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EFFECTS OF SAMPLE WEIGHT, PARTICLE SIZE, PURGE GAS AND CRYSTALLINE STRUCTURE ON THE OBSERVED KINETIC PARAMETERS OF CALCIUM CARBONATE DECOMPOSITION

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ABSTRACT

The effects of experimental variables (ie. sample weight, particle size, purge gas velocity and crystalline structure) on the observed kinetic parameters of calcium carbonate decomposition were studied. The calcite and aragonite decompositions can be described with a separable variables model. A two-dimensional (cylindrical geometry) phase boundary reaction model describes both decomposition reactions. Within the range of experimental conditions used in the extensive TG literature, the kinetic parameters observed were found to be slightly affected by the experimental variables. The activation energy of aragonite decomposition is smaller than that of calcite decomposition. The difference is due to crystalline structure and/or the effects of impurities.

INTRODUCTION

The kinetic models which have been developed to describe decomposition reactions do not consider the influence of variables such as sample weight, solid particle size, linear velocity of purge gas, etc. However, these variables influence the behaviour of solid decomposition. Different authors [1-4] have dealt with the influence of sample weight on the observed activation energy and pre-exponential factor. Some of these [1,2] have found that the kinetic parameters are also dependent on the heating rate which could be the result of an error in choosing the kinetic model. Therefore the thermal dehydration of calcium oxalate monohydrate must be described with a non-separable variables model [5] and this has not been taken into account.

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To study the influence of experimental variables it is useful to choose a solid with a decomposition that can be described with a separable variables model. In this study we examine the thermal decomposition of calcium carbonate. This reaction is described in a simple model which allows the influence of crystalline structure and the experimental variables: (sample mass, solid particle size, and linear velocity) on decomposition to be studied. Within the wide range of experimental variables, these variables have been observed to have some influence. The main influence corresponds to particle size and purge-gas velocity. The larger the particle size and/or the less the gas velocity, the smaller the activation energy observed. However, the influences are not large enough to change the controlling decomposition step.

EXPERIMENTAL

Calcite and aragonite from La Silva (Spain) containing 100 ± 1.8% and 98.7 ± 1.7% of calcium carbonate were used.

TABLE 1

Experimental conditions: central composite design

Run	Sample size, x_1 (mg)	Gas velocity, x_2 (cm^3 s^{-1})	Particle size, x_3 (mm)
E-1	78	6.5	0.84
E-2	78	1.5	0.84
E-3	18	6.5	0.84
E-4	18	1.5	0.84
E-5	78	6.5	1.41
E-6	78	1.5	1.41
E-7	18	6.5	1.41
E-8	18	1.5	1.41
E-9	48	4	1
E-10	48	4	1
E-11	48	4	1
E-12	48	4	1
E-13	48	4	1
E-14	48	4	1
E-15	48	4	0.25
E-16	48	4	3.05
E-17	48	–	1
E-18	48	8	1
E-19	4	4	1
E-20	100	4	1

The decomposition behaviour of the samples was observed using a Dupont model 951 thermogravimetric (TG) analyzer connected to a nitrogen-flow-control system.

The sample temperature was measured using a chromel-alumel thermocouple placed only a few millimeters from the sample. The weight variation of the sample was recorded as a function of the sample temperature.

The experiments were carried out at five different heating rates (0.5, 1, 2, 5, and 10 K min^{-1}) to find the kinetic model which best describes the decomposition behaviour. To study the influence of experimental variables, experiments at three different heating rates (2, 5, and 10 K min^{-1}) were performed.

Table 1 shows the experimental conditions which reflect a statistical design [6] that corresponds to a central composite design for the three-factor case. The experimental order was randomized and three α–T curves at different heating rates were obtained in each experiment.

Experimental conditions corresponding to experiment E-15 were used to determine the kinetic model for both calcite and aragonite decomposition.

RESULTS AND DISCUSSION

Experimental α–T data from the decomposition of calcite and aragonite are shown in Figs. 1 and 2, respectively. With an analysis at constant temperature [7], α–t data were obtained from the α–T curves for each temperature. The α–t points must fulfill the following equation

$$g(\alpha) = K_n t \tag{1}$$

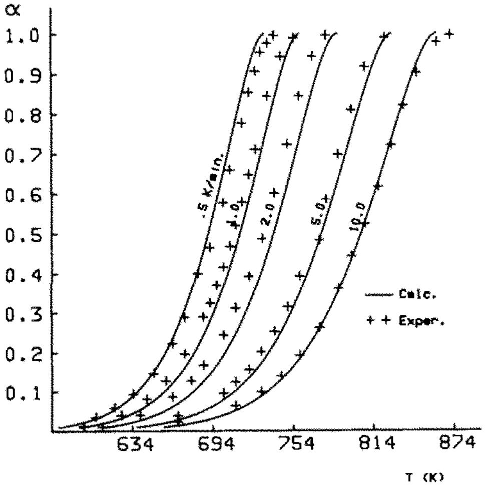

Fig. 1. Experimental and calculated α–T curves for calcite.

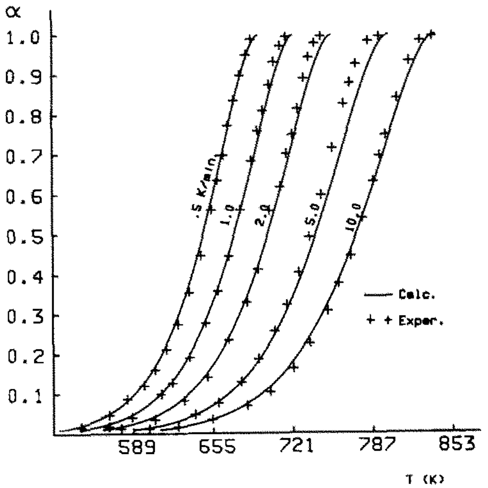

Fig. 2. Experimental and calculated α–T curves for aragonite.

where

$$K_n = \frac{\int_{T_0}^{T} A \exp(-E/RT)\, \mathrm{d}T}{(T - T_0)} \tag{2}$$

Figure 3 shows eqn. (1) applied to aragonite decomposition. The $g(\alpha)$ values plotted were ideal for the correlation with experimental data, and the same was true when the data corresponding to calcite were analysed. This allows us to conclude that the kinetic model which describes the decomposi-

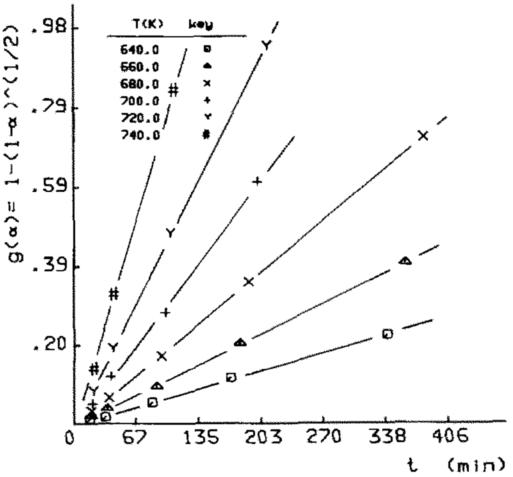

Fig. 3. Analysis at constant temperature for aragonite.

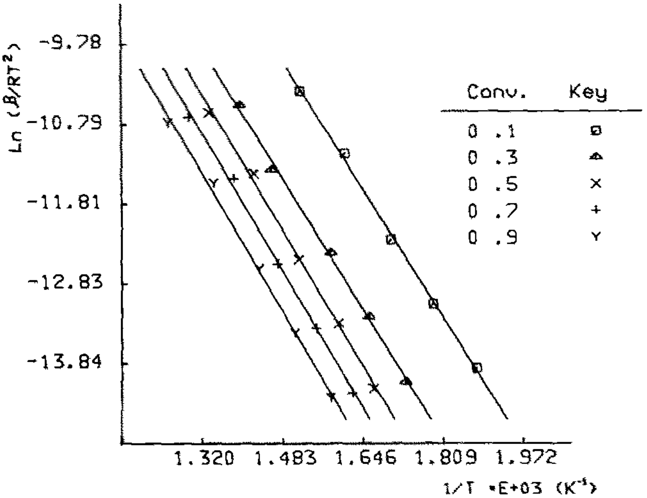

Fig. 4. Analysis at constant conversion for aragonite.

tion of calcite and aragonite is the cylindrical phase boundary reaction with $g(\alpha) = 1 - (1 - \alpha)^{1/2}$.

From an analysis at constant conversion [7], the temperature values for a prefixed conversion and different heating rates were used to obtain the temperature influence, i.e. to obtain the kinetic parameters. The relationship between temperature, heating rate and kinetic parameters at a prefixed conversion is given by

$$\frac{\beta}{RT^2} = \frac{A/E}{g(\alpha)} \exp(-E/RT) \tag{3}$$

Using a linear expression of eqn. (3) it is possible to obtain the kinetic parameters. Figure 4 shows, as an example, the data for aragonite fitted by the logarithmic form of eqn. (3). For both calcite and aragonite, parallel straight lines are obtained for the entire conversion range. Table 2 shows mean *E* and *A* obtained at identical experimental conditions. The differences observed could be due to a different crystalline structure and/or the influence of impurities.

By using the analysis at constant conversion to evaluate the kinetic parameters corresponding to the 20 experiments described in Table 1, we

TABLE 2

Mean *E* and *A* values for calcite and aragonite: run E-15

	E (kcal mol^{-1})	A (min^{-1})
Calcite	26.43	1.3 E6
Aragonite	20.85	4.5 E4

TABLE 3

The activation energies (kcal mol^{-1}) for different experimental conditions

Run	α					Mean E
	0.1	0.3	0.5	0.7	0.9	
E-1	24.41	24.29	23.28	24.81	23.99	24.25
E-2	22.01	22.46	22.62	21.97	21.42	22.10
E-3	–	23.68	23.55	23.52	22.84	23.40
E-4	–	19.72	20.60	20.49	20.26	20.27
E-5	27.38	28.83	28.04	28.27	–	28.13
E-6	23.38	23.30	23.17	22.79	22.78	23.08
E-7	24.02	24.85	25.56	25.29	24.66	24.88
E-8	25.23	24.23	24.39	24.59	24.32	24.55
E-9	25.92	26.12	26.49	26.12	26.10	26.15
E-10	22.39	24.34	24.97	23.55	23.90	23.83
E-11	24.53	26.66	26.78	27.34	26.75	26.41
E-12	23.22	24.17	25.83	26.16	26.24	25.12
E-13	24.26	24.75	25.21	25.24	25.22	24.94
E-14	24.67	25.81	26.62	27.07	26.31	26.10
E-15	26.96	25.99	26.46	26.33	26.38	26.43
E-16	–	20.19	20.23	20.12	20.20	20.19
E-17	26.88	25.34	25.63	26.61	26.64	26.22
E-18	–	29.51	29.23	28.58	29.56	29.22
E-19	24.08	25.16	24.92	24.53	–	24.67
E-20	22.70	23.78	23.32	22.52	22.21	22.90

obtain as many E and A values as constant conversions are established in each experiment. These E and A values and their mean values are given in Tables 3 and 4.

The values of the observed kinetic parameters depend on the experimental variables as can be established with statistical analysis, although the dependence is slight. Thus, the difference in the E value for experiments E-19 and E-20 is less than 8%. These experiments were done with different sample sizes and without any changes in other experimental variables.

The influence of the purge gas velocity (E-17, E-18) is less than 10% within the range of the velocity values used in this study.

The main influence is that of particle size (E-15, E-16). However, none of the three influences introduced enough changes in the experimental results to consider changes in the reaction mechanism. In any case, the model to be used in the description of this decomposition is the two-dimensional phase-boundary reaction. The changes in the observed kinetic parameters are due to the slight influences of physical phenomena.

With statistical analysis it is possible to determine the influence of the three variables studied and any of their combinations.

TABLE 4

The pre-exponential factors [$A/g(\alpha)$, min^{-1}] for different experimental conditions

	α					Mean
	0.1	0.3	0.5	0.7	0.9	A (min^{-1})
E-1	0.47 E7	0.13 E7	0.55 E6	0.76 E6	0.28 E6	0.23 E6
E-2	0.75 E6	0.37 E6	0.25 E6	0.11 E6	0.53 E5	0.52 E5
E-3	–	0.15 E7	0.78 E6	0.52 E6	0.21 E6	0.21 E6
E-4	–	0.92 E5	0.10 E6	0.69 E5	0.40 E5	0.26 E5
E-5	0.44 E8	0.35 E8	0.10 E8	0.78 E7	–	0.37 E7
E-6	0.89 E6	0.29 E6	0.15 E6	0.82 E5	0.54 E5	0.43 E5
E-7	0.57 E7	0.32 E7	0.30 E7	0.17 E7	0.64 E6	0.57 E6
E-8	0.15 E8	0.22 E7	0.13 E7	0.10 E7	0.54 E6	0.48 E6
E-9	0.17 E8	0.58 E7	0.40 E7	0.20 E7	0.12 E7	0.95 E6
E-10	0.11 E7	0.14 E7	0.13 E7	0.33 E6	0.28 E6	0.20 E6
E-11	0.60 E7	0.87 E7	0.50 E7	0.46 E7	0.19 E7	0.13 E7
E-12	0.21 E7	0.14 E7	0.26 E7	0.21 E7	0.14 E7	0.62 E6
E-13	0.51 E7	0.22 E7	0.17 E7	0.11 E7	0.76 E6	0.43 E6
E-14	0.66 E7	0.45 E7	0.44 E7	0.37 E7	0.14 E7	0.10 E7
E-15	0.37 E8	0.54 E7	0.43 E7	0.26 E7	0.18 E7	0.13 E7
E-16	–	0.49 E5	0.31 E5	0.19 E5	0.14 E5	0.89 E4
E-17	0.14 E8	0.13 E7	0.92 E6	0.12 E7	0.87 E6	0.44 E6
E-18	–	0.50 E8	0.21 E8	0.86 E7	0.10 E8	0.63 E7
E-19	0.10 E8	0.67 E7	0.28 E7	0.12 E7	–	0.76 E6
E-20	0.98 E6	0.73 E6	0.31 E6	0.12 E6	0.68 E5	0.73 E5

Equations (4) and (5) can be used to determine the kinetic parameters within the experimental range with an accuracy of more than 95%.

$$\begin{aligned} \mathrm{E} = {} & 12704 + 281.6x_1 + 1598x_2 + 9898x_3 - 31.4x_1x_2 - 133.4x_1x_3 \\ & -1505x_2x_3 + 33.4x_1x_2x_3 - 1.5x_1^2 + 34.0x_2^2 - 1615.7x_3^2 \end{aligned} \tag{4}$$

$$\begin{aligned} A = {} & -1.4\mathrm{E}6 + 3.8\mathrm{E}4x_1 + 3.8\mathrm{E}5x_2 + 1.7\mathrm{E}6x_3 - 1.7\mathrm{E}4x_1x_2 - 4.5\mathrm{E}4x_1x_3 \\ & -4.1\mathrm{E}5x_2x_3 + 2.1\mathrm{E}4x_1x_2x_3 \end{aligned} \tag{5}$$

where x_1 is the sample size, x_2 the purge-gas velocity and x_3 the particles size.

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