzian mixing ratio.

Moreover the method used for baseline (background in XPS) subtraction proves to be formally identical [7] to that proposed [2–4,14] for DSC/DTA signals, when values of c_p for both reagents and products are assumed to be constant during reaction, although different from each other.

2. Experimental and basic theory

The personal computer (PC) configuration and programs have been fully described previously [1–7], as has the basic theory. Special functions were written in QUICK-BASIC 4.0 to convert data formats from TA simulation to NLLSRC and to display the trend of obtained peak parameters versus simulation parameters. NLLSRC were performed by using estimated values roughly read on the curve: the displayed maximum was used to identify H and P, left and right displacements at $H/2$ were measured for LHWHM and RHWHM respectively, and LGL = RGL = 1 was used. Allowed ranges of variation were set to $\pm 50\%$ (always positive) around estimated values as constraints, while the range 0–1 was assigned for LGL and RGL variation. To help the reader the basic theory of the simulation process [1–6] is summarised in this section and extended to DTG/DTA/DSC as a pseudo-experimental description. For TG, an energy flow balance can be written as

$$dq/dt = k(T_p - T) = C_h(dT/dt) + m_i c_{mix}(dT/dt) - m_i \Delta H(dW/dt)$$

or, dividing by k and introducing over-all coefficients a_1-a_3, as

$$T_p - T = a_1 m_i B + a_2 m_i WB - a_3 m_i B_p (dW/dT_p) \tag{2}$$

where T_p is the programmer temperature (i.e. the experimental abscissa), T is the sample temperature, $B_p = dT_p/dT$ constant controlled heating rate, $B = dT/dt$ sample heating rate, t is the time from the start, m_i is the initial reagent mass, and $W = [m - m_f]/[m_i - m_f] = 1.0$ where m is the actual mass and m_f the final mass, c_1 is the specific heat of the reactant and c_2 the specific heat of the product (referred to initial mass m_i), $c_{mix} = c_1 W + c_2(1 - W)$, ΔH is the reaction enthalpy, k the heat transfer coefficient, C_h the sample holder thermal capacity, and $a_1 = (C_h/m_i + c_2)/k$, $a_2 = (c_1 - c_2)/k = \Delta c_p/k$, $a_3 = \Delta H/k$.

Such a balance in Eq. (2) is combined with Eq. (1) and with the programmed heating function

$$T_p = B_p t + T_0$$

Starting with an initial temperature $T_0 = T_p = T$ and increasing t by small enough increments the system is solved by finite elements to obtain W versus T_p or $\{W, T_p\}$ pseudo-experimental normalised TG curves. As a rough but realistic [2–6] approximation, c_1, c_2, C_h and k are assumed to be constant in the temperature (time) range spanned by such a simulation. From Eq. (2) a normalised DTG or $\{dW/dT_p, T_p\}$ becomes

$$dW/dT_p = [a_1 B/B_p + a_2 WB/B_p - (T_p - T)/(m_i B_p)]/a_3 \tag{3}$$

which can be calculated by the numerical derivative of $\{W,T_p\}$. By combining the energy flow balance reference side, where symbols are given the subscript r

$$T_p - T_r = (C_{hr}/k_r)B_r$$

with the sample side represented by Eq. (2) and taking into account that $B_r = dT_r/dt = dT_p/dt = B_p$ in the steady state, a DTA $\{T_r - T, T_r\}$ expression can be obtained as

$$T_r - T = a_1 m_i B + a_2 m_i WB - a_3 m_i B_r(dW/dT_r) \qquad (4)$$

where the constant baseline shift $(C_{hr}/k_r)B_r$ is ignored. In the same way, when heat flows dq_r/dt and dq/dt are considered, for the reference side and sample side respectively, with the constraint that $T = T_r$ (implying that $B = B_r$), a DSC or $\{d\Delta q/dt, T_r\}$ expression can be obtained as

$$d\Delta q/dt = a_1 m_i B_r + a_2 m_i WB_r - a_3 m_i B_r(dW/dT_r) \qquad (5)$$

where $d\Delta q/dt$ is the heat flow difference ($\Delta q = q - q_r$) shifted with respect to a baseline $C_{hr}B_r$. In such a representation k, appearing in $a_1 - a_3$ terms, becomes just a scale factor. Eq. (5) and also Eq. (4) are formally similar to Eq. (2) when T_p (abscissa in TG) is replaced by T_r (abscissa in DTA/DSC) and B_p by B_r, so simulation can be performed with the same mathematical representation, just taking into account the additional constraint that $T = T_r$ when dealing with pure DSC. Since many commercial DSC instruments display DTA-like architecture, the sample temperature T is generally different from T_r. Moreover this difference always exists because of thermal contact with the holder and/or because of temperature distribution into the sample [13]. A real DSC can, therefore, best be modelled by DTA with high k values.

A reference set of parameters included in Eqs. (1) and (2) or (4) or (5) was used for simulations. Such a reference set was that already found [3,4] for $CaC_2O_4 \cdot H_2O$ dehydration in the used equipment. Values are summarised in Table 1 by classifying

Table 1
Reference set of parameters used for simulations

Symbol	Subset	Unit	Value
m_i	OS	mg	10
B_p	OS	K min^{-1}	20
k	EF	mcal K^{-1} s^{-1} [a]	0.367
C_h	EF	mcal K^{-1}	0.402
Z	SK	s^{-1}	1.87×10^8
E	SK	kJ mol^{-1}	86.5
N	SK		0.619
ΔH	ST	cal g^{-1}	86
$\Delta c_p = c_1 - c_2$	ST	cal g^{-1} K^{-1}	0.0
c_1	ST [b]	cal g^{-1} K^{-1}	0.25
c_2	ST [b]	cal g^{-1} K^{-1}	0.25

[a] Dimensionless when DSC. [b] Not included in ST discussion.

parameters as belonging to the following different subsets: operational setting (OS), equipment features (EF), sample kinetics (SK), sample thermodynamics (ST).

3. Results

With respect to the reference set, all other simulations were performed by varying each parameter separately using values reported in Table 2 with units used in Table 1.

Simulated peaks were obtained for DTG, DTA and DSC. Such peaks were refined by NLLSRC until elimination of all parameters from refining occurred [7] without regard to values for chi-squared. When dealing with $\Delta c_p > 0$, baselines were subtracted before NLLSRC. By using peak shape parameters, geometrical characters were calculated as defined below

$$FW = LHWHM + RHWHM$$

$$GL = LGL[LHWHM/(LHWHM + RHWHM)]$$
$$+ RGL[RHWHM/(LHWHM + RHWHM)]$$

$$A = \pi H\{LHWHM[LGL(f - 1) + 1] + RHWHM[RGL(f - 1) + 1]\}/B_p$$

$$AS = LHWHM/RHWHM - 1$$

with $f = (\pi \ln 2)^{-1/2} \approx \ln 2$ as gaussian shape factor. Together with height H and position P, such geometrical characters can easily describe each peak in terms of full width at half maximum (FW), GL which is the mean of LGL and RGL weighted on LHWHM and RHWHM respectively, A which is the peak area divided by the heating rate, and asymmetry (AS).

Observed variation ranges for H, P and geometrical characters are summarised in Tables 3–5, as depending on values used for simulation. To improve readability, each range is described by a symbol ($=$, $+$, $-$ or U) to mean that peak

Table 2
Simulation values other than reference set (units as per Table 1)

Symbol	Values				
m_i	1	2	5	20	
B_p	1	2	5	10	50
k	0.70	1.05	1.40		
C_h	0.80	1.20	1.60		
$Z/10^8$	0.94	3.74			
E	70	80	92	110	
N	0.5	1.0	1.5	2.0	
ΔH	10	50	150		
Δc_p	0.05	0.10	0.15		

Table 3
DTG peak shape

Parameter	H/arb. units		P/°C		FW/°C		GL		A/arb. units		AS	
m_i	−	25–17	+	184–205	+	37–56	U	0.85–1.00	+	144–153	U	1.54–3.57
B_p	−	31–16	+	131–226	+	31–60	U	0.86–1.00	−	2964–60	U	0.90–2.09
Z	+	19–21	−	206–182	−	48–46	U	0.86–1.00	=	1% (148)	U	1.37–2.09
E	−	21–19	+	162–220	+	46–49	U	0.86–1.00	=	2% (149)	U	1.21–2.09
N	−	21–12	=	3% (193)	+	43–74	U	0.86–1.00	=	4% (147)	U	0.11–2.09
ΔH	−	25–18	+	186 202	+	37–53	U	0.83–1.00	U	143–151	U	1.22–2.59
Δc_p	=	1% (20)	=	0% (200)	=	1% (46)	=	1% (0.98)	=	0% (148)	=	4% (5.01)
k	+	20–23	−	200–187	−	46–39	−	0.98–0.87	=	2% (146)	−	4.91–3.20
C_h	=	0% (20)	=	0% (200)	=	1% (47)	=	2% (0.99)	=	0% (148)	=	5 (4.87)

Key: +, positively correlated; −, negatively correlated; =, constant within 5%; U, uncorrelated.

parameter/character is constant within 5%, positively correlated, negatively correlated or uncorrelated, respectively. The same symbol is also followed by a letter "s" or "h" when correlation is recognisable as straight line or hyperbolic, respectively. The range of variation is also reported or, when symbol " = " appears, the percentage variation in parentheses, together with the lowest value.

4. Discussion

As stated in Section 2, simulations were performed by varying each parameter individually when others were kept constant at reference values. Hence discussion of Tables 3–5 could be carried out only by assuming that there was no significant cross correlation between such parameters. Whilst correlations between SK parameters are well known as the previously discussed kinetic compensation effect [6], observed trends can however be used as a rough approximation of expected peak shapes for one step heterogeneous reactions, occurring with OS, SK, ST and EF parameters close to chosen reference values. Otherwise new sets of simulations should be performed.

With such a theoretical limitation, Tables 3–5 suggest very interesting considerations about peak shapes.

(1) Peak asymmetry AS is always very high and falls to approximately zero, and the gaussian/lorentzian mixing GL approaches unity, only when the pseudo reaction order N lies between 1.5 and 2.0. Because a pure gaussian peak must have $GL = 1$ and $AS = 0$, the parameter N seems to be the only one able to produce gaussian peaks in a RO model. However, the same result can be obtained when it is considered that assuming gaussian peaks implies that a modified form of Eq. (1) must match the normalised gaussian one

$$-\mathrm{d}W/\mathrm{d}T = (Z/B)\mathrm{e}^{-E/[R(T_m + t)]}W^N = [1/(2\pi)^{1/2}]\mathrm{e}^{-t^2/2}$$

Table 4
DTG peak shape

Parameter	H/arb. units		P/°C		FW/°C		GL		A/arb. units		AS	
m_i	+	2×10^3–27×10^3	+	184–213	+	37–54	+	0.86–0.99	+	1×10^4–23×10^4	U	2.70–4.01
B_p	+	1×10^3–30×10^3	+	133–236	+	29–60	+	0.78–0.97	=	3% (1×10^5)	U	2.57–4.01
Z	+	15×10^3–16×10^3	–	213–188	–	48–45	=	1% (0.96)	=	0%(1×10^5)	=	2% (3.99)
E	–	16×10^3–15×10^3	+	168–228	+	45–48	=	1% (0.96)	=	0% (1×10^5)	U	3.72–0.11
N	–	16×10^3–10×10^3	=	4% (196)	+	44–74	U	0.91–1.00	=	3% (1×10^5)	–	5.12–0.11
ΔH	+	2×10^3–24×10^3	+	188–209	+	38–52	+	0.85–100	+	1×10^4–20×10^4	+	2.32–5.38
Δc_p	=	1% (16×10^3)	=	1% (201)	=	3% (46)	=	2% (0.98)	=	2% (1×10^5)	=	4% (4.09)
k	–	16×10^3–5×10^3	–	201–188	–	47–39	–	0.97–0.89	–	11×10^4–3×10^4	–	4.01–3.16
C_h	=	1% (16×10^3)	=	05 (201)	=	1% (47)	=	1% (0.96)	=	1% (1×10^5)	–	4.01–3.28

Key: see Table 3.

Table 5
DSC peak shape

Parameter	H/arb. units		P/°C		FW/°C		GL		A/arb. units		AS	
m_i	+	2×10^3–40×10^3	=	2% (184)	=	1% (36)	=	1% (0.84)	+	1×10^4–22×10^4	=	4% (2.43)
B_p	+	1×10^3–46×10^3	+	132–205	+	28–38	+	0.78–0.85	=	1% (1×10^5)	U	2.35–2.51
Z	+	19×10^3–21×10^3	–	197–172	–	38–34	=	3% (0.83)	=	0% (1×10^5)	=	4% (2.40)
E	–	24×10^3–16×10^3	+	100–302	+	30–45	U	0.80–0.85	=	1% (1×10^5)	–	2% (2.40)
N	–	22×10^3–11×10^3	=	4% (181)	+	32–64	U	0.76–0.88	=	5% (1×10^5)	–	3.59–0.0
ΔH	+	2×10^3–35×10^3	=	0% (184)	=	1% (36)	=	1% (0.84)	+	1×10^4–20×10^4	=	4% (2.43)
Δc_p	=	0% (20×10^3)	=	1% (185)	=	1% (36)	=	4% (0.86)	=	1% (1×10^5)	U	2.38–2.62
k	–	20×10^3–5×10^3	=	1% (183)	=	0% (36)	=	0% (0.84)	–	11×10^4–3×10^4	U	0% (2.38)
C_h	=	0% (20×10^3)	=	1% (184)	=	0% (36)	=	0% (0.84)	=	0% (1×10^5)	=	0% (2.39)

Key: see Table 3.

when for simplicity it is assumed that $T = T_p$ with $t = (T_m - T)/\sigma$ and T_m is the temperature at peak maximum. By approximating $1/(T_m + \sigma t)$ to $(1/T_m)(1 - \sigma t/T_m)$ and by passing to logarithms

$$\ln(Z/B) - E/RT_m + \sigma t E/RT_m{}^2 + N \ln W = -t^2/2 - \ln(2\pi)^{1/2}$$

is obtained. Around $t \approx 0$ and $W \approx 1/2$, i.e. in the most significant range of the peak, when considering the kinetic compensation effects [6] $\ln(Z/B) - E/RT_m \approx$ constant ≈ 0 and

$$N \ln(1/2) \approx -\ln(2\pi)^{1/2}$$

is found, the solution of which is $N \approx 1.33$. Such an analytical solution is very close to the numerically found range, within the domain of approximations used.

(2) Whilst specific heat variation Δc_p and holder thermal capacity C_h affect AS in DSC (10% variation with Δc_p) and DTA (25% variation with C_h), the transfer coefficient k shifts position P and influences AS only in DTG and DTA: as already stated it is just a scale factor in DSC.

(3) Peak asymmetry AS in DTG and DTA depends on all OS, SK, ST and EF parameters: such a dependence is very strong in DTG, whilst in DTA both E and Δc_p display a poor influence on AS. On the contrary the same AS results are quite constant at around 2.4 in DSC, except when they fall to zero due to the values of N as discussed above.

(4) Peak height H, position P and full width FW show an almost linear correlation with the activation energy E, whilst, particularly for DSC, H seems to be highly correlated with sample mass m_i, heating rate B_p and reaction enthalpy ΔH. This latter correlation could support quantitative analysis performed by peak height alone, so avoiding tedious peak integration.

(5) The well known correlation between peak area A (normalised with respect to heating rate) and ΔH or m_i is better displayed in DSC than in DTA, thus confirming the better performance of DSC for quantitative analysis.

Considerations (1) to (3) above can be retained as the main contribution of this study, whilst considerations (4) and (5) merely confirm what was already known, accounting for the reliability of the chosen model. Relationships between such main considerations and other recent models and/or approaches to same argument are discussed below.

Through simulations based on highly flexible kinetic functions, instead of considering the heat transfer process as previously observed [6], Malek and Smrcka also found asymmetric DSC peaks when fitting data from crystallisation of sulphides [15]. The results of the present study agree with such a finding, i.e. asymmetry strongly depends on the kinetic model, and also on N when RO is considered. On the contrary some authors assumed DSC peaks be symmetric gaussians [8–12]. When a gaussian is arbitrarily used for peak sum resolutions and subsequent kinetic analysis, the value found for N (1.5) in the RO model [8,9] should be considered an artifact, because this value is implicit in the assumed peak shape. In addition multiple peak resolution by assuming a (not real) gaussian shape [10–12] can lead to mistakes in enthalpy measurements.

Though DSC performs better than DTA, real experiments should be modelled like DTA (with k high enough), both because of equipment architecture and because the sample mean temperature should be always assumed to be different from that of the sample holder; this is also the case in balance equipment [13] where a contact term and a temperature distribution into the sample have to be taken into account.

Dealing with the problem of solving kinetics by TA (most commonly DSC) peak analysis, several approaches can be recognised and summarised with respect to that used in this work.

(a) As previously reported [6], many authors prefer to fit peaks with flexible kinetic models (e.g. SB (Šesták–Berggren) or JMA (Johnson–Mehl–Avrami)), without taking into account heat transfer phenomena. They recognise, however, that the physical meaning of the kinetic parameters obtained is doubtful [16] when no other information is available. We pointed out previously [1–6] that with our approach true kinetic parameters, which have good predictive power, can be derived.

(b) Other authors [13,17–20] deconvolute observed signals in order to desmear peaks from the equipment transfer function before kinetic analysis. It must be emphasised that both experimental and empirical transfer functions contain k and C_h, as stated by Yamane et al. [19] or a similar parametric function [18]. Rather than just C_h, they should contain $C_h + m_i c_{mix}$ (i.e. the total heat capacity including sample) so even when assuming k, C_h, c_1 and c_2 as constant, the equipment transfer function becomes dependent on the sample and cannot be measured with energy spikes on an empty holder. The present results on DTA peak shapes, which can be extended to real DSC as stated above, agree with such a dependence. In addition the proposed method for obtaining true kinetic parameters [6] should be regarded as a way of "deconvoluting curves when calculating parameters". Dealing with the deconvolution of TA peaks, even when taking into account the limitations discussed above, it is interesting to note that the direct one, performed in the time domain [20], is similar to the satellite subtraction in XPS, once more extending the general approach of NLLSRC [7].

(c) An original approach to homogeneous kinetics has been presented by Koch [21] through pattern recognition based on the mechanistic concentration code (MCC) derived from peak shape. Because the author claims the possibility of extending the same approach to heterogeneous kinetics, our model could be useful both for extracting MCC from peaks by NLLSRC and for simulating reference patterns by extending Eqs. (1) and (2) to the Two Reactions Model. Instead of deconvoluting real peaks from theoretically unknown transfer functions, to compare MCC with data-bank, the as read MCC obtained from experimental peaks could be compared with the simulated patterns, including convolution with an autogenerated transfer function.

5. Conclusions

The present study on TA peak shapes has shown that peaks are generally asymmetric and their assumption as gaussian curves can produce artifacts. More-

over, excluding pure DSC which is a theoretical case, peak shapes (asymmetry) strongly depend on OS, EF and on chosen kinetic functions (on N in the RO model). When considering peak height and position, the strong dependence is extended to all SK and ST parameters, thus supporting the good choice performed [21] to introduce a pattern recognition approach to kinetics. In our opinion, whilst worse in principle, approaches based on peak convolution and/or on fitting with more sophisticated kinetic models, remain valid only when masses and heating rates are low enough and when k is very high (as in DSC equipment). When such conditions do not occur, the proposed method [6] should be the only one available by which to obtain true kinetic parameters. Peak sum resolution should be performed by using asymmetric peaks [7].

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