

INFLUENCE OF DECONVOLUTION ON KINETIC STUDIES BY DTA. PART I. DETERMINATION OF THE REACTION MECHANISM

E. CESARI *, J. FONT, J. MUNTASELL and J. NAVARRO

Departament de Física, E.T.S.E.I.B., U.P.C., Barcelona (Spain)

** Departament de Termologia, Facultat de Física, U.B., Barcelona (Spain)*

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ABSTRACT

In this paper we analyse the influence that inverse filtering has on kinetic studies carried out with the DTA technique. The reaction mechanism $f(\alpha)$ has been selected graphically and analytically. Both filtered and direct thermograms yield the same functions; nevertheless, agreement to linear behaviour of $\ln[\int_0^\alpha d\alpha'/f(\alpha')]$ vs. $1/T$ is optimal when deconvoluted signals are used.

INTRODUCTION

In previous papers we developed an RC model [1,2] to study the influence of different model parameters and experimental factors on our DTA system. This model allowed us to identify the first two time constants of the experimental device as a function of temperature. Using standard inverse-filtering techniques, it was possible to partially eliminate the inertia of the system by compensation of these time constants.

The registers that are obtained from deconvolution of the thermograms present different shapes to those of direct signals, specially when they correspond to the fastest processes.

In kinetic studies of a process carried out with dynamic techniques, methods that take account of the shape of the thermograms must be used. In this manner, the application of these procedures to filtered signals must be analysed because they can give quite different results to those calculated from direct thermograms. They must give a more accurate representation of the studied thermal effect.

In order to manifest the influence of deconvolution, we have analysed the transition III \rightarrow I of potassium nitrate at atmospheric pressure. We have compared the peak and the onset temperatures at several different heating rates, both for filtered and non-filtered thermograms. We have also analysed several $f(\alpha)$ in order to describe the reaction mechanism.

TABLE 1

Onset and peak temperatures (average values) in K for direct and deconvoluted thermograms

β (K min ⁻¹)	Direct thermogram		Deconvoluted thermogram	
	T_{onset}	T_{peak}	T_{onset}	T_{peak}
3.3	400.4	404.1	399.8	402.8
5.2	401.4	406.0	400.5	403.9
7.3	403.1	408.3	401.6	405.6
9.2	404.1	410.6	402.9	407.1

EXPERIMENTAL

The transition III \rightarrow I of potassium nitrate at atmospheric pressure is a first-order process of the order-disorder type, which takes place at ca. 400 K. Phase III is trigonal with a space group C_{3v}^5 , one molecule per unit cell, with ferroelectric properties. Phase I is also trigonal, but with a space group D_{3d}^6 and two molecules per unit cell. It is para-electric and stable at high temperatures [3].

In order to isolate phase II (stable at room temperature) from phase III [4], we heated the potassium nitrate to 600 K and let it cool down until the transformation I \rightarrow III occurred. A second heating gives rise to the above-described order-disorder process.

Four runs were completed for each of the four heating rates used ($\beta = 3.3, 5.2, 7.3$ and 9.2 K min⁻¹). In all cases, numerical data acquisition was performed with a sampling period of 2 s. The differential signal was amplified 5000 times. We used Merck "pro analysi" potassium nitrate with a particle size in the range 60–100 μm . The sample mass for each thermogram was of the order of 30 mg.

The average values of the peak and onset temperatures for both direct and filtered thermograms are shown in Table 1.

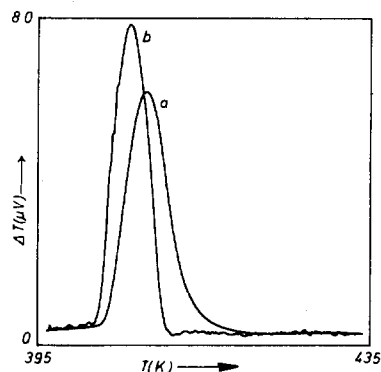


Fig. 1. Transition III \rightarrow I of potassium nitrate (a) and their deconvoluted register (b) ($\tau_1 = 23$ s and $\tau_2 = 5$ s). Heating rate $\beta = 5.2$ K min⁻¹.

The mean values of the enthalpy change ΔH are 6.45 and 6.46 cal g⁻¹ (± 0.40 cal g⁻¹ in both cases) for the integrated direct and filtered differential signals, respectively. They are practically coincident, as is assured by inverse filtering. In Fig. 1 we present an example of a thermogram and its deconvoluted register with the first two time constants.

As the temperature interval of this process is of the order of 15 K, we filtered the whole peak assuming that the time constants do not vary with temperature. These are the conditions of the isothermal three-bodies model previously described [1].

The selection of $f(\alpha)$

Assuming that the instantaneous reaction rate depends only on the conversion degree (α) and on the temperature (T), it can be stated that

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The rate constant $k(T)$ can be expressed by the Arrhenius law. Letting $\beta = dT/dt$ we have

$$\frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \exp(-E/RT)dT \quad (2)$$

From this equation, the activation energy E and the frequency factor k_0 may be determined from the known $f(\alpha)$. Function $f(\alpha)$ is, in most cases, unknown for solid state processes, generally being of the form [5]

$$f(\alpha) = (1 - \alpha)^n \alpha^m [-\ln(1 - \alpha)]^P \quad (3)$$

where m, n and P are constants.

It is usually accepted that all heterogeneous reactions can be described by a simpler function than eqn. (3), in which no more than two exponents must intervene. These functions $f(\alpha)$ are [5]

$$\alpha^m \quad m = 3/4, 2/3, 1/2, 0, -1/2, -1, 1$$

$$(1 - \alpha)^n \quad n = -1, -2, -3, 1, 2/3, 1/2$$

$$\alpha^m (1 - \alpha)^n \quad \begin{cases} m = 1 \\ n = 1 \end{cases}$$

$$(1 - \alpha)^n [-\ln(1 - \alpha)]^P \quad \begin{cases} n = 0 & P = -1 \\ n = 1/3 & P = -1 \\ n = 1 & \begin{cases} P = 3/4 \\ P = 2/3 \\ P = 1/2 \\ P = 1/3 \end{cases} \end{cases}$$

In the present study, we have used two different ways for selecting $f(\alpha)$.

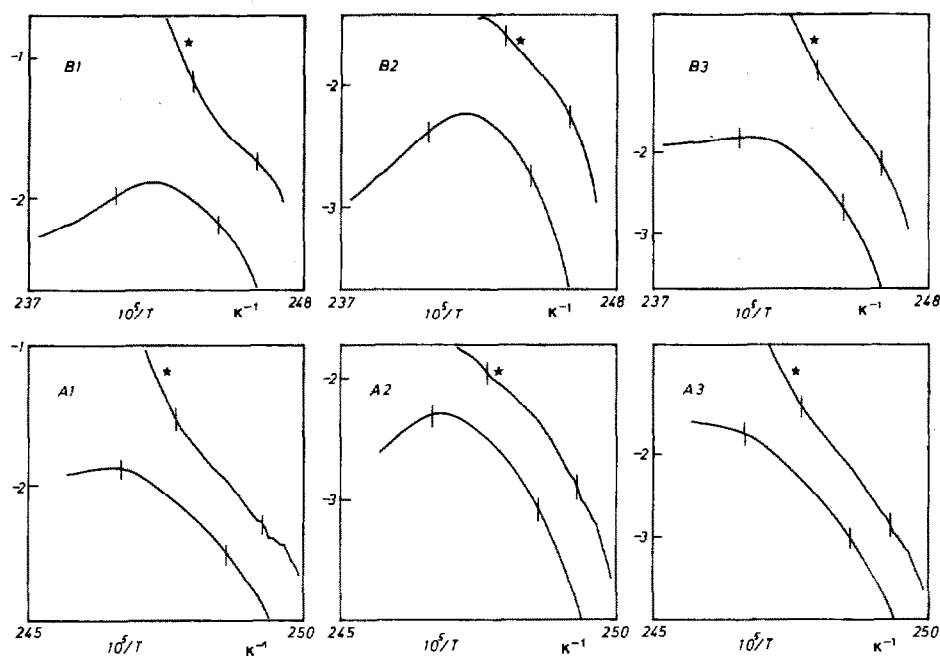


Fig. 2. Representation of eqn. (4) for different $f(\alpha)$ functions, (1) $(1 - \alpha)(-\ln(1 - \alpha))^{1/3}$; (2) $(1 - \alpha)^{2/3}$; (3) $(1 - \alpha)$, corresponding to direct and deconvoluted (\star) thermograms, with two heating rates: (A) 3.3 K min^{-1} ; (B) 9.2 K min^{-1} .

Graphic method

Many authors [6–9] approximate the integrated expression of eqn. (2) in logarithmic form to

$$\ln g(\alpha) = \ln \left[\int_0^\alpha \frac{d\alpha'}{f(\alpha')} \right] = A - \frac{E}{RT} \quad (4)$$

where A is a parameter that depends on k_0 , β and T . In this case, we will assume that A is constant because the peak forms in only a few degrees.

For each thermogram and its filtered register, we represented graphically the left-hand side of eqn. (4) vs. $1/T$ between α values of 0.2 and 0.8. The function $f(\alpha)$ with the most linear representation will be the best one to represent the process, if we assume E to be constant.

The functions giving negative slopes and the best regression coefficients for both direct and deconvoluted thermograms are: $(1 - \alpha)[-\ln(1 - \alpha)]^{1/3}$; $(1 - \alpha)^{2/3}$; $1 - \alpha$. We have to note that the linearity is greater for the filtered registers than for the direct thermograms.

In Fig. 2, the representation of $\ln g(\alpha)$ vs. $1/T$ can be observed for the three functions just described.

Analytical method

Urbanovici and Segal [10] propose a method that allows the kinetic

TABLE 2

Average values of E and standard deviations for $f(\alpha) = (1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$ and $f(\alpha) = 1 - \alpha$, at different β , corresponding to direct and deconvoluted thermograms

β (K min ⁻¹)	Direct thermogram		Deconvoluted thermogram	
	E (kJ mol ⁻¹)	SD (kJ mol ⁻¹)	E (kJ mol ⁻¹)	SD (kJ mol ⁻¹)
$f(\alpha) = (1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$				
3.3	283	31	383	20
5.2	145	50	264	28
7.3	120	36	212	21
9.2	73	44	174	43
$f(\alpha) = 1 - \alpha$				
3.3	589	66	733	37
5.2	349	81	532	34
7.3	291	61	433	12
9.2	213	67	370	17

parameters of a process to be determined by using different $f(\alpha)$ functions. This method is based on the determination of E as an average value of several E_i . In the present work, we choose α values in the range 0.2–0.8 and use five equal temperature intervals. For three consecutive temperatures, we determine one E_i value; so three E_i are calculated for each $f(\alpha)$ in the range 0.2–0.8. The selected $f(\alpha)$ is the one for which the standard deviation of the E_i values is minimal.

In our application of this method to the process III \rightarrow I of potassium nitrate, the $f(\alpha)$ found are $1 - \alpha$ and $(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$.

The average activation energies with the corresponding standard deviations from the mean are shown in Table 2 for direct and deconvoluted thermograms at each β and for the two considered functions ($0.2 \leq \alpha \leq 0.8$).

As can be observed in Table 2, the deviations are smaller for the deconvoluted registers. Analysis of the values of E from Table 2 shows that the relative difference in activation energies from filtered and direct thermograms increases when β increases.

CONCLUSIONS

For filtered signals, the linearity of the representation of eqn. (4) is better for the functions $(1 - \alpha)$, $(1 - \alpha)^{2/3}$ and $(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$ in all measurements. Likewise, in the analytical method, the standard deviations are smaller when using deconvoluted thermograms.

As a consequence, in accepting the approximation of $\ln g(\alpha)$ as a linear function of $1/T$, the kinetic parameters obtained from the filtered signals

will be more representative of the real process. The main reason for this is that, being deconvoluted, they are less influenced by the inertia of the measuring system.

In a future study with these functions, we will determine the values of the kinetic parameters (activation energy and frequency factor) of the process using different methods, and we shall analyse the influence that each of these parameters has on the deconvolution of the thermograms.

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