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COMPARISON OF ISOTHERMAL AND NON-ISOTHERMAL TG DATA. KINETIC ANALYSIS OF CALCIUM OXALATE DEHYDRATION

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ABSTRACT

An isothermal study of the kinetic behaviour of calcium oxalate monohydrate dehydration is reported. The results were compared with those obtained in a non-isothermal study.

It is shown that kinetic parameters obtained from non-isothermal experiments describe isothermal experiments better than those obtained from the experiments themselves.

The kinetic behaviour of calcium oxalate dehydration in both isothermal and non-isothermal conditions is described with accuracy according to a two-step model, namely nucleation, $n = 1/2$, $E_1 = 168$ kJ mol^{-1}, and reaction at the cylinder interface, $E_2 = 70$ kJ mol^{-1}.

INTRODUCTION

The non-isothermal method of kinetic analysis of thermal decompositions has been widely accepted, since, among other advantages, experiments can be carried out over the whole conversion range, also covering a wide range of temperatures [1,2].

Some authors think that the number of experimental runs necessary in a kinetic study is smaller for the non-isothermal method [3]. However others, accepting the advantages of non-isothermal analysis [2], perform the experiments in isothermal conditions [4] because of the trouble of separating temperature and conversion influences in non-isothermal studies.

There are authors who consider it necessary to use isothermal methods in kinetic analysis: De Bruijn et al. [5] suggest that it is not possible to obtain the right conversion influence and E value by using dynamic methods; Tang [6] affirms that the conversion influence has to be established using at least an isothermal experiment; O'Brien and Ross [7] point out that the determination of kinetic parameters for calcium oxalate dehydration by non-isothermal methods is likely to be unreliable; while Guler et al. [8] consider the agreement between isothermal and non-isothermal results to be

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reasonable, although f(α) cannot always be chosen from non-isothermal experiments. Gorbachev [9], using mathematical analysis, demonstrates that kinetic parameters with linear temperature programming are identical to those obtained from isothermal experiments when the chemical transformation is irreversible; however, a similar statement cannot be made for reversible non-isothermal transformations, since kinetic parameters depend on the heating rate.

Tanaka [10] found different kinetic models using isothermal and dynamic analyses in the dehydration stages of $BaBr_2 \cdot 2H_2O$. This author attributed the differences to factors such as the distribution of the shape particles or "thermal agitation".

There are also some other different opinions [11] about the relation between isothermal an non-isothermal kinetics.

The objective of this study is to compare the results obtained in an isothermal kinetic analysis with those obtained in a non-isothermal analysis. The reaction studied was the dehydration of a calcium oxalate.

In a previous work [12], the discrepancies between results obtained by different authors in the kinetic studies of this reaction, using both isothermal and non-isothermal methods, were pointed out. Also, a non-isothermal kinetic study using a non-separable variables model was reported [13]. This work shows results obtained isothermally compared with non-isothermal results.

EXPERIMENTAL

Experiments were performed with a Carlo Erba RPE calcium oxalate monohydrate. The dehydration behaviour of samples, weighing 10 ± 0.05 mg and with a random distribution of solid in the sample pan, was observed in a Du Pont model 951 thermogravimetric analyser (TGA) connected to a nitrogen flow control system which maintained a flow rate of 2 $cm^3\ s^{-1}$. The sample temperature was controlled by the TGA furnace and measured by a chromel–alumel thermocouple placed adjacent to the sample pan. The output of this thermocouple and the weight of the sample were recorded as a function of time.

The dehydration experiments were carried out at five different temperatures (370, 380, 390, 400 and 410 K). Experimental data were recorded when the difference between programmed and recorded temperatures was kept to less than 2 K.

RESULTS AND DISCUSSION

The experimental conversion–time data are shown in Fig. 1. The lowest α point in each curve is the α_0 value, at which the programmed temperature is obtained. This point is taken as the initial time, t_0.

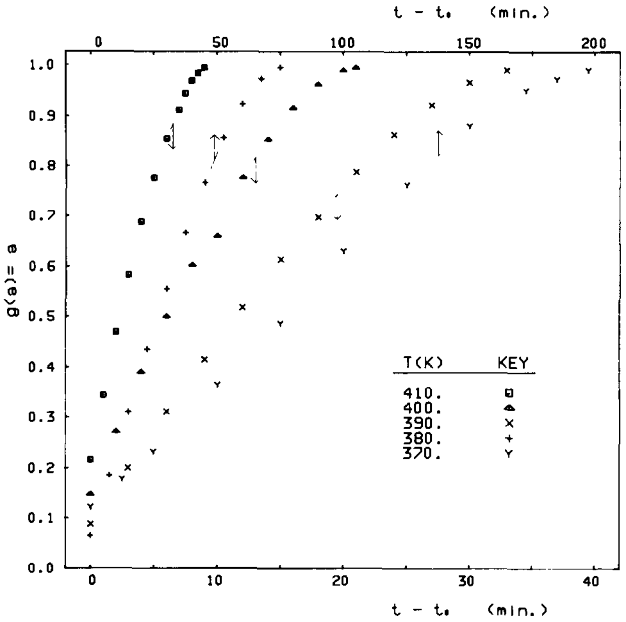

Fig. 1. Experimental data and g(α) vs. time for a reaction at the interface of a flat plate model.

If the dehydration kinetics could be described with a separable variables model, the g(α)– Δt relationship would be a straight line in agreement with the following equation:

$$\Delta t = t - t_0 = g(\alpha)/K(T) - g(\alpha_0)/K(T) \qquad (1)$$

This equation can be obtained easily by integrating the reacton rate with α_0 as the lowest limit, at $t = t_0$.

Among all possible models, e.g. nucleation, reaction at the interface and diffusion, only the interface reaction model can be fitted at all temperatures. Nucleation models, with high correlation coefficients, provide $1/K$ values much lower than the experimental time for complete reaction. By fitting the experimental data to diffusion models, with a linear least-squares method, high, positive intercepts opposite to the meaning of eqn. (1) were obtained.

The interface reaction model can be fitted according to three geometries. The cylindrical geometry, R_2, provides the highest correlation coefficient; however, other geometries also fit the data with good correlation coefficients.

Figure 1 shows experimental data and g(α)–time values from the reaction at the interface of a flat plate. Figures 2 and 3 show the representation for spherical and cylindrical geometries, respectively, and it can be seen that R_2 fits the experimental data very well, especially at high α values. Values of the slope ($1/K$) are shown in Table 1. These values can be fitted according to the Arrhenius equation to obtain kinetic parameters for this model. The parameters are also given in this table.

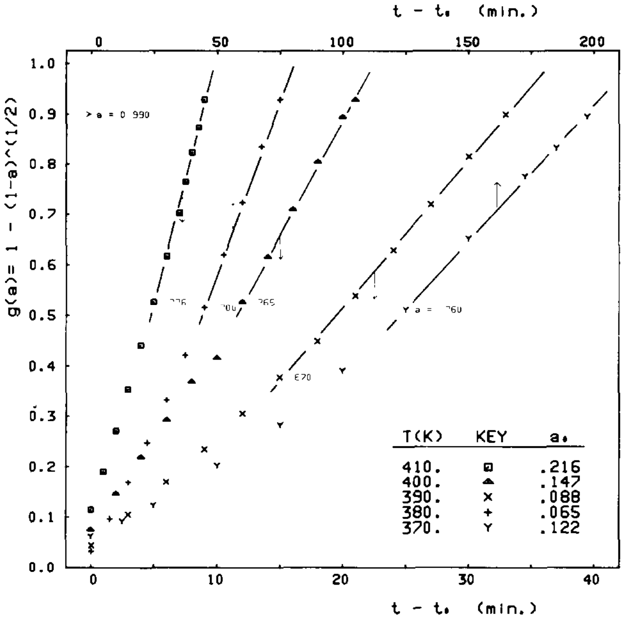

Fig. 2. g(α) vs. time for the R_2 model.

To explain the disagreement between the R_2 model and experimental data at low conversions it is necessary to use a non-separable variables model. If it is supposed that the steps connect in series, at a given

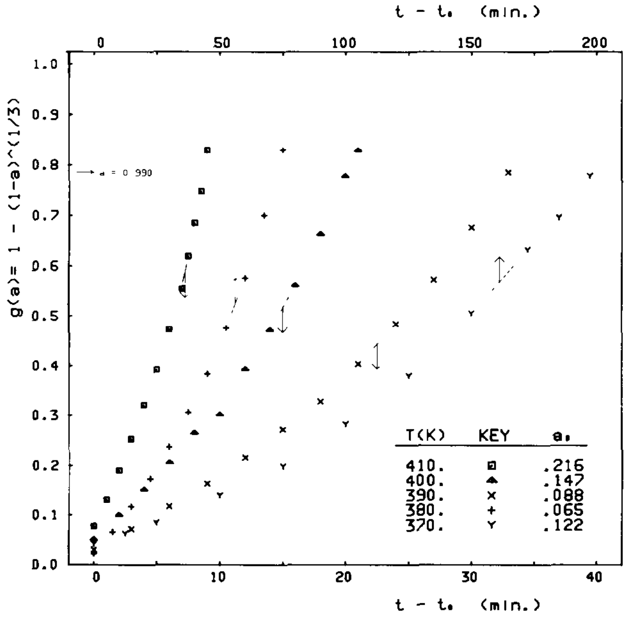

Fig. 3. g(α) vs. time for the R_3 model.

TABLE 1

Kinetic parameters for R_2 model

T (K)	$1/K$ (min)	From Arrhenius equation
410	11.2	$E = 96.0$ kJ mol^{-1}
400	24.1	$A = 1.8 \times 10^{11}$ min^{-1}
390	38.2	$r = 0.9970$
380	81.8	
370	238.2	

temperature, and integrating from $\alpha = \alpha_0$ as the lowest limit, we obtain:

$$\Delta t = g_1(\alpha)/K_1 + g_2(\alpha)/K_2 - [g_1(\alpha_0)/K_1 + g_2(\alpha_0)/K_2] \quad (2)$$

Logically, the model that should fit the low conversion data better would be a nucleation step connected to a reaction step. The reaction step used was R_2 but it was necessary to verify that any other geometry did not improve this approach.

The influence of the nucleation step is smaller than that of the reaction step, and as α increases this influence becomes smaller. By fitting the experimental data to eqn. (2), by multiple linear regression, K_1 values without any physical meaning are obtained. Therefore, it is necessary to separate the influences of each step to study the nucleation step. By supposing that the influence of nucleation is negligible at high conversion levels, the reaction at the interface could be studied.

In Fig. 2 the point over which a one-step control is assumed and the corresponding α value are shown. The kinetic parameters calculated for this step are shown in Table 2.

The influence of the nucleation step should be obtained by subtracting from each experimental time that calculated from step R_2. Fitting with eqn. (1) of these new α–t data, at each temperature, would allow the kind of nucleation to be chosen. This fitting is available for F_2 or F_3 functions at low conversion levels, below 0.5; however, it is impossible to decide between them. The kinetic parameters for steps F_2 and F_3 are shown in Table 2.

TABLE 2

Kinetic parameters for a non-separable variables model: R_2 and F_2 or F_3 steps

	R_2	F_2	F_3
A (min^{-1})	4.03×10^{10}	1.41×10^{12}	2.51×10^{11}
E (kJ mol^{-1})	90.86	99.10	94.37

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The relation between experimental conversions and those calculated supposing a one-step model, reaction at the interface with a cylindrical shape, and using the kinetic parameters of Table 1, are shown in Fig. 4. When the

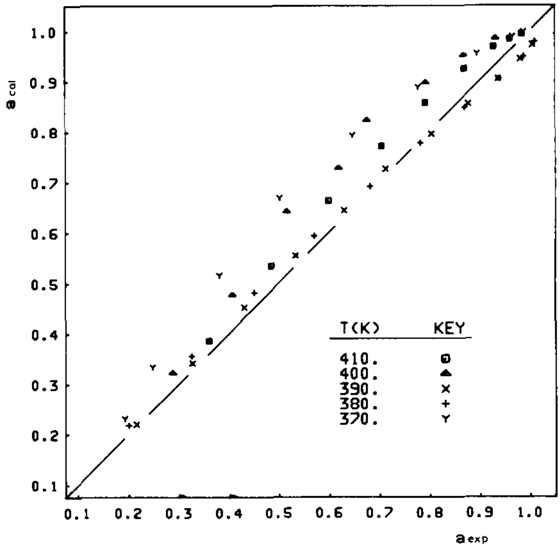

Fig. 4. Comparison of experimental data with R_2 model.

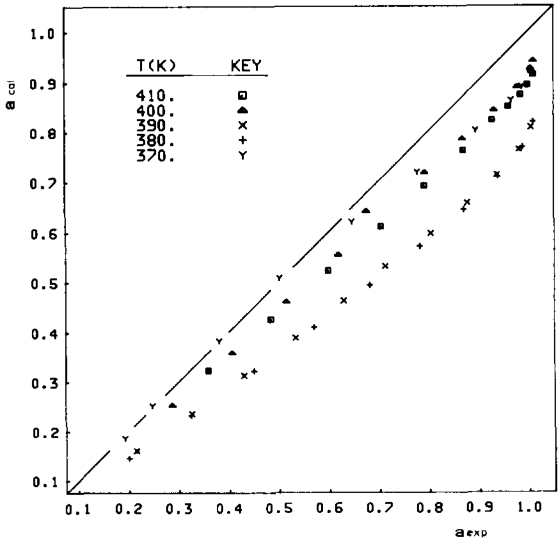

Fig. 5. Comparison of experimental data with F_2R_2 model.

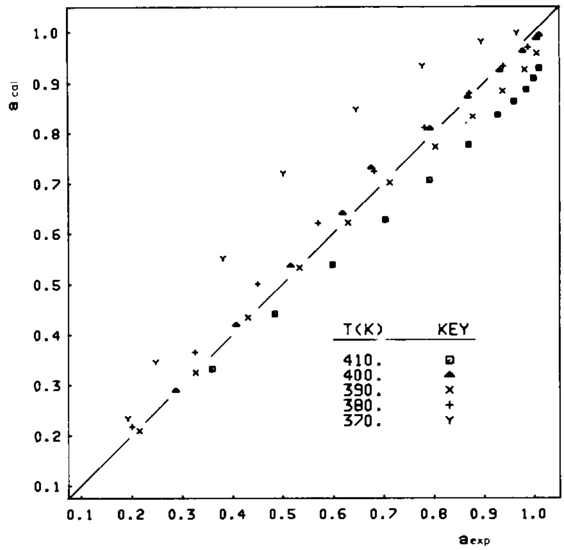

Fig. 6. Experimental data vs. F_2R_2 model using the kinetic parameters of a non-isothermal analysis [13].

calculated conversions are obtained using a two-step model, F_2R_2, with the kinetic parameters of Table 2, the relation shown in Fig. 5 is found. Finally, in Fig. 6 the same relation is shown using the model and kinetic parameters obtained with the non-isothermal analysis [13].

The best description of experimental data in isothermal conditions was obtained using non-isothermal analysis data, as can be seen in Figs. 4–6. Therefore, when two steps influence a reaction and they change their effects during the course of the reaction, the non-isothermal method is very useful so long as it allows kinetic study at low conversion levels and the influence of the principal step at these conditions is known.

NOTATION

A, A_1, A_2	pre-exponential factors (min^{-1})
E, E_1, E_2	activation energies (kJ mol^{-1})
F_2, F_3	random nucleation steps, $n = 1/2$ and $n = 1/3$, respectively
$g(\alpha)$, $g(\alpha_0)$, $g_1(\alpha)$, $g_1(\alpha_0)$, $g_2(\alpha)$, $g_2(\alpha_0)$	kinetic model functions at every conversion and at initial conversion
$K(T)$, K_1, K_2	rate constants (min^{-1})
n	exponent in the α function of random nucleation steps

R_2, R_3	reaction at the interface of a cylinder or sphere
F_2R_2	model or step of a model
r	correlation coefficient
t, t_0	time, and time when the programmed temperature is reached (min)
Δt	$= t - t_0$
α, α_0	conversion, and conversion at $t = t_0$

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