KINETIC ANALYSIS OF TG DATA: STUDY OF CALCIUM OXALATE MONOHYDRATE DEHYDRATION WITH A NON-SEPARABLE VARIABLES MODEL

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ABSTRACT

A study of the kinetic behaviour of calcium oxalate dehydration using TG data is reported. The discrimination among non-separable variables models was carried out in a differential form.

It was found that a two step model namely nucleation, $E_1 = 168$ kJ mol^{-1}, and reaction at the cylinder interface, $E_2 = 70$ kJ mol^{-1} is required to descibe the reaction course.

Good agreement between experimental and calculated $\alpha-T$ curves is observed.

INTRODUCTION

The calcium oxalate dehydration is one of the most extensively investigated decomposition reactions, among other reasons, because of its hypothetic simplicity. In a previous work [1], divergences in the results obtained from different authors in the study of this reaction were clearly established. In that work, the need to use non-separable variables models to describe the behaviour of this reaction was pointed out.

The amount of work involved to discriminate among different models is reduced if those models are compared in their differential form, especially if the experimental work is carried in non-isothermal mode.

In experiments at constant heating rate, the reaction rate is obtained in the same form as for the isothermal mode, as was shown before [2].

In this work, we describe the calcium oxalate dehydration kinetics with a non-separable variables model. The discrimination among models was made by comparing the experimental reaction rates with those calculated from different models. To obtain reaction rates from the models, we used the approximate kinetic parameters found on an integral analysis at constant α [1]. Once the kinetic model is chosen, the optimal values of kinetic parameters are obtained from non-linear regression.

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EXPERIMENTAL

The details of the sample and instruments used are described in our earlier publication [1]. Five heating rates (0.5, 1, 2, 5 and 10 K min^{-1}) were employed in the study.

RESULTS AND DISCUSSION

The experimental reaction rates obtained at various temperatures and different heating rates are shown in Table 1. Those rates were calculated from DTG curves.

For a given temperature, the number of values of reaction rate is insufficient for model discrimination. Having approximate values of the kinetic parameters, the experimental reaction rates can be compared with the ones obtained from different models in order to choose the best model to describe the experimental rates.

Approximate kinetic parameters estimation

In Fig. 2(C) of an earlier work [1] it is observed that slopes (E/R) and intercepts (A/E g(α)) change with the conversion level. It is pointed out that one of the causes of that change can be variations in the relative influence of the controlling steps in the reaction.

If we assume that the reaction is one step controlled at the beginning ($\alpha = 0$) and at the end ($\alpha = 1$), we can obtain the approximate E values by extrapolation of those calculated at different conversion levels in that integral analysis. The A values can also be obtained in a similar way.

The E and A values obtained in this manner are shown in Table 2.

Model discrimination

Supposing that the controlling steps of the reaction are connected in series, reaction rate can be written as

$$\frac{1}{r} = \frac{1}{A_1 \exp(-E_1/RT) \, f_1(\alpha)} + \frac{1}{A_2 \exp(-E_2/RT) \, f_2(\alpha)} \tag{1}$$

If the approximate kinetic parameters are substituted in this equation, it can be used to find $f_i(\alpha)$ corresponding to the model.

Combinations of rate control by nucleation, reaction at the interface of flat plates, cylinders and spheres, and diffusion with the same geometries were used.

The only combinations that generate values of reaction rates similar to the experimental one are those corresponding to nucleation for $f_1(\alpha)$ and chem-

TABLE 1

Experimental reaction rates (min^{-1})

T (K)	380		390		400		410		420	
β (K. min^{-1})	α	r	α	r	α	r	α	r	α	r
10			0.040	0.041	0.100	0.074	0.195	0.122	0.345	0.181
5	0.020	0.150	0.060	0.039	0.165	0.071	0.335	0.111	0.585	0.148
2	0.060	0.190	0.192	0.038	0.410	0.060	0.740	0.072	0.955	0.013
1	0.150	0.220	0.400	0.037	0.790	0.044				
0.5	0.350	0.230	0.815	0.022						

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TABLE 2

Approximate kinetic parameters

α	E/R (K)	A (min^{-1})
0	19000	$2.0 \cdot 10^{22}$
1	8700	$1.1 \cdot 10^{8}$

ical reaction with spherical geometry ($R_2 = 2(1-\alpha)^{1/2}$) for $f_2(\alpha)$. In Fig. 1, experimental and calculated reaction rates are compared. Calculated rates were obtained with $f_1(\alpha)$ corresponding to

$$F_1 = (1-\alpha)$$

$$F_2 = 2(1-\alpha)[-\ln(1-\alpha)]^{1/2} \qquad (2)$$
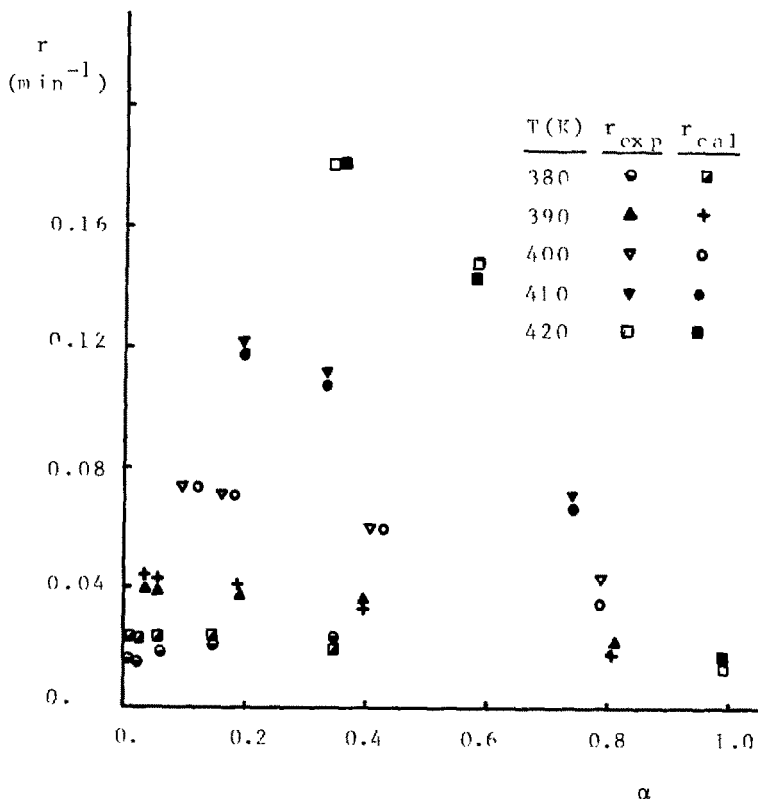
$$F_3 = 3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$$

Fig. 1. Reaction rates comparison.

TABLE 3

Optimal kinetic parameters for eqn. (1)

Parameter	Model		
	F_1R_2	F_2R_2	F_3R_2
E_1 (kJ mol^{-1})	169.1	168.2	167.5
A_1 (min^{-1})	$2.0 \cdot 10^{22}$	$2.0 \cdot 10^{22}$	$2.0 \cdot 10^{22}$
E_2	71.6	69.2	70.2
A_2	$9.4 \cdot 10^7$	$4.7 \cdot 10^7$	$6.3 \cdot 10^7$

Optimal parameter estimation

Once having established the kinetic model, optimal parameters can be determined by non-linear regression using eqn. (1) and the experimental values of reaction rate in Table 2. The kinetic parameters calculated in this manner are shown in Table 3.

$\alpha - T$ curves generation

The calculated $\alpha-T$ curves can be obtained by integration of eqn. (1), using the Runge–Kutta method. Figure 2 shows calculated and experimental
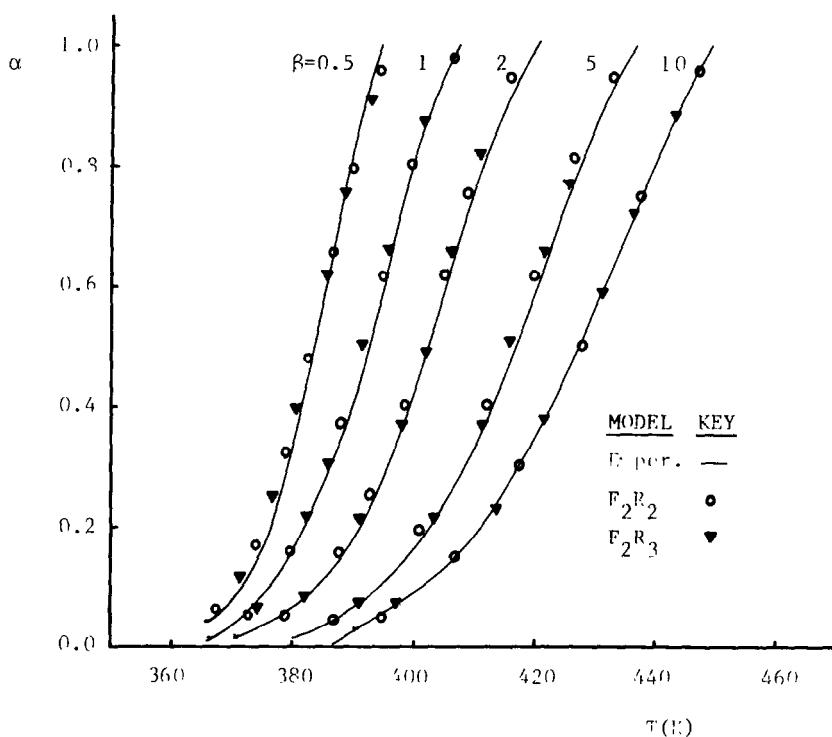

Fig. 2. Experimental and calculated $\alpha-T$ curves.

curves. Those calculated are for two kinetic models, F_2R_2 and F_3R_2. It can be observed that there is very good agreement between experimental and calculated curves, but it is not possible to choose between these two models.

The F_1R_2 model disagrees slightly with experimental values for low T and/or α. The $\alpha-T$ curves of this model were not printed in Fig. 2 because of its disagreement.

REFERENCES

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