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INFLUENCE OF DECONVOLUTION ON KINETIC STUDIES BY DTA. PART II. DETERMINATION OF THE KINETIC PARAMETERS

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ABSTRACT

In a previous paper we analysed the influence of deconvolution in the selection of the reaction mechanism f(α) corresponding to the kinetics of a process. In this article we determine the kinetic parameters with both the direct and deconvoluted signals using the Kissinger, Ozawa, Coats and Redfern, and Piloyan methods, and one based on the Avrami equation.

INTRODUCTION

In a previous article [1] we analysed the influence of standard inverse filtering on the determination of the function f(α) corresponding to the kinetics of a process. As an example, the III → I transition of KNO_3 at atmospheric pressure was studied, using graphical and analytical methods to choose f(α). We have verified that the three functions chosen were more accurate for the deconvoluted thermograms than for the direct ones. Filtering the thermograms we obtain different values for the activation energy, E.

The purpose of this paper is to determine the equation of the reaction rate from kinetic parameters obtained from direct and filtered signals. A discussion is made of the different results obtained for the III → I transition of KNO_3. Five methods using dynamic techniques have been used for evaluating the kinetics of solid-state reactions. For the Kissinger [2] and Ozawa [3] methods, it is necessary to work with recordings at different heating rates, β. The other three methods require only one thermogram: the Coats and Redfern method [4], one based on the Avrami equation [5] and the Piloyan method [6], which uses differential signals. Of the five methods, those of Kissinger and Piloyan have been specifically developed for the technique used in this study (DTA).

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EXPERIMENTAL

The experimental conditions under which the thermograms have been obtained for the III → I transition of KNO_3 at atmospheric pressure are: $\beta = 3.3$, 5.2, 7.3 and 9.2 K min^{-1}; amplification of the differential signal, 5000; sampling period, 2 s [1].

RESULTS AND DISCUSSION

Kissinger method

With this method it is possible to determine the activation energy and the frequency factor (or pre-exponential factor) of the process from the equation

$$\ln(\beta/T_p^2) = \ln(K_0 R/E) - E/(RT_p) \qquad (1)$$

where E, K_0, T_p and R are the activation energy, the frequency factor, the peak temperature and the universal gas constant, respectively. Plotting the first part of eqn. (1) against $1/T_p$ gives a straight line, its slope giving E and its value at the origin giving K_0. The value of E obtained with this method is independent of β. The values of E and K_0 obtained from the direct readings are: $E = 207$ kJ mol^{-1}, $K_0 = 8 \times 10^{24}$ s^{-1}, $r = -0.9823$; and from the filtered registers are: $E^* = 306$ kJ mol^{-1}, $K_0^* = 10^{38}$ s^{-1}, $r^* = -0.9768$. Note that E is 50% greater for the deconvoluted thermograms. Figure 1 shows eqn. (1) for both the direct and filtered thermograms.

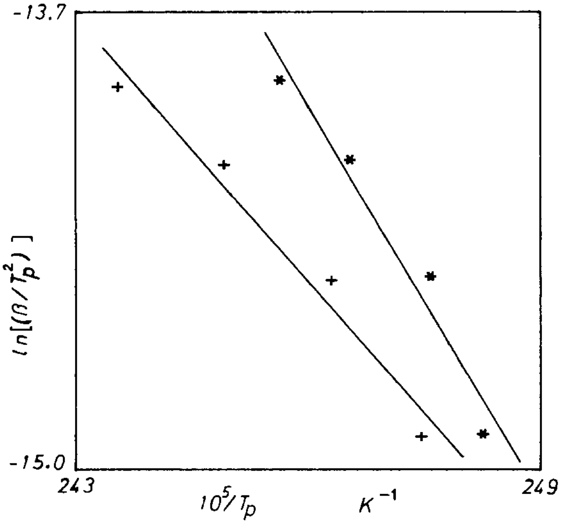

Fig. 1. Representation of eqn. (1) for the direct (+) and deconvoluted (*) readings.

TABLE 1

Activation energies and regression coefficients for the direct and deconvoluted (*) readings, obtained for different values of $(1-\alpha)$ and using Ozawa's method

$1-\alpha$	E (kJ mol^{-1})	E^* (kJ mol^{-1})	ΔE (%)	r	r^*
0.2	325	498	53	−0.9880	−0.9825
0.4	383	559	46	−0.9861	−0.9785
0.6	433	620	43	−0.9819	−0.9728
0.8	502	688	39	−0.9777	−0.9607

$\Delta E(\%) = 100(E^* - E)/\mathrm{E}$

Ozawa method

The basis of this method is that for a changing β, different temperatures correspond to each specific value of $(1-\alpha)$. The relation between β and T given by Ozawa for each value of $(1-\alpha)$ is

$$\log \beta + 0.4567E/RT = \text{constant} \tag{2}$$

We have used this method for the following values of $(1-\alpha)$: 0.2, 0.4, 0.6, 0.8. Table 1 shows the values obtained for E.

At the end of the peak it can be observed that E decreases with $(1-\alpha)$. This variation is of the order of 50% for the direct thermograms and 40% for the filtered ones. The effect of filtering is greater for values of E corresponding to the end of the peak $(1-\alpha = 0.2)$. On average, E varies 45% between the direct and deconvoluted thermograms.

Piloyan method

According to Piloyan et al. [6], if $0.05 \leqq \alpha \leqq 0.8$ and $\beta \leqq 20$ K min^{-1} then the following relation holds:

$$\ln(\Delta T) = C - E/(RT) \tag{3}$$

where ΔT is the differential signal (thermogram) and C is a constant. In the

TABLE 2

Values of the activation energy obtained with the method of Piloyan, corresponding to direct and filtered (*) thermograms

β (K min^{-1})	E (kJ mol^{-1})	E^* (kJ mol^{-1})	ΔE (%)
3.3	550	539	−2
5.2	367	408	11
7.3	324	334	3
9.2	259	344	33

present case for $\alpha > 0.45$ the slope of eqn. (3) changes sign. We have used this method for values of α between 0.05 and 0.45. In Table 2 we present the average values of E for each β.

The regression coefficients are smaller in this case and vary between -0.9378 and -0.9635 for the direct thermograms and between -0.9002 and -0.9654 for the filtered thermograms.

E varies greatly as a function of β mainly for the direct thermograms. These variations are relatively small for one β value, with the one exception of $\beta = 9.2$ K min^{-1}, comparing direct and filtered readings.

Coats and Redfern method

This was initially developed for $f(\alpha)$ functions of the type $f(\alpha) = (1-\alpha)^n$. Expressions relating this function with the kinetic parameters are:

$$\ln\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \ln\left[\frac{k_0 R}{E\beta}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \text{ for } n \neq 1 \tag{4}$$

and

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{k_0 R}{E\beta}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \text{ for } n = 1 \tag{5}$$

We have used this method for the two kinds of thermograms, but only for $n = 1$ and $n = 2/3$, which correspond to two of the three $f(\alpha)$ functions chosen to represent the III → I transition of KNO_3 [1]. Table 3 shows the average values of the kinetic parameters for each β and the two values of n.

Although E varies greatly with β, in this case the variations are also more significant for the direct rather than for the deconvoluted thermograms.

TABLE 3

Activation energy and frequency factor for the direct and filtered (*) readings, obtained with the method of Coats and Redfern, for $f(\alpha) = 1 - \alpha$ and for $f(\alpha) = (1-\alpha)^{2/3}$

β (K min^{-1})	E (kJ mol^{-1})	k_0 (s^{-1})	r	E^* (kJ mol^{-1})	k_0^* (s^{-1})	r^*	ΔE (%)
$n = 1$							
3.3	855	$>10^{100}$	-0.9962	1025	$>10^{100}$	-0.9973	20
5.2	612	10^{72}–10^{77}	-0.9936	791	$>10^{100}$	-0.9954	29
7.3	501	10^{58}–10^{61}	-0.9935	668	10^{78}–10^{86}	-0.9957	33
9.2	411	10^{45}–10^{51}	-0.9918	590	10^{67}–10^{74}	-0.9943	44
$n = 2/3$							
3.3	768	10^{97}–10^{98}	-0.9926	911	$>10^{100}$	-0.9945	18
5.2	542	10^{67}–10^{69}	-0.9905	715	10^{89}–10^{94}	-0.9924	32
7.3	443	10^{54}–10^{56}	-0.9894	592	10^{71}–10^{77}	-0.9923	34
9.2	363	10^{42}–10^{49}	-0.9872	523	10^{63}–10^{69}	-0.9904	44

Avrami equation

According to the literature [5], this equation is the most convenient for representing phase transitions under isothermal conditions. From Avrami's equation

$$\alpha = 1 - \exp\{-[k_0 t \exp(-E/RT)]^q\} \tag{6}$$

and considering $t = (T - T_0)/\beta$ (where T_0 is the initial peak temperature)

$$\ln\left[-\frac{\ln(1-\alpha)}{(T-T_0)^q}\right]^{1/q} = \ln(k_0/\beta) - E/RT \tag{7}$$

For $q = 1.5$ in eqn. (7) the corresponding $f(\alpha)$ function is

$$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{1/3} \tag{8}$$

This is one of the functions chosen [1] for representing the process studied. We have used eqn. (7) in all the measurements, direct and deconvoluted, for values of α between 0.2 and 0.8. The average values of E are given in Table 4.

A graphical representation of eqn. (7) with $q = 1.5$ appears in Fig. 2.

Variations of E are small and increase with β in both thermograms. The changes of E with heating rate, β, are smaller for the filtered thermograms. Therefore, eqn. (7) is better adjusted to the deconvoluted data.

With all the pairs of values E, k_0 we have verified that a compensation effect occurs. It is given by the equations

$\ln k_0 = 0.282E - 2.16$; $r = 0.9976$ (direct thermograms)

$\ln k_0^* = 0.288E^* - 2.07$; $r^* = 0.9989$ (filtered thermograms)

where k_0 is in s^{-1} and E in kJ mol^{-1}. Using these equations we have calculated k_0 and k_0^* from values of E determined by methods not giving the frequency factor directly (Ozawa, Piloyan). Considering that the accepted values of k_0 for solid-state processes are in the range 10^{12}–10^{18} s^{-1}, acceptable frequency factors are calculated by the Kissinger method and the Avrami equation.

TABLE 4

Activation energy and frequency factor obtained from eqn. (7) with $q = 1.5$, for the direct and deconvoluted thermograms

β (K min^{-1})	E (kJ mol^{-1})	k_0 (s^{-1})	r	E^* (kJ mol^{-1})	k_0^* (s^{-1})	r^*	ΔE (%)
3.3	212	10^{24}–10^{28}	−0.9987	229	10^{26}–10^{30}	−0.9998	8
5.2	121	10^{14}–10^{15}	−0.9946	136	10^{15}–10^{18}	−0.9986	12
7.3	101	10^{10}–10^{12}	−0.9955	111	10^{12}	−0.9993	10
9.2	81	10^{8}–10^{9}	−0.9901	95	10^{8}–10^{11}	−0.9994	17

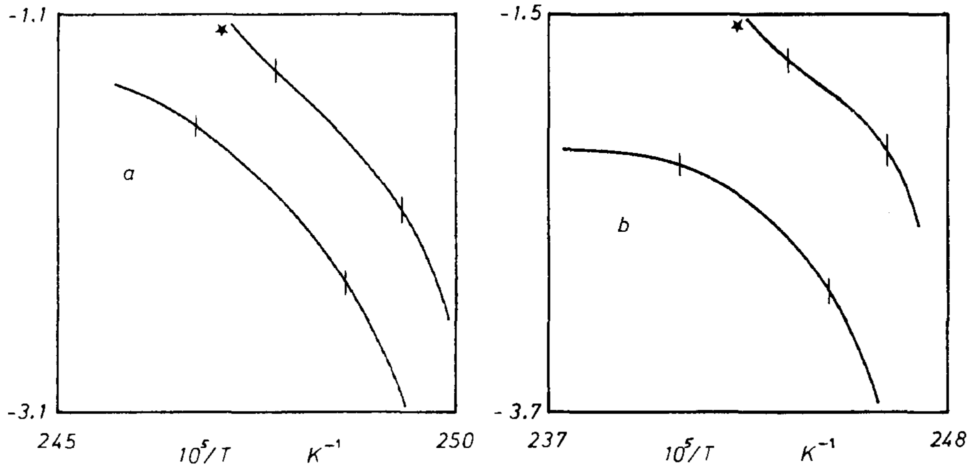

Fig. 2. Representation of eqn. (7) with $q = 1.5$ for the direct and deconvoluted (*) thermograms. Heating rate $\beta = 3.3$ K min^{-1} (a) and $\beta = 9.2$ K min^{-1} (b). The marks on the graphs indicate $\alpha = 0.2$ and $\alpha = 0.8$.

Furthermore, the smallest dependence of E on β is desirable. With all methods giving E from β, the values of E obtained from the filtered thermograms vary less with β than those obtained from the direct readings.

In order to obtain from Avrami's equation one single value for E, more comparable to that of an isothermal regime, a simple linear extrapolation of the values of E at $\beta = 0$ has been performed. We have obtained the following extrapolated values:

$E = 259$ kJ mol^{-1}; $E^* = 277$ kJ mol^{-1}

If we compare these values with those found with the Kissinger method, the agreement is clearly better in the case of the filtered signals, which allows the activation energy to be determined within a reasonable uncertainty interval.

With the mean value of E obtained by the Kissinger method and the extrapolation at $\beta = 0$, we have calculated the frequency factor, making use of the compensation effect. Accepting eqn. (8) as f(α), the equation for the reaction rate of the transition studied becomes (T in K)

$$\mathrm{d}\alpha/\mathrm{d}t = 2 \times 10^{27} \exp\left(-\frac{2.78 \times 10^4}{T}\right)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$$

for the direct signals, and

$$\mathrm{d}\alpha/\mathrm{d}t = 2 \times 10^{35} \exp\left(-\frac{3.50 \times 10^4}{T}\right)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$$

for the filtered signals.

We can therefore conclude that use of the deconvoluted thermograms with a simple technique such as standard inverse filtering produces good results.

It improves the quality of the adjustments in search of an adequate f(α) function and, therefore, of the process studied itself. Moreover, E is influenced less by the heating rate when filtered instead of direct thermograms are used. If the values of E corresponding to frequency factors unacceptable for solid-state processes are discarded, then extrapolation to zero heating rate of the values given by Avrami's equation presents a better concordance with values obtained using Kissinger's method with filtered thermograms. We believe that this allows a value for the activation energy to be obtained with notably lower uncertainty.

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