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THE INVESTIGATION OF THE DECOMPOSITION KINETICS OF CALCIUM CARBONATE ALONE AND IN THE PRESENCE OF SOME CLAYS USING THE RISING TEMPERATURE TECHNIQUE

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ABSTRACT

The kinetic parameters for the decomposition of calcium carbonate are established using a rising temperature programme experiment and from isothermal experiments. The effects on the decomposition of adding various clays are then established. Four methods of analysing the rising temperature data are then attempted.

INTRODUCTION

Calcium carbonate decomposition studies are numerous [1–6] and it would seem appropriate to use this material as a model to test rising temperature methods of establishing kinetic parameters [7]. The actual decomposition reaction is simply

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

It was decided to extend the investigation into the more complicated system of calcium carbonate reacting with clays. This is, of course, the basic reaction leading to the formation of cement clinker [8–10]. The loss of water from the kaolin [8] is first seen, followed by decomposition of the calcium carbonate with reaction between the lime and the clay residue occurring in the region up to 1500°C [11]. This temperature is beyond the range of the thermal analysis equipment used in the study so only the first two reactions are detailed in the present investigation.

Over many years, various methods for the analysis of thermogravimetric data have been evolved in order to evaluate kinetic parameters such as the energy of activation for solid decomposition reactions [12–30]. Four dynamic analysis techniques were used in this study and the results compared with the isothermal technique.

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The Ozawa method [*18,22*]

The derivation of the method is fully outlined in the original papers. Here, the use of the final operative equation is investigated. This takes the form

$$\log \beta = \log\left(\frac{AE}{R}\right) - 2.315 - 0.4567\frac{E}{RT} - \log g(\alpha) \tag{2}$$

where β is the heating rate (°C min^{-1}), A is the pre-exponential factor (min^{-1}), R is the gas constant (1.387 cal mole^{-1}), E is the activation energy (cal mole^{-1}), and

$$g(\alpha) = \int_0^{\alpha} \frac{\alpha d}{f(\alpha)}$$

where the reaction is described by an equation of the form

$$\frac{d\alpha}{dt} = k_T f(\alpha) \tag{3}$$

under isothermal conditions. Here, $d\alpha/dt$ is the rate of the process, α is the fraction decomposed at time t, $f(\alpha)$ is the function of α which describes the variation of the rate, and k_T is the temperature-dependent constant corresponding to the specific reaction rate in homogeneous reaction kinetics. The function $f(\alpha)$ assumes different forms depending on the model put forward to describe the rate process.

In the Ozawa method, plots of log β against the reciprocal of absolute temperature give parallel lines for each α value. The method therefore entails repetition of the TG data at varying values of β. The slope (-0.4567 E/R) of these plots gives the activation energy. The next step in the analysis is the determination of A and $g(\alpha)$. The theoretical curves of $1-\alpha$ vs. log $g(\alpha)$ have been determined before, but have been recalculated and reproduced here to enable the data presented here to be

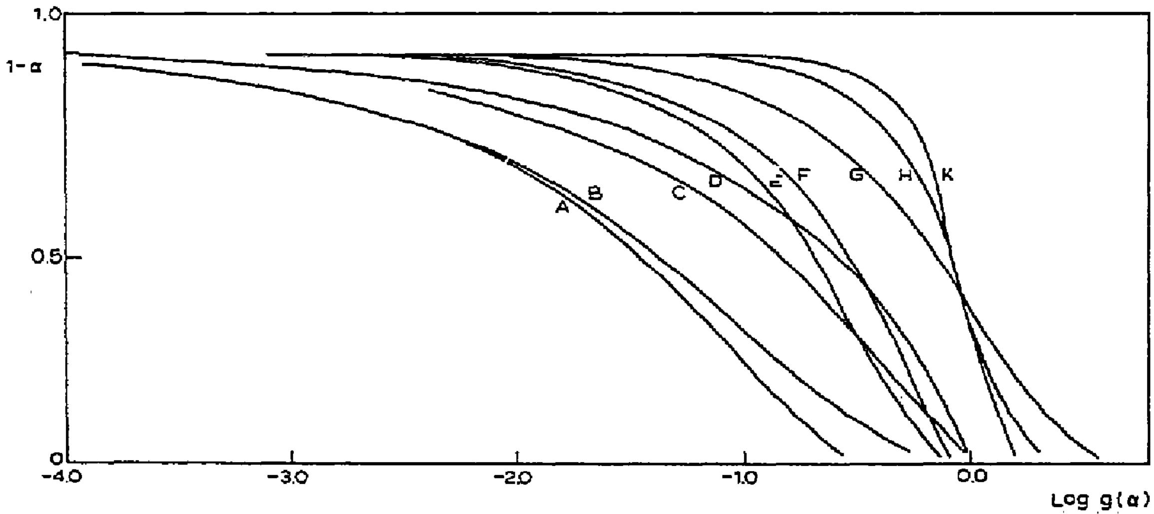

Fig. 1. The theoretical thermogravimetric curves for some kinetic equations. A, D_4; B, D_3; C, D_2; D, D_1; E, R_3; F, R_2; G, F_1; H, A_2; K, A_3.

understood (see Fig. 1). The various models tested and their algebraic forms are as follows.

Diffusion-controlled reactions

$$D_1(\alpha) = \alpha^2 = kt \qquad \text{One-dimensional diffusion} \tag{4}$$

$$D_2(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha = kt \qquad \text{Two-dimensional diffusion, cylindrical symmetry} \tag{5}$$

$$D_3(\alpha) = \left[1-(1-\alpha)^{1/3}\right]^2 = kt \qquad \text{Three-dimensional diffusion, spherical symmetry, Jander equation} \tag{6}$$

$$D_4(\alpha) = \left[1-(2\alpha/3)\right] - (1-\alpha)^{2/3} = kt \qquad \text{Three-dimensional diffusion, spherical symmetry, Ginstling–Brounshtein equation} \tag{7}$$

Phase-boundary controlled reactions

$$R_2(\alpha) = 1-(1-\alpha)^{1/2} = kt \qquad \text{Cylindrical symmetry} \tag{8}$$

$$R_3(\alpha) = 1-(1-\alpha)^{1/3} = kt \qquad \text{Spherical symmetry} \tag{9}$$

Kinetic equations based on the concept of an order of reaction

$$F_1(\alpha) = -\ln(1-\alpha) = kt \tag{10}$$

Avrami–Erofe'ev equations

$$A_2(\alpha) = \left[-\ln(1-\alpha)\right]^{1/2} = kt \qquad \text{Random nucleation; Avrami equation I} \tag{11}$$

$$A_3(\alpha) = \left[-\ln(1-\alpha)\right]^{1/3} = kt \qquad \text{Random nucleation, Avrami equation II} \tag{12}$$

The plots of $1-\alpha$ against $\log[(E/\beta R)\, P(E/RT)]$ are obtained by using experimental data. Here, one makes use of the relationship given by Ozawa, namely

$$g(\alpha) = \frac{AE}{\beta R} P(x) \tag{13}$$

where

$$x = \frac{E}{RT} \tag{14}$$

and

$$P(x) = e^{-x}x^{-1} - \int_x^0 e^{-x}x^{-1}\,dx \tag{15}$$

This experimental plot may be superimposed to fit upon one of the curves in Fig. 1. The best fit determines $g(\alpha)$ and the length of the lateral shift is found to be equal to $\log A$.

The Kissinger method [*19,23*]

Kissinger's method has been criticised mainly because it has been generally applied to DTA data and subjected to an error in attributing the maximum rate of reaction to the peak temperature [24–26]. However, applied to TG data there would seem to be no difficulty. For a first-order reaction

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A(1-\alpha)\,\mathrm{e}^{-E/RT} \tag{16}$$

At the maximum reaction rate

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}=0$$

$$=\frac{\mathrm{d}\alpha}{\mathrm{d}t}\left(\beta E/RT_{\mathrm{m}}^2-A\,\mathrm{e}^{-E/RT_{\mathrm{m}}}\right) \tag{17}$$

Therefore

$$\ln\left(\frac{\beta}{T_{\mathrm{m}}^2}\right)=\ln\frac{AR}{E}-\frac{E}{RT_{\mathrm{m}}} \tag{18}$$

and

$$\frac{\mathrm{d}\ln(\beta/T_{\mathrm{m}}^2)}{\mathrm{d}(1/T_{\mathrm{m}})}=-\frac{E}{R} \tag{19}$$

or

$$\log\frac{\beta}{T_{\mathrm{m}}^2}=\log\frac{AR}{E}-\frac{E}{2.303\,RT_{\mathrm{m}}} \tag{20}$$

where β, T_{m}, E and R are heating rate, maximum rate temperature, activation energy and gas constant, respectively. The plot of $\ln(\beta/T_{\mathrm{m}}^2)$ against $1/T_{\mathrm{m}}$ then has a slope equal to $-E/R$. Kissinger claimed that the method is approximately true for other orders of reaction.

The differential method

This has been outlined by Dollimore et al. [27,28]. Starting with the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k\mathrm{f}(\alpha) \tag{21}$$

and combining this with the equation describing the programmed rise in temperature, viz.

$$T=T_0+\beta t \tag{22}$$

where T_0 is the initial temperature in degrees Kelvin, and β is the heating rate, then noting that $\beta=\mathrm{d}T/\mathrm{d}t$

$$k_{\mathrm{T}}=\frac{\beta(\mathrm{d}\alpha/\mathrm{d}T)}{\mathrm{f}(\alpha)} \tag{23}$$

This can be substituted into the Arrhenius equation to give

$$\log\left[\frac{(\mathrm{d}\alpha/\mathrm{d}T)\beta}{\mathrm{f}(\alpha)}\right]=\log k=\log A-\frac{E}{2.303RT} \tag{24}$$

The plot of log[$(\mathrm{d}\alpha/\mathrm{d}T)\ \beta/\mathrm{f}(\alpha)$] against the reciprocal absolute temperature must give a straight line, the slope of which $(-E/2.303R)$ gives the activation energy.

Doyle's integral method [*20,29*]

The rate of reaction of a process can be generally written as [17]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\ \exp(-E/RT)\ \mathrm{f}(\alpha)(1-\mathrm{e}^{-\Delta G/RT}) \tag{25}$$

where ΔG is the free energy change of the process and $\mathrm{f}(\alpha)$ depends on the type of rate-controlling process. If the velocity of the reverse reaction can be neglected (far from the equilibrium temperature), then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\ \exp(-E/RT)\ \mathrm{f}(\alpha) \tag{26}$$

If the temperature is rising during the reaction, then writing $\beta=\mathrm{d}T/\mathrm{d}t$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\ \exp(-E/RT)\ \mathrm{f}(\alpha)$$

and by the integration to the temperature, T, at which the fraction decomposed is α, the following relationship is obtained according to Doyle [20,29]

$$\mathrm{g}(\alpha)=\frac{AE}{\beta R}\ \mathrm{P}(x) \tag{27}$$

where $\mathrm{P}(x)$ and x have the same definition as that used in the consideration of Ozawa's method discussed earlier.

The difficulty posed here is the fact that the integration $\int_{T_0}^{T}\mathrm{e}^{-E/RT}\,\mathrm{d}T$ is not possible analytically (note, in foregoing equation, $x=E/RT$). Doyles approximation for log $\mathrm{P}(x)$ is

$$\log \mathrm{P}(x)=-2.315-0.4567x \tag{28}$$

From these equations, log $\mathrm{g}(\alpha)$ can be written as [30]

$$\log \mathrm{g}(\alpha)=\log\left(\frac{AE}{R\beta}\right)-2.315-0.4567\frac{E}{RT} \tag{29}$$

where, as before

$$\mathrm{g}(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} \tag{30}$$

Values of log $\mathrm{g}(\alpha)$ should be plotted against $1/T$ and this then allows both A and E to be calculated. The forms of $\mathrm{g}(\alpha)$ for various models have been listed earlier in the text. In addition, for

$$\mathrm{g}(\alpha)=\alpha^n=kt \tag{31}$$

the values of n may be extended to $n=1/4$, $1/3$, $1/2$, 1 and 2.

The Avrami–Erofe'ev relationship will include

$$g(\alpha) = \left[-\ln(1-\alpha)\right]^{1/n} = kt \tag{32}$$

with $n = 1$, 4/3, 3/2, 2 and 3.

In addition to those already listed, one may include the Prout–Tomkins equation

$$g(\alpha) = \ln\left[\alpha/(1-\alpha)\right] = kt \tag{33}$$

the second-order equation

$$g(\alpha) = \frac{1}{(1-\alpha)} = kt \tag{34}$$

and the exponential relationship

$$g(\alpha) = \ln \alpha = kt \tag{35}$$

EXPERIMENTAL

These methods were applied to six reaction samples, namely finely ground calcite in the form of limestone from the Cawdor Quarry of the Derbyshire Stone Co. Ltd. (sample $CaCO_3$), a 50% mixture (by weight) of the calcite with dehydrated supreme grade china clay (sample S1), a 50% mixture (by weight) of calcite with china clay also dehydrated designated RT (sample S2), a 50% mixture of calcite and dehydrated Wyoming bentonite (sample S3), a 50% mixture of calcite and supreme grade china clay which had been preheated at 430°C for 1 h (sample S1A), a 50% mixture

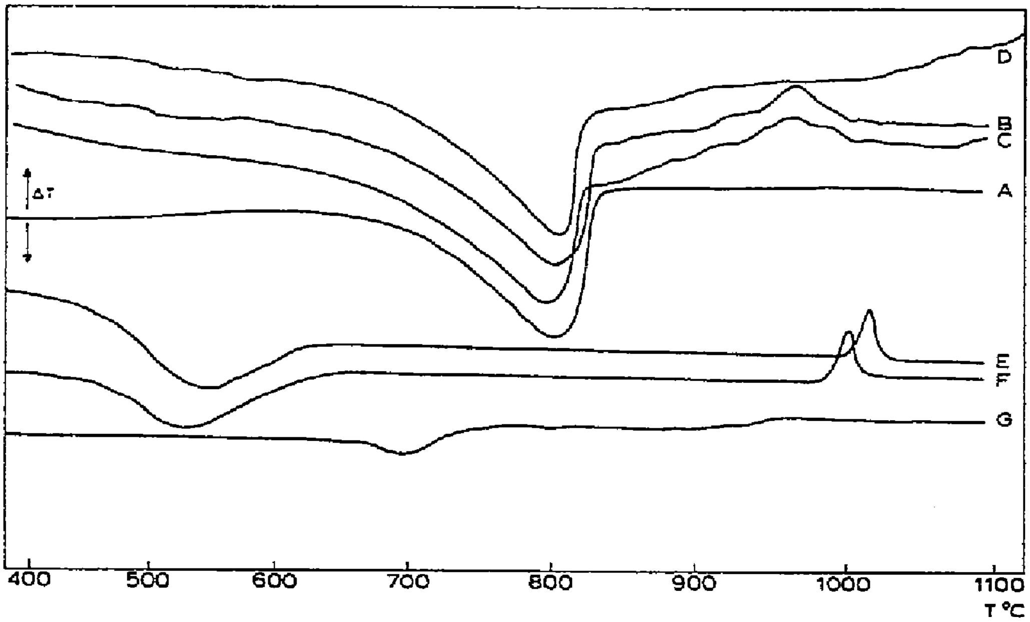

Fig. 2. DTA curves of $CaCO_3$, some clays and mixtures. A, $CaCO_3$; B, S1; C, S2; D, S3; E, supreme clay; F, china clay; G, Wyoming bentonite.

of calcite and supreme grade china clay which had been preheated at 730°C for 1 h (sample S2A). The analysis for the two grades of china clay has been previously published together with other details of their behaviour [31,32]. The DTA plots indicate that the decomposition of the calcite can be considered as a separate reaction distinct from the processes identified in the clay samples (see Fig. 2). The DTA traces were obtained using a Netzsch DTA unit at a heating rate of 10 K min^{-1} in a stream of nitrogen (5 cm^3 min^{-1}). The TG data subsequently reported in this study was determined using a Stanton TG 750 unit in a nitrogen atmosphere (flow rate 5 cm^3 min^{-1}).

RESULTS AND DISCUSSION

TG data was determined at various heating rates on all the samples. The samples were also decomposed on the TG unit at various temperatures, plotting the fraction decomposed (α) against time (t) in each isothermal experiment. Each of the methods mentioned in the Introduction was then used to analyse the data and determine the kinetic parameters.

The Ozawa method

The logarithms of the heating rates were plotted against the reciprocal of absolute temperature for the six samples for different α values. The activation energies determined by this method are listed in Table 1.

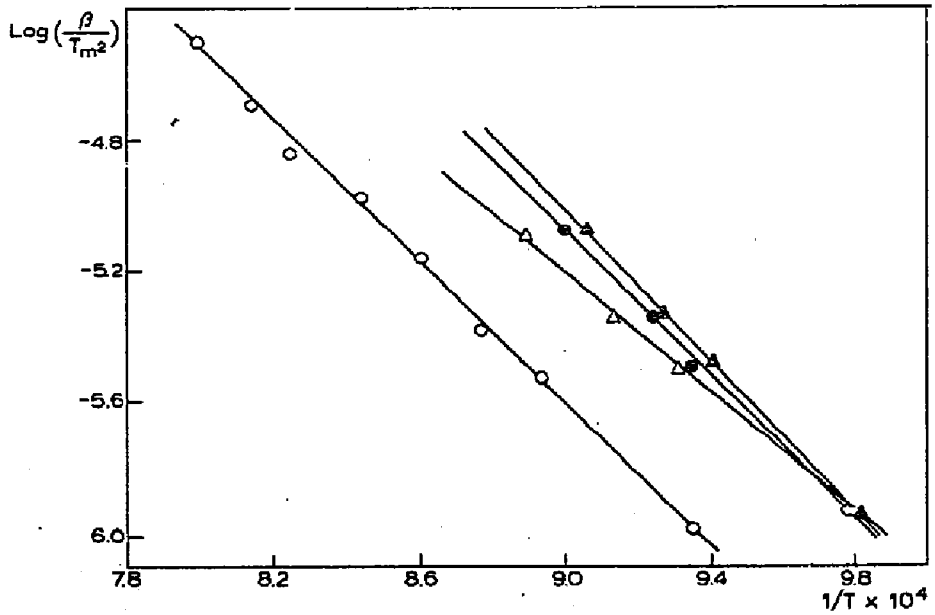

Fig. 3. Kissinger method. Plots for $CaCO_3$ and mixtures with clays. ○, $CaCO_3$; ●, S1; △, S2; ▲, S3.

TABLE 1

Activation energies of decomposition of the samples studied

Material	Activation energies of decomposition (kJ $mole^{-1}$)			
i	The Ozawa method	The Kissinger method	The differential method	
			1.20 deg. min^{-1}	3.69 deg. min^{-1}
$CaCO_3$	211.60 ± 4.65	209.76 ± 0.12	196.58 ± 0.36	193.00 ± 0.30
S1	227.08 ± 7.38	208.07 ± 0.42	191.54 ± 0.45	184.25 ± 0.29
S2	182.60 ± 0.45	173.48 ± 0.54	186.14 ± 0.18	204.42 ± 0.33
S3	218.95 ± 8.98	217.58 ± 0.25	177.91 ± 0.14	193.53 ± 0.22
S1A	218.26 ± 2.38	209.11 ± 1.06	218.53 ± 1.07	231.18 ± 1.18
S2A	209.98 ± 2.35	202.95 ± 1.02	177.98 ± 0.22	177.53 ± 0.30

By using the activation energies thus determined, the weight changes were plotted against $\log[(E/\beta R)\ P(E/RT)]$ and compared with the curves in Fig. 1. From these comparisons, the mechanism of the decomposition of calcium carbonate may be determined to conform to a first-order equation. The pre-experimential factors were determined as outlined in the introduction to give the following results.

Sample	$\log_{10}A$ (A in s^{-1})
$CaCO_3$	8.823 ± 0.018
S1	10.032 ± 0.063
S2	7.804 ± 0.034
S3	3.832 ± 0.013
S1A	9.217 ± 0.076
S2A	8.920 ± 0.029

The Kissinger method

Typical plots of $\log(\beta/T_m)$ vs. $1/T_m$ are seen in Fig. 3. Table 1 lists the values of E.

The differential method

The values of $d\alpha/dT$ are calculated at appropriate α values and the corresponding values of $f(\alpha)$ are also calculated. In this calculation, it has been demonstrated [27,28] that making the approximation of $f(\alpha) \simeq 1 - \alpha$ for decelerating mechanisms is reasonable for most carbonate decompositions. Typical plots are seen in Fig. 4

			Isothermal
5.36 deg. min^{-1}	10.12 deg. min^{-1}	Mean	
184.43 ± 0.28	203.44 ± 0.31	194.38 ± 7.91	
187.10 ± 0.23	180.56 ± 0.56	185.56 ± 4.60	197.32 ± 0.61
193.54 ± 0.01	196.71 ± 0.02	195.20 ± 7.58	205.71 ± 0.76
189.82 ± 0.01	202.82 ± 0.18	191.02 ± 10.30	199.84 ± 0.36
218.51 ± 1.10	191.63 ± 1.14	219.15 ± 9.34	
178.89 ± 0.28	183.15 ± 0.20	179.39 ± 2.57	

(similar plots were obtained for the other samples) and the activation energies are given in Table 1.

Doyle's integral method

The values of log g(α) calculated for the various rate processes using TG data can be plotted against the corresponding $1/T$ values [see eqn. (4)]. A straight line should

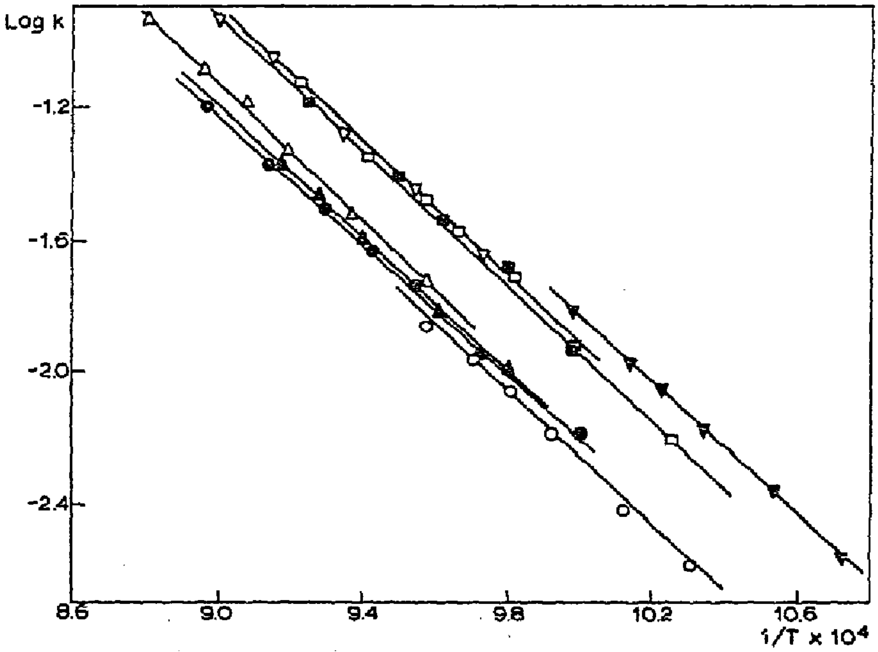

Fig. 4. Differential method. Plot of log $k = \log[(d\alpha/dT)\ \beta/f(\alpha)]$ against $1/T$ and $f(\alpha) = 1-\alpha$. $CaCO_3$ heating rates (deg. min^{-1}): ○, 1.20; ◉, 3.68; ▲, 5.36; △, 10.12. S2A heating rates (deg. min^{-1}): ▼, 1.20; □, 3.68; ▣, 5.36; ▽, 10.12.

TABLE 2

Activation energies and pre-exponential factors for the decomposition of the mixtures studied by Doyle's integral method

Function	$CaCO_3$			S1		
	E (kJ mole^{-1})	log A	St. dev. 10^{+2}	E (kJ mole^{-1})	log A	St. dev. 10^{+2}
$-\ln(1-\alpha)$	203.8	8.04	1.87	200.6	8.34	2.11
$[-\ln(1-\alpha)]^{1/2}$	93.3	2.77	0.94	92.2	2.94	1.05
$[-\ln(1-\alpha)]^{1/3}$	56.8	0.97	0.63	56.3	1.09	0.70
$[-(\ln(1-\alpha)]^{1/4}$	38.7	0.02	0.47	38.5	0.12	0.53
$[-(\ln(1-\alpha)]^{3/4}$	148.5	5.42	1.41	146.3	5.65	1.58
$[-(\ln(1-\alpha)]^{2/3}$	130.1	3.54	1.25	128.3	4.75	1.41
$1-(1-\alpha)^{1/2}$	169.8	6.42	3.97	163.97	6.38	3.26
$1-(1-\alpha)^{1/3}$	181.4	6.77	3.05	174.5	6.82	2.33
$[1-(1-\alpha)^{1/3}]^{1/2}$	83.5	2.12	1.53	79.2	2.16	1.17
$[1-(1-\alpha)^{1/3}]^{1/2}$	49.5	0.23	1.02	47.8	0.57	0.78

result, according to Doyle, if the correct form of $g(\alpha)$ is chosen. The data are shown in Table 2. It should be noted that, in practice, various functions of $g(\alpha)$ gave linear plots.

Isothermal decomposition

The rates of decomposition of S1, S2 and S3 were studied in dry nitrogen using a Stanton TG 750 thermobalance. A sample weight of 100 mg was used for all the decompositions at constant temperature as follows: S1 at 659, 684, 715, 738 and 767°C; S2 at 652, 681.5, 701.5, 724 and 753°C; and S3 at 654, 688.5, 702, 727 and 757.5°C.

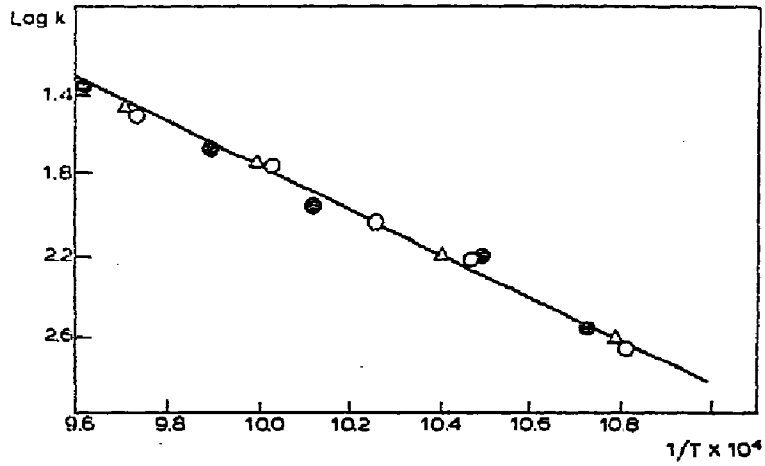

Fig. 5. Arrhenius plot for mixtures of $CaCO_3$ and clays (isothermal). ●, S1; ○, S2; △, S3.

S2			S3		
E (kJ mole^{-1})	log A	St. dev. 10^{+2}	E (kJ mole^{-1})	log A	St. dev. 10^{+2}
167.5	6.55	6.03	203.4	8.46	2.47
75.6	2.01	3.01	110.1	3.08	1.23
45.4	0.46	2.01	56.9	1.23	0.82
30.3	−0.37	1.51	38.9	0.26	0.62
121.5	4.30	4.30	148.3	5.78	1.85
106.2	3.50	4.02	130.0	4.89	1.64
137.1	5.166	1.95	165.6	6.53	1.94
146.4	5.28	2.79	177.2	6.98	1.27
65.2	1.37	1.40	80.4	2.31	0.63
38.4	−0.01	0.93	48.4	0.71	0.42

The constant temperature decomposition data for all samples were first plotted as fraction reacted (α) vs. $t/t_{0.5}$ (where t is the time of reaction and $t_{0.5}$ is the time for half reaction) according to the method of Brindley and co-workers [15] and shown to be isokinetic. For results over wide ranges of α (0.1−~0.95), the best fit was described by the Mampel intermediate equation with $n = 2$ [eqn. (31)].

Arrhenius activation energies were calculated over the complete range of the decomposition reaction (Table 1 and Fig. 5).

Comment on the results

The agreement between the results of isothermal and non-isothermal methods was considered reasonable. In the rising temperature methods, the sensitivity (especially in Doyle's integral method) of selecting the correct rate equation is not very great and the method does not discriminate very well between certain groups of rate equations. Thus, in the Doyle's integral method, the Avrami–Erofe'ev equation with $n = 1$ (i.e. first-order), 4/3, 3/2, 2 and 3 and the contracting geometry equation with $n = 2$ and 3 all gave reasonable linear plots. The activation energies calculated from such plots are listed in Table 2 together with the value of log A. If these results are compared with other methods utilising the first-order equation, then the agreement is again reasonable. It should also be noted that a compensation effect is seen when results obtained by a consistent method are compared (Fig. 6) and the linear relationship, viz.

$$\log A = aE + b \tag{36}$$

is observed. However, the validity of this observation is somewhat diminished if it is

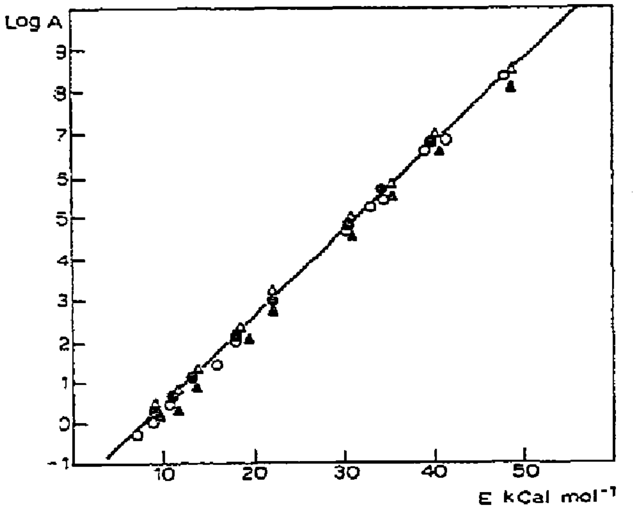

Fig. 6. Kinetic compensation effect in the thermal decomposition of $CaCO_3$ and clay mixutres (1 kcal = 4.18 kJ). ▲, $CaCO_3$; ●, S1; ○, S2; △, S3. $\log A = 0.208E - 1.80$ (E in kcal) or $\log A = 0.0498E - 1.80$ (E in kJ).

noted that results for E and A obtained by the use of alternative kinetic equations lie on the extension of the same compensation plot. Similar plots, which are in close agreement with the data shown here, have been obtained by Zsako and Arz [4]. This emphasizes the need to decide on a common kinetic mechanism before seeking a compensation plot.

The results show (see Fig. 2 and Tables 1 and 2) that calcium carbonate decompositions are affected by the clay with which they are heated, but not greatly so, and this is reflected by the small differences in the activation energy. This could be important in site consideration in cement manufacture and in terms of energy conservation, as considerable quantities of material are involved. The absolute validity of E may be questioned, but the selection of a common method of analysis allows comparisons to be made which can be relied upon. Table 2 demonstrates, in particular, the need to find the correct choice for f(α) which cannot always be made from an analysis of rising temperature experiments. Inspection of Table 2 and the values of E and A enable a selection of reasonable functions of g(α) to be chosen, but this is only after a comparison with other methods.

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