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SIMULATION OF A DTA SYSTEM BY THE RC MODEL. APPLICATION TO A REAL PROCESS

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ABSTRACT

We have analysed the RC model for our DTA system in the case of the real II → I transition of KNO_3, which occurs around 400 K at atmospheric pressure. The model allows a perfect simulation of the experimental conditions of the measurements, such as the effect of working with an open or covered crucible or the influence of mass and compactness changes.

There is concordance between the time constants corresponding to the signals generated by the Joule effect and those found from the return to baseline of the thermogram of the transition. It is therefore possible to identify the time constants by filtering the real process thermogram and to partially eliminate the influence of the inertia of the measuring system.

We have finally compared the values of the kinetic parameters found from direct signals and from previously filtered signals.

INTRODUCTION

In a previous communication [1] a localized constants model for our DTA experimental system was developed. Using it, we simulated the evolution of sensibility and of the time constants with temperature in the 300–600 K range. Also, we have analysed the influence on the thermograms, of several experimental parameters such as the crucible type and the variation of the thermal resistance between the crucible and the thermocouples. This was done through generation of diverse electrical signals by the Joule effect.

In the present study the validity of our model for the simulation of a real process has been analysed under different experimental conditions. The coherence of the model with the real experimental conditions justifies the possibility of identifying the time constants of the DTA system from the thermogram of the physical process. The time constants thus obtained can be used to partially reduce the influence of the inertia of the experimental system by deconvolution of the thermogram by inverse filtering.

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The real process used is the II → I transition of potassium nitrate, which is a structural change from orthorhombic to trigonal. It occurs at atmospheric pressure at about 400 K [2,3] and, therefore, in the work range of our model. We have analysed the effect of variations of the sample mass, its compactness degree and the fact of working with open or covered crucibles on the output of our experimental system.

In order to confirm the validity of the time constants obtained by the return to the baseline of the thermogram corresponding to the KNO_3 transition we have compared them with those obtained from Joule signals generated by an electrical resistance put in the crucible, also containing KNO_3. These signals were generated at temperatures close to the transition temperature and for different experimental conditions.

The last step is an introductory analysis of the influence of the elimination of the system's inertia on the results obtained during the kinetic study of the process. The comparison of the results obtained from the direct thermograms and from the deconvoluted ones (in which the time constants are eliminated by inverse filtering) was done with different conventional dynamic methods: Kissinger [4] and Ozawa [5].

EXPERIMENTAL

In all measurements we used aluminium crucibles of mass close to 35 mg directly lying on the thermocouples. It is the case of the three-body model previously described [1] and schematized in Fig. 1.

With this model we have been able to follow the evolution of the time constants and of the sensibility of the experimental system, under isothermal conditions, by dissipation of energy by the Joule effect at temperatures between 300 and 600 K. Working under isothermal conditions and having a furnace with a high thermal resistance between the crucibles permits us to consider the reference crucible and the thermostat group as forming only one body at a temperature T_0 [1].

We acquired numerical data with a sampling period of 2 s. Through inverse filtering we have identified the first two time constants of each measurement with an indetermination error of ±1 s for each of the values.

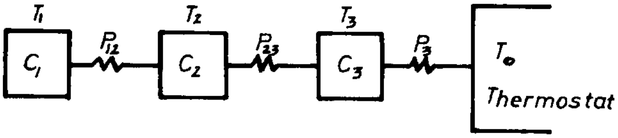

Fig. 1. Model used to represent our system of measurement. (1) Sample; (2) crucible; (3) thermocouples.

A total of 50 measurements with the following eight configurations were made.

Configuration	Open crucible	Covered crucible	KNO_3	Mass of KNO_3 (mg)
A		×	*	35
B		×	*	35
C	×		*	35
D	×		*	70
E	×		×	35
F	×		×	70
G	×		×	80
H		×	×	17

The covers of the crucibles weighed 15 mg each. × indicates that the salt was previously melted and resolidified before measurement. * indicates that the salt was not melted and presented a grain size of 60–100 μm. In both cases the KNO_3 used was Merck pro analysi grade of 99% minimum purity.

The average sensibility in all measurements is 4.3 mV W^{-1}. All measurements that were used to identify the time constants were made in a static air atmosphere with a heating rate of 5 K min^{-1} and an amplification of the differential signal of 5×10^3.

As for the kinetic study, we worked with open crucibles and masses of non-melted KNO_3 of 35 mg, with several different heating rates: 3.8, 5.2, 7.6, 9.6, 11.8 and 14.1 K min^{-1}. In every case the time constants were identified.

RESULTS AND DISCUSSION

As it was stated in a previous paper [1] we propose an invariant model because the studied transition ranges over only a few degrees (about 20 K). This makes possible the assumption that T_0 is almost constant during the whole process. The differential signal is therefore $T_3 - T_0$ ($= T_3$ if we make $T_0 \equiv 0$) (see Fig. 1).

We have considered different causes of variation of the thermal capacities C_i.

(a) The thermal capacity increases when the mass of KNO_3 increases. When a wire is introduced in the crucible to dissipate energy by the Joule effect (experiments A and G) its thermal capacity is added to that of the salt.

(b) The thermal capacity of the crucible is increased when the crucible is covered because the cover is included in group number 2 of Fig. 1.

The experimental results obtained through inverse filtering (values of the time constants shown in Table 1) have led us to make the following consideration on the parameters of the model.

(a) When the constantan wire is introduced into the crucible with the KNO_3, the thermal sample–crucible coupling coefficient, P_{12}, diminishes.

TABLE 1

Values of C_i, P_{ij}, P_k ($\times 10^4$) of the model that give the time constants most similar to the values obtained by inverse filtering

	A	B	C	D	E	F	G	H
C_1 (J K^{-1})	500	410	400	800	400	800	1000	200
C_2(J K^{-1})	475	475	340	340	340	340	340	475
C_3 (J K^{-1})	53	53	53	53	53	53	53	53
P_{12} (W K^{-1})	54	100	90	90	700	700	450	800
P_{23} (W K^{-1})	69	51	46	70	46	70	75	45
P_3 (W K^{-1})	96	96	96	96	96	96	96	96

This effect is due to the poorer heat transmission between bodies 1 and 2. However, when working with KNO_3 previously melted or when covering the crucible (the compactness of the substance increases compared to that when working with an open crucible or with a crystallized substance) we have incremented the value of P_{12} because the transmission of heat between the substance and the crucible is facilitated.

(b) Any mass increase of body number 1 (increase of the mass of KNO_3 or introduction of the wire) or of body number 2 (covering the crucible) produces an increase in the crucible–thermocouple coupling, P_{23}. This fact can be explained as the effect of a more important pressure that lessens the contact resistance between bodies 2 and 3 of the model.

We show in Table 1 the values of the parameters of the model (C_i, P_{ij}, P_k) that give the time constants values as close as possible to the ones experimentally determined by inverse filtering.

We present in Table 2 the values of the first two time constants obtained from the model with the values of the parameters shown in Table 1, and those obtained by inverse filtering.

In order to see how the partial correction of the influence of the inertia of our system on real measurements can modify the results, we have done a

TABLE 2

Values (s) of the first two time constants determined by standard inverse filtering (τ_{1F}, τ_{2F}) and determined by the model (τ_{1M}, τ_{2M}) with the values of parameters C_i, P_{ij}, P_k shown in Table 1

	A[a]	A[b]	A	B	C	D	E	F	G[a]	G[b]	G	H
τ_{1F}	30	30	29	30	27	34	23	29	35	36	35	21
τ_{2F}	5	5	3	3	5	5	4	5	6	6	6	4
τ_{1M}	30.1	30.1	30.1	28.8	26.6	35.1	24.3	29.2	34.2	34.2	34.2	22.1
τ_{2M}	3.7	3.7	3.7	2.1	1.9	2.2	0.4	0.4	2.7	2.7	2.7	0.4

[a] Joule effect to 390 K.

[b] Joule effect to 410 K.

TABLE 3

Method of Kissinger (the peak temperatures are of the direct (*) and filtered (**) signals for different heating rates, β)

β (K $\min^{-1}$)	T_{peak} (K) *	T_{peak} (K) **
3.8	413.8	412.2
5.2	416.1	414.3
7.6	417.5	414.7
9.6	419.2	416.0
11.8	420.5	416.6
14.1	421.8	417.1

TABLE 4

Method of Ozawa (temperature (K) values for $1-\alpha = 0.3, 0.4, 0.5, 0.6$ (α = fraction of sample reacted) corresponding to direct (*) and filtered (**) thermograms)

β (K $\min^{-1}$)	$T^{*}_{0.3}$	$T^{**}_{0.3}$	$T^{*}_{0.4}$	$T^{**}_{0.4}$	$T^{*}_{0.5}$	$T^{**}_{0.5}$	$T^{*}_{0.6}$	$T^{**}_{0.6}$
3.8	415.2	413.0	414.4	412.3	413.6	411.7	412.8	410.9
5.2	417.9	415.0	417.0	414.3	416.1	413.6	415.3	412.9
7.6	420.1	416.0	418.9	415.1	417.7	414.2	416.7	413.5
9.6	422.0	417.6	420.7	416.6	419.5	415.7	418.4	414.7
11.8	424.5	418.5	422.8	417.4	421.4	416.3	420.1	415.4
14.1	426.4	419.5	424.6	418.3	422.8	417.1	421.3	416.0

TABLE 5

Values of the kinetic parameters determined with the methods of Kissinger and Ozawa from the direct (*) and deconvoluted (**) thermograms

	E (kJ mol^{-1})*	r*	E (kJ mol^{-1})**	r**
Ozawa: $1-\alpha = 0.3$	166	0.9932	281	0.9937
$1-\alpha = 0.4$	183	0.9935	305	0.9914
$1-\alpha = 0.5$	200	0.9940	335	0.9880
$1-\alpha = 0.6$	216	0.9939	355	0.9865
Kissinger	237	−0.9951	379	−0.9783

comparative study of the kinetic parameters of the II → I transition of KNO_3 using the direct and the deconvoluted signals. For this study we have used two conventional dynamic methods: Kissinger [4] and Ozawa [5]. Tables 3–5 present the results obtained.

The values obtained for the activation energies using the methods of Kissinger and Ozawa are shown in Table 5 for each value of $1-\alpha$ and for direct and filtered thermograms.

CONCLUSIONS

The values of the time constants obtained from different configurations of the model are coherent with those obtained from different experimental conditions. The variations introduced in the parameters have good physical grounds, which indicates that this kind of model is useful for the theoretical evaluation of the influence of experimental conditions on real processes.

Furthermore, the coherence of the time constants that result from the return to the baseline of the thermogram corresponding to the KNO_3 transition and those that result from Joule signals justifies the validity of identification from the real thermogram.

We have used the II → I transition of KNO_3 in the said conditions as an example of how the kinetic results may be affected by a variation of the peak's shape produced by the deconvolution of the thermogram. The purpose is not to determine the activation energies with precision, but to see how they disperse. The values of the kinetic parameters determined present, between both cases, an average difference of 60%.

All kinetic studies made by DTA are based on the shape of the thermogram, either on its variation with different heating rates or on the determination of the function, $f(\alpha)$, of the reaction rate ($d\alpha/dt = kf(\alpha)$). Thus, the discrepancies found in this study seem important enough to say that the inertia of the system (and the deformation introduced in the thermogram) will have to be considered in most kinetic studies.

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