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THE MEASUREMENT OF MEANINGFUL KINETIC PARAMETERS FOR SOLID STATE DECOMPOSITION REACTIONS

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Following previous work on the measurement of meaningful activation energies and the application of Constant Rate Thermal Analysis (CRTA) to the determination of kinetic parameters [1, 2], here we further examine sources of error in determining activation energies and go on to consider the form of the alpha function and the value of A. Using theoretical arguments based on transition state theory, we conclude that allowing significant pressures of product gas to appear in the reaction environment will lead to very high values for apparent activation energies. We note that, although this is observed in practice for calcium carbonate, it in no way invalidates the application of the Arrhenius equation to solid state decomposition reactions, provided care is taken to avoid this type of distortion of experimental results. We attempt to determine the alpha function for the decomposition of calcium carbonate using data gathered from a variety of different types of temperature programme and reaction conditions. We find that the apparent alpha function depends on the method adopted and the experimental conditions used. We propose an explanation of why this occurs and tentatively introduce a new way of looking at the development of a reaction interface for this type of reaction. We review the literature and conclude that, while significant variations for the activation energy for the decomposition of calcium carbonate exist, a critical appraisal leads to good agreement amongst values that follow good experimental practice and reliable methods of data reduction. The apparent divergence of results can be explained in the light of the theoretical arguments advanced and the easily understood sourc-es of experimental error.

Introduction

This article is a companion of two previous articles [1, 2] and they are best read in chronological order. Some knowledge of these articles and the kinetic conventions used therein is assumed in the text. In these previous articles we recalled an observation made in a comprehensive review of the

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literature of solid state reactions [3], namely: "the kinetic parameters most frequently used to provide information about the (reaction) step identified as rate limiting are A and E. Values for nominally the same chemical change often show significant deviations". We then went on to consider the case of the thermal decomposition of calcium carbonate in some detail. We confined our attention to the activation energy and presented results that suggested the widely dispersed values for this parameter reported in the literature could be explained, in large measure, by poor choice of experimental conditions and/or the method chosen for the subsequent analysis of experimental data to extract kinetic information. In particular, the results suggested that on both theoretical and practical grounds the method known as Constant Rate Thermal Analysis (CRTA) has significant advantages for studying the kinetics of solid state decomposition reactions. The potential of this technique was explored in some detail and the Reduced Temperature Plot as a method for determining the alpha function for a reaction, was introduced.

In this article we present a theoretical treatment of the kinetics of solid state decomposition reactions that investigates the effect of the partial pressure of the product gas on the apparent activation energy. The results of this analysis go further in providing an explanation of the observed disparity in published values for the activation energy for the decomposition of calcium carbonate and other compounds. We also extend the analysis of our experimental data to consider the pre-exponential factor and the alpha function using the Reduced Temperature Plot method and other more established techniques.

Theoretical Treatment of the Influence of Product Gas Pressure on Reversible Solid State Decomposition Reactions

Consider the general reaction;

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)} \tag{1}$$

where the subscript 's' denotes a solid and 'g' a gas.

In this treatment we will take the molecule A to be BC, and assume, in accordance with usual approach of transition state theory, that the reaction proceeds via some activated intermediate viz;

$$BC \rightarrow [B - - - C]^{\ddagger} \rightarrow B + C \tag{2}$$

Postulating a pseudo equilibrium between the reactant and the activated intermediate we obtain

$$BC \underset{K^{\ddagger}}{\rightleftarrows} [B---C]^{\ddagger} \rightarrow B + C \tag{3}$$

where the pseudo equilibrium constant is given by

$$K^{\ddagger} = \frac{[B----C]^{\ddagger}}{[BC]} \tag{4}$$

From transition state theory we may write

$$\text{Rate} = wv\,[B---C]^{\ddagger} \tag{5}$$

Where w = some transmission coefficient, typically between 0.5 and 1
ν = classical vibration frequency of the reaction co-ordinate
From Eq. (4) we may write

$$[B---C]^{\ddagger} = K^{\ddagger}\,[BC] \tag{6}$$

$$\therefore \text{Rate} = w\nu\; K^{\ddagger}[BC] \tag{7}$$

Continuing with pseudo-thermodynamic arguments we may write

$$\Delta G^{\ddagger\theta} = \Delta H^{\ddagger\theta} - T\Delta S^{\ddagger\theta} \tag{8}$$

Where

$\Delta G^{\ddagger\theta}$ = Gibbs free energy of activation
$\Delta H^{\ddagger\theta}$ = enthalpy of activation
$\Delta S^{\ddagger\theta}$ = standard entropy of activation

From standard thermodynamic arguments

$$\Delta G^{\ddagger\theta} = -RT\,\ln K^{\ddagger} \tag{9}$$

$$\therefore K^{\ddagger} = e^{(-\Delta G^{\ddagger\theta}/RT)} \tag{10}$$

$$\therefore \text{Rate} = w\;\nu\, e^{(-\Delta G^{\ddagger\theta}/RT)}\,[BC] \tag{11}$$

Let the reaction rate constant = k, then

$$k = w\,\nu\, e^{(-\Delta G^{\ddagger\theta}/RT)} \tag{12}$$

$$\therefore k = w\nu e^{(-\Delta S^{\ddagger\theta}/R)} e^{(-\Delta H^{\ddagger\theta}/RT)} \tag{13}$$

Where

$$\Delta H^{\ddagger\theta} = E \tag{14}$$

Where E is the activation energy from the usual form of the Arrhenius equation. This point is further delt with below.

From statistical mechanics we may write

$$e^{(\Delta S^{\ddagger\theta}/R)} = \frac{\bar{k}T}{h\nu}\frac{Q^{\ddagger}}{Q} \tag{15}$$

Where

$Q^{\ddagger}$ = the partition function for the activated complex excluding that for the reaction co-ordinate

$\frac{\bar{k}T}{h\nu}$ = the partition function for the classical oscillator assumed to be the raction co-ordinate

Q = the complete partition function for the reactant

Thus one obtains the well known expression

$$k = w\frac{\bar{k}T}{h}\frac{Q^{\ddagger}}{Q}e^{(-\Delta H^{\ddagger\theta}/RT)} \tag{16}$$

In order to understand the effect that significant concentrations of product gases in the reaction environment may have, we can extend the above argument to include the effects of the reverse reaction in the following manner:

Consider Eq. (11) modified to denote the forward reaction by use of the subscript 'f', viz;

$$\text{forward rate of reaction} = w_f \nu_f e^{\Delta G_f^{\ddagger\theta}/RT}[BC] \tag{17}$$

We may postulate that the reverse reaction proceeds through the same activated intermediate as the forward reaction thus

$$B + C \rightleftarrows \quad [B---C]^{\ddagger} \rightarrow BC \tag{18}$$

Following the same arguments presented above to arrive at Eq. (11) we can derive the equation for the backward reaction viz;

$$\text{backward rate of reaction} = w_b \nu_b e^{-\Delta G_b^{\ddagger\theta}/RT} [C][B] \qquad (19)$$

Thus the net rate of reaction is given by

$$\text{net rate of reaction} = w_f \nu_f e^{-\Delta G_f^{\ddagger\theta}/RT} [BC] - w_b \nu_b e^{-\Delta G_b^{\ddagger\theta}/RT} [C][B] \qquad (20)$$

It is convenient to consider the reaction rate in terms of the specific reaction rate constant for the forward overall reaction thus;

$$\text{rate of reaction} = k_f [BC] \qquad (21)$$

$$\therefore k_f = w_f \nu_f e^{-\Delta G_f^{\ddagger\theta}/RT} - w_b \nu_b e^{-\Delta G_b^{\ddagger\theta}/RT} \frac{[C][B]}{[BC]} \qquad (22)$$

Given

$$\Delta G^{\theta} = \Delta G_f^{\ddagger\theta} - \Delta G_b^{\ddagger\theta} \qquad (23)$$

Where

ΔG^{θ} = standard Gibbs free energy for the reaction

$\Delta G_f^{\ddagger\theta}$ = standard Gibbs free energy for the formation of the activated intermediate from the reactant

$\Delta G_b^{\ddagger\theta}$ = standard Gibbs free energy for the formation of the activated intermediate from the products

$$-\Delta G_b^{\ddagger\theta} = \Delta G^{\theta} - \Delta G_f^{\ddagger\theta} \qquad (24)$$

$$\therefore k_f = w_f \nu_f e^{-\Delta G_f^{\ddagger\theta}/RT} - w_b \nu_b e^{-\Delta G_f^{\ddagger\theta}/RT} e^{\Delta G^{\theta}/RT} \frac{[C][B]}{[BC]} \qquad (25)$$

Assuming, as the reaction co-ordinate for the forward and reverse reaction is the same,

$$w_f \nu_f = w_b \nu_b \qquad (26)$$

$$k_f = w_f \nu_f e^{-\Delta G_f^{\ddagger\theta}/RT} \left[1 - e^{\Delta G^{\theta}/RT} \frac{[C][B]}{[BC]} \right] \qquad (27)$$

Now, from standard thermodynamics

$$\Delta G = \Delta G^{\theta} + RT \ln \frac{[C][B]}{[BC]} \qquad (28)$$

Where ΔG = change in Gibbs free energy

$$\therefore \ln \frac{[C]\,[B]}{[BC]} = \frac{\Delta G - \Delta G^{\theta}}{RT} \tag{29}$$

$$\therefore \frac{[C]\,[B]}{[BC]} = e^{(\Delta G - \Delta G^{\theta})/RT} \tag{30}$$

$$\therefore e^{\Delta G^{\theta}/RT} \frac{[C]\,[B]}{[BC]} = e^{\Delta G^{\theta}/RT} e^{(-\Delta G^{\theta} + \Delta G)/RT} \tag{31}$$

$$= e^{\Delta G/RT} \tag{32}$$

From (32) and (27)

$$k_{\mathrm{f}} = w_{\mathrm{f}} \nu_{\mathrm{f}} e^{-\Delta G_{\mathrm{f}}^{\ddagger\theta}/RT} [1 - e^{\Delta G/RT}] \tag{33}$$

From standard thermodynamics for the case of

$$AB_{(s)} \rightarrow A_{(s)} + B_{(g)}$$

$$\Delta G = \Delta G^{\theta} + RT \ln P_{\mathrm{B}} \tag{34}$$

Where

P_{B} = pressure of gas B

Now

$$\Delta G^{\theta} = -RT \ln P_{\mathrm{B}}^{*} \tag{35}$$

Where

P_{B}^{*} = equilibrium pressure of the gas B at temperature T

From Eqs (34) and (35) we may write;

$$\frac{\Delta G}{RT} = \ln \frac{P_{\mathrm{B}}}{P_{\mathrm{B}}^{*}} \tag{36}$$

From Eqs (33) and (36) we may write:

$$k_{\mathrm{f}} = w_{\mathrm{f}} \nu_{\mathrm{f}} e^{-\Delta G_{\mathrm{f}}^{\ddagger\theta}/RT} [1 - e^{\ln [P_{\mathrm{B}}/P_{\mathrm{B}}^{*}]}] \tag{37}$$

$$= w_{\mathrm{f}} \nu_{\mathrm{f}} e^{-\Delta G_{\mathrm{f}}^{\ddagger\theta}/RT} [1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*}] \tag{38}$$

Following the procedure given above to obtain Eq. (13) we may obtain the following from Eq. (38):

$$k_{\mathrm{f}} = w_{\mathrm{f}} \nu_{\mathrm{f}} e^{-\Delta S_{\mathrm{f}}^{\ddagger\theta}/R} e^{-\Delta H_{\mathrm{f}}^{\ddagger\theta}/RT} [1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*}] \tag{39}$$

Remembering

$$[1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*}] = e^{\ln(1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*})} \tag{40}$$

$$\therefore k_{\mathrm{f}} = w_{\mathrm{f}} \nu_{\mathrm{f}} e^{\Delta S_{\mathrm{f}}^{\ddagger\theta}/R} e^{-[\Delta H_{\mathrm{f}}^{\ddagger\theta} - RT \ln(1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*})]/RT} \tag{41}$$

Thus, by comparison with the usual form of the Arrhenius equation, the apparent activation energy, at any given temperature and product gas pressure, is given by

$$E_{\mathrm{apparent}} = \Delta H_{\mathrm{f}}^{\ddagger\theta} - RT \ln(1 - P_{\mathrm{B}}/P_{\mathrm{B}}^{*}) \tag{42}$$

Equation (42) may be used to examine whether any experimental measurements were made too close to the equilibrium gas pressure. If we assume that the entropy of activation for the forward reaction is independent of temperature, a tacit assumption of the Arrhenius equation (a point considered further below), together with Eqs (14) and (39) can be simplified to produce

$$k = A\, e^{-E/RT} (1 - P/P^{*}) \tag{43}$$

This expression has been derived by others. Barret derived this relationship by assuming an adsorbed intermediate layer [4], Benito and Searcy [5] by assuming one of the diffusion steps of the gaseous product to be rate limiting. Cutler *et al.* derived a similar expression [6] by postulating that, for calcium carbonate, CaO is first formed in some special activated form that occupies a constant fraction of the surface. Our derivation shows that no special assumption is necessary beyond that the reaction is reversible. However, it is reassuring that the same result can be reached by a variety of routes. Experimental confirmation that the relationship between the rate constant and the presseure of product gas is of the form given in Eq. (43), has been obtained by several workers [6–9], thus we can have some confidence that the general thrust of the arguments presented here must be correct.

The well known Van't Hoff relationship provides a means of predicting equilibrium pressure as a function of temperature, viz.

$$\ln P^{*} = -\frac{\Delta H}{RT} + \text{constant} \qquad (44)$$

Plotting the data given in reference [10] gives a good straight line plot and provides a value for the standard enthalpy of formation of calcium carbonate of 177 kJ/mol (see Fig. 1), which is in good agreement with literature values [11]. The equilibrium pressure is, thus, given by:

$$p^{*} = 2.6489\text{x}\,10^{10}\ e^{20298/T}\ \text{torr} \qquad (45)$$

We will assume the following values for the kinetic parameters;

$$A = 1\,\text{x}\,10^{8}\,\text{sec}^{-1} \qquad E = 210\ \text{kJ/mol}$$

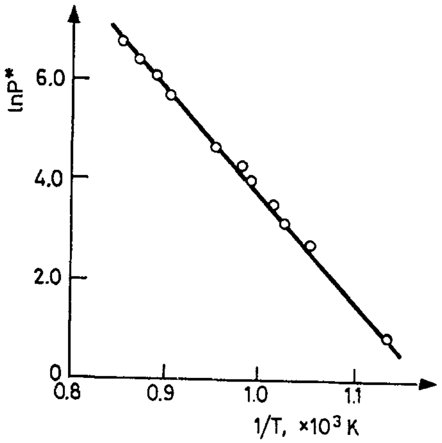

Fig. 1

The value for E is taken from [1] while the value for A is taken as an approximate value taken from the work given below.

Thus, Eq. (43) combined with (44) enables us to predict the shape of an Arrhenius plot at any given constant pressure of product gas. In Fig. 2 results are presented that show the effect of 4 different pressures. It can be clearly seen how a combination of high pressure and low temperature leads to a steeply descending plot that would give a vast overestimate of the value of the activation energy. While such a plot would be curved, this fact could easily be lost if only a small temperature interval were used or a curve fitting procedure with rising temperature data was employed [12].

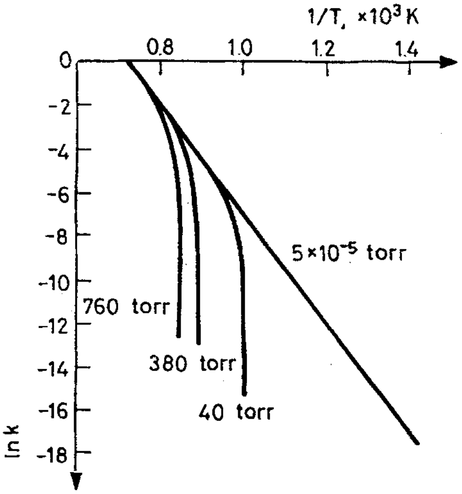

Fig. 2

The CRTA experiments previously presented [1] were carried out at the lowest pressure considered, 5×10^{-5} torr. It can be seen that at this low pressure no distortion of the Arrhenius plot is detectable even at the lowest temperature considered, 700 K. All of the data presented in Ref. [1] were gathered above this temperature and thus should provide the correct value for the activation energy, provided the assumed values for A and E are near to the true values. This argument may appear circular, but in [1] we went to some trouble to investigate the reaction over a very wide temperature range and obtained consistent results. It is unlikely that all of our measurements using CRTA were distored by excess product gas pressure. Given that the other experiments, where the product gas pressure is less well controlled, yield the same value, it must be assumed that during these experiments, the pressure of carbon dioxide also, did not rise to a value that impeded the forward reaction significantly.

We can again consider the table of literature values presented in Ref. [1], reproduced as Table 1, in the light of the results given above. In category a) are given the results of those experiments that conformed to the three criteria for good experimental practice suggested in Ref. [1] viz.

1) Rejection of methods based on a single rising temperature measurement.

2) The partial pressure of product gas in the sample environment should kept as low as possible, especially for reversible reactions.

3) Sample masses should be as low as possible, in order to minimise self-cooling effects.

Included in this category is the result obtained by Rouquerol [21] as, although the sample size is high, it was obtained by Rate Jump Constant Rate Thermal Analysis and can, therefore, be considered reliable. It can be seen that the results are in good agreement amongst themselves and also with those results presented by us earlier [1].

Table 1 Literature activation energies for the decomposition of calcium carbonate

Category	Reference	E, kJ/mol	Sample, mg	Atmosphere	Method*
a)	17	190–208	1–32	O_2	I
	18	201	4	Ar	I
	19	205	35–70	Vacuum	I
	20	210–212	10**	N_2	SRT
	21	201–217	100	Vacuum	JCRTA
b)	18	950	4	5% CO_2 in Air	I
	18	607–715	4	5% CO_2 in Air	RT
	18	2046–2155	4	CO_2	RT
	22	565–3828	1–16	CO_2	RT
c)	23	184	100	N_2	RT
	24	180–192	1000	–	RT
	25	163	290	air	RT
	26	216	100	air	RT
	27	170	250	N_2	RT
	17	142–297	1–16	O_2	RT
	18	213–226	4	Ar	RT
d)	17	170	455	air	I
	28	397	500–2000	air	I
	11	146–176	500	Vacuum	I
	30	172	300–450	N_2	I

*Methods are as follows: I = Isothermal, RT = single Rising Temperature experiment, SRT = several Rising Temperature experiments, JCRTA = Jump Constant Rate Thermal Analysis.

**Sample size supplied by Authors.

In category b) are given all those results that were obtained in atmospheres that contain significant amounts of carbon dioxide, the lowest value corresponding to approximately 40 torr. It can be seen that the values obtained are very much higher than those obtained under conditions designed to minimise product gas pressure category a). From the above results it can be seen that, far from this being and indication that we cannot apply the Arrhenius equation in the usual way to these types of reaction, as has been suggested [13], they are entirely in agreement with conventional kinetic theory. While most of the results in this category were obtained with methods based on a single rising temperature experiment (a method that gives unreliable results) this technique does not usually give values that are in error by an order of magnitude, whereas, some of the values are a factor of 10 higher than the real value. The most reliable result is that given by the isothermal methods which gives a value of 950 kJ/mol.

The significance of the other categories will be dealt with later in thus paper.

The effect of sample environment on the apparent α function and pre-exponential constant

Introduction

We start by recalling the basic equations usually used to describe the course of solid state thermal decomposition reactions:

$$\frac{d\alpha}{dt} = f(\alpha)\,Ae^{-E/RT} \tag{46}$$

Where

α = extent of reaction

t = time

$f(\alpha)$ = some function that is characteristic of the way the reaction interface proceeds through the sample

E = the activation energy

A = the pre-exponential constant

T = the absolute temperature

We also define the function $g(\alpha)$ such that

$$\int_{o}^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) \tag{47}$$

In this scheme the reaction rate constant k is given by

$$k = Ae^{-E/RT} \tag{48}$$

The correspondence between this treatment and the transition state approach used above can be seen by comparing Eqs (48) and (13). The pre-exponential factor is shown to be a function of the frequency of the reaction coordinate and the entropy of the activated intermediate. This is assumed, to a first approximation, not to change with temperature and can, therefore, be treated as a constant, A. In this section we are concerned with the alpha function and the value of A.

There are a large number of possible alpha functions that might apply to solid sate reactions. Here we will consider ten of the most commonly used, are given in Table 2. The theory behind these equations is well covered elsewhere [3]. However, it is worth observing that they fall into three categories; 1-3 describe the behaviour of a system in which nucleation is the rate determining process, 4-6 a system in which it is the geometric nature of the growth of the reaction interface that is important, while for 7-10, diffusion is the rate controlling process.

The isothermal results were analysed using the well known reduced time method [15], all plots are reduced to the time at alpha = 0.9. The CRTA results were analysed using the reduced temperature method described in Ref. [2], all plots are reduced to alpha = 0.3 and 0.9. Single rising temperature results were analysed using a variation of the method proposed by Whitehead [16] and used by us [1] for the analysis of multiple heating rate methods. The two relevant equations are

$$\ln\left[\frac{g(\alpha)}{T^2 I(E,T)}\right] = \ln\left[\frac{AR}{bE}\right] - \frac{E}{RT} \tag{49}$$

Where b = the heating rate
and

$$I(E,T) = 1 - \frac{2!}{(E/RT)} + \frac{3!}{(E/RT)^2} \tag{50}$$

Initially $I(E, T)$ is assumed to be 1 and the l. h. s of Eq. (49) is plotted against $1/T$. This gives an initial value for E which can then be fed into Eq. (50) for a re-evaluation of the integral $I(E, T)$. This iterative process can be continued until the desired accuracy is achieved, rapid convergence is the rule. In practice the iterative process was only applied to the three ex-

Table 2 Commonly used α functions for solid state decomposition reactions (see Ref. [3] for details)

No.		$f(\alpha)$ $[=(\mathrm{d}\alpha/\mathrm{d}t)/k]$	$g(\alpha)$ $[=kt]$	label
	Sigmoid Rate Equations			
1		$(1-\alpha)(-\ln(1-\alpha))^{\frac{1}{2}}$	$2[-\ln(1-\alpha)]^{\frac{1}{2}}$	A2
2	Avrami Erofe'ev	$(1-\alpha)(-\ln(1-\alpha))^{\frac{2}{3}}$	$3[-\ln(1-\alpha)]^{\frac{1}{3}}$	A3
3		$(1-\alpha)(-\ln(1-\alpha))^{\frac{3}{4}}$	$4[-\ln(1-\alpha)]^{\frac{1}{4}}$	
	Deceleratory			
4	first order	$(1-\alpha)$	$\ln(1-\alpha)$	F1
	Based on Geometric Models			
5	Contracting area	$(1-\alpha)^{\frac{1}{2}}$	$2[1-(1-\alpha)^{\frac{1}{2}}]$	R2
6	Contracting volume	$(1-\alpha)^{\frac{2}{3}}$	$3[1-(1-\alpha)^{\frac{1}{3}}]$	R3
	Based on Diffusion Mechanism			
7	One dimensional diffusion	α–1	$\frac{1}{2}\alpha^2$	D1
8	Two dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	D2
9	Three dimensional diffusion	$[1-(1-\alpha)^{\frac{1}{3}}]^{-1}(1-\alpha)^{\frac{2}{3}}$	$\frac{3}{2}[1-(1-\alpha)^{\frac{1}{3}}]^2$	D3
10	Ginstling Brounshtein	$[(1-\alpha)^{-\frac{1}{3}}-1]^{-1}$	$\frac{3}{2}[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]$	D4

pressions giving the most linear initial plots as iteration did little to improve the regression coefficient of a non-linear result. In principle, the expression giving the best regression coefficient should be the correct choice and thus provide the alpha function, the activation energy and pre-exponential factor from one experiment. In practice, however, we shall show that this procedure is not reliable.

Experimental

The details are given in [1]; in brief, Analytical Grade precipitated calcium carbonate was studied using two thermobalances, one for vacuum work, (Mettler Thermoanalyser No. 76), the other for flowing atmospheres, (Stanton Redcroft TG 750). The vacuum microbalance was modified to enable it to perform CRTA experiments which were all carried out at a regulated pressure of 5×10^{-5} torr. During the rising temperature and isothermal experiments performed under vacuum, the pressure never exceeded $5x10^{45}$ torr. Isothermal and rising temperature experiments were carried out under flowing nitrogen at 20 ml/min and 200 ml/min. All samples were about 10 mg except two CRTA experiments, which used 100 mg samples.

Results

CRTA

The reduced temperature plot for a 10 mg sample decomposed at a rate of 1.684×10^{-4}/sec, is given in Fig. 3. Comparison with master curves given in Ref. [2] clearly indicates that the alpha function is an order expression. This is confirmed by plotting theoretical reduced temperature for this function against experimental reduced temperature, given in Fig. 4. A good fit should give a regression coefficient close to 1, with a slope of 1 and an intercept at the origin. It can be seen that the agreement is excellent. All of the CRTA experiments show similar behaviour. Two samples of 10 mg and two samples of 100 mg were investigated. It should be recalled that, with the CRTA apparatus used here, the reaction rate is inversely proportional to the mass of the sample. It was decided to examine both fast and slow reaction rates, thus it was contrived that the slow rate of the small sample should be roughly equivalent to the fast rate of the large sample, in this way the effect of sample size could be compared. In this analysis the alpha function can be of the general form

$$f(\alpha) = (1 - \alpha)^n \tag{51}$$

where

n = the reaction order

Thus the reaction order is not limited to a particular value such as those given in Table 2. Following the procedure given in [2] and taking E to be 210 kJ/mol, as determined in [1], n can be found. Table 3 summarises the results, they are also compiled in Table 4.

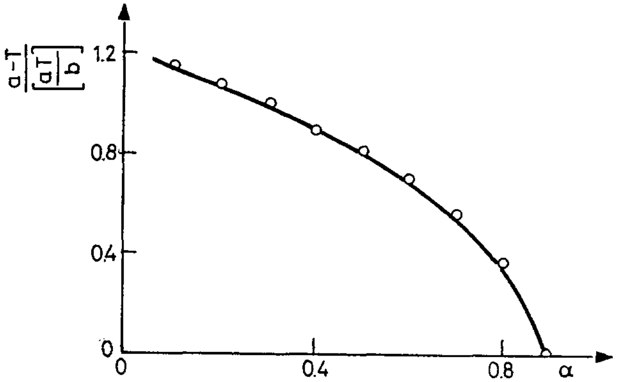

Fig. 3

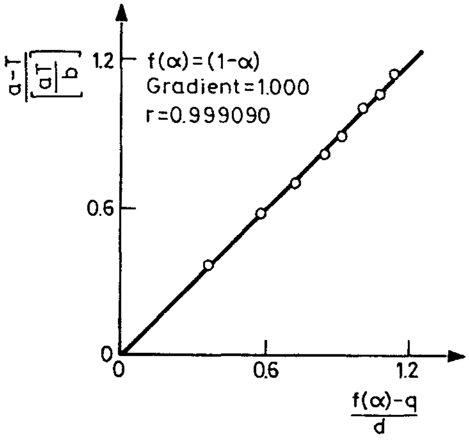

Fig. 4

Isothermal

Figure 5 shows a collected reduced time plot for calcium carbonate sieved between 53-45 micron. The data were collected under flowing nitrogen at 200 ml/min at 883, 891, 901, 910, 918 and 935.5 K. The error bars illustrate that the results show good isokinetic behaviour, this is typical of all the other isothermal results. The best fit from the equations in Table 2 was

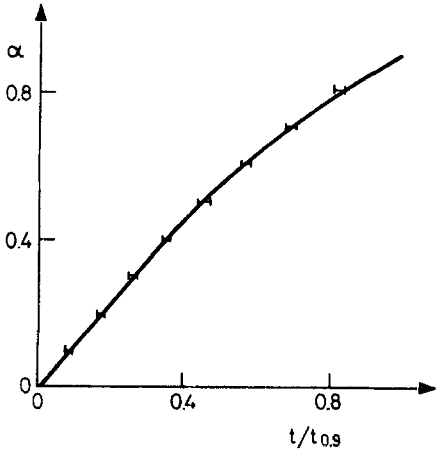

Fig. 5

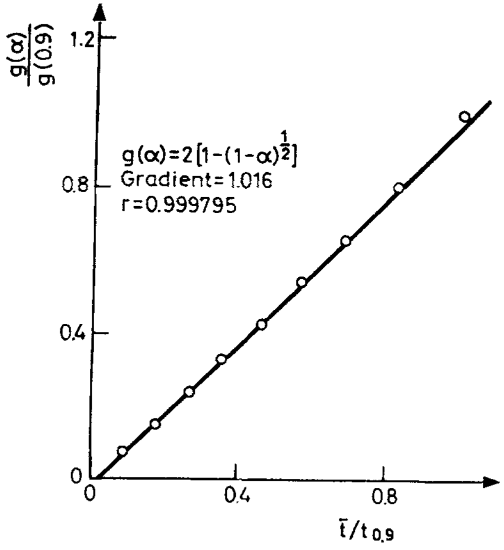

Fig. 6

found to be Eq. R2 (No. 5). A plot of theoretical reduced time against experimental is given in Fig. 6, the agreement is excellent. In common with the CRTA results, this procedure should ideally give a regression coefficient close to 1 with a slope of 1 and an intercept at the origin. This procedure to determine the alpha function was used for all the isothermal results, Table 4 gives the collected results for the best fits. Figure 7 shows the collected reduced time plots. The clear conclusion is that the alpha function changes with experimental conditions. It is to be expected that sieving the sample should change $f(\alpha)$. However, the way it changes with flow rate and when moving from atmospheric pressure to vacuum conditions is an indication that the function being determined is not the 'true' kinetic function. The function indicated by the CRTA results, given above, of a reaction order of 1.5 for the 10 mg sample, was investigated for the vacuum experiments.

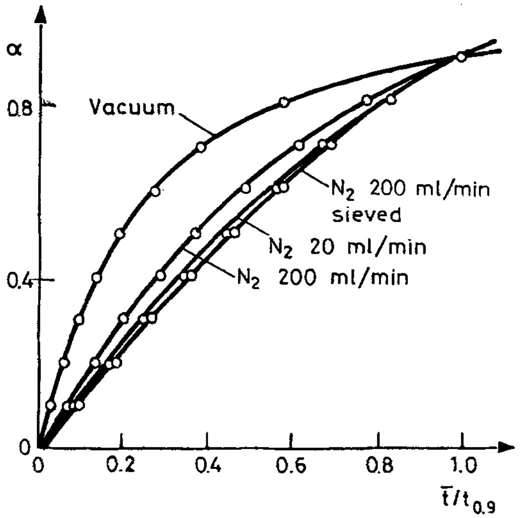

Fig. 7

Table 3 Reaction orders determined from constant rate thermal analysis results

No.	Weight, mg	Rate	n	A/sec^{-1}
1	10	1.684x10^{-4}	1.500	5.935x10^{8}
2	10	2.671x10^{-5}	1.489	6.719x10^{8}
3	100	2.380x10^{-5}	1.193	4.466x10^{8}
4	100	1.828x10^{-6}	1.148	2.613x108

Comparatively poor agreement was obtained, regression coefficient = 0.990155, gradient 0.965 and an intercept of −0.05.

Rising temperature

The procedure outlined above for this type of experiment was applied to all of the experiments carried out at a heating rate or 1 deg/min (nominal heating rates were not assumed, they were measured in each case). The

Table 4 Summary of apparent α functions and A values for the decomposition of calcium carbonate under a variety of conditions

Expt. No.	Sample Size, mg	Method	Conditions	$f(\alpha)$	A/sec^{-1} (E/kJ mol^{-1})**
1	10	Constant Rate Thermal Analysis	5x10^{-5} torr	$(1-\alpha)^{1.5}$	5.935x10^{8}
2	10	Constant Rate Thermal Analysis	5x10^{-5} torr	$(1-\alpha)^{1.5}$	6.719x108
3	100	Constant Rate Thermal Analysis	5x10^{-5} torr	$(1-\alpha)^{1.2}$	4.466x108
4	100	Constant Rate Thermal Analysis	5x10^{-5} torr	$(1-\alpha)^{1.1}$	2.613x108
5	10	Single Rising* Temperature	Following N_2 at 200 ml/min	$(1-\alpha)^{0.5}$	7.535x107 (217)
6	10	Single Rising* Temperature	Following N_2 at 200 ml/min	$(1-\alpha)^{1.0}$	5.307x108 (219)
7	10	Single Rising Temperature	Following N_2 at 20 ml/min	$(1-\alpha)^{0.67}$	1.786x107 (211)
8	10	Single Rising Temperature	Vacuum <5x10–4 torr	$(1-\alpha)^{1.5}$	2.985x108 (217)
9	10	Isothermal*	Following N_2 at 200 ml/min	$(1-\alpha)^{0.5}$	1.664x108
10	10	Isothermal	Following N_2 at 200 ml/min	$(1-\alpha)^{0.67}$	7.352x108
11	10	Isothermal	Following N_2 at 20 ml/min	$(1-\alpha)^{0.5}$	1.212x107
12	10	Isothermal	Vacuum <5x10–4 torr	$(1-\alpha)^{1.0}$	1.151x108

* Sample sieved between 53-45 microns (other samples not sieved)

**Activation energy, E, given for Single Rising Termperature experiments where it was used as a criterion for selecting the correct alpha function.

most appropriate alpha function was chosen on the basis of which expression gave an activation energy closest to the previously determined [1] value of 210 kJ/mol. In only one case (Expt. No. 6, Table 4), the unsieved sample under a nitrogen flow rate of 200 ml/min, was the function from Table 1 that gave the highest regression coefficient also the function that fulfilled this criterion. For the sieved sample under nitrogen at 200 ml/min, (Expt. No. 5, Table 4), the best fit was given by equation D3 in Table 2 (No. 9) regression coefficient = 0.999588, with an activation energy of 475 kJ/mol. The third best fit was give by Eq. R2, in Table 2 (in No. 5) regression coefficient = 0.998960, with an activation energy of 217 kJ/mol. Given that our previous work presents very strong evidence that the true activation energy for this reaction is about 210 kJ/mol, the above example illustrates why the analysis of a single rising temperature experiment can give rise to very misleading conclusions. For the sample under vacuum, (Expt. No. 8 Table 4) the best fit was given by function F1, in Table 2 (in No. 4) regression coefficient = 0.998700, with an activation energy of 180 kJ/mol, this was the closest obtained to the correct value. The CRTA results for the 10 mg samples give a reaction order of 1.5. This function was tried and an activation energy of 217 kJ/mol with a regression coefficient = 0.999357 was obtained, thus giving both the best fit and the E value closest to 210 kJ/mol.

Discussion of results

Table 4 summarises the different alpha function and A values obtained by the different methods and experimental conditions used. One interesting feature is the fact that all of the alpha functions are of the order type, none of the results indicates that nucleation or diffusion are the rate limiting process. However, the apparent order varies from 0.5 up to 1.5. The A value varies by more than an order of magnitude.

The variation in the A value is, perhaps, not too surprising as this would be very sensitive to errors on the slope of the Arrhenius plot, which inevitably do occur. The massive variation in the apparent order of the reaction is, however, very surprising.

A consistent trend in the change in reaction order can be identified. It is reasonable to assume that in moving from flowing nitrogen at 20 ml/min to 200 ml/min and that to vacuum, the average pressure of product gas in the sample environment decreases. Taking the isothermal results first (neglecting the sieved samples, which will behave differently from the others) we obtain a reaction order of 0.5, 0.6 then 1 when moving from high to low pressure. The same comparison for the rising temperature results reveals a trend of 0.6, 1 then 1.5 (this last value is 1 if the choice is confined to Table 1 but it is known that 1.5 gives a better fit and an activation energy much closer to the known value for the vacuum experiment). The CRTA experiments, that undoubtedly maintained the lowest pressure over the majority of the reaction, give a value of 1.5 for the 10 mg samples, though lower values were obtained for the 100 mg samples. When an apparent reaction order increases, this means that, relatively speaking, the early part of the reaction is faster in comparison the latter part i.e., when looking at a reduced time plot, a higher extent of rection is achieved at a lower reduced time value. There are two reasons why this might occur.

The first is clear when the first section of this article is considered. In the isothermal experiment the early part of the reaction is fast, thus giving rise to a relatively high product gas pressure. This pressure then slows down the reaction through the back reaction. This effect is greater at the start of the reaction than at the end, thus it will tend to decrease the apparent reaction order. This effect will become more important as the efficiency of product gas removal declines, this is consistent with the isothermal results. The application of this argument is less clear in the case of the rising temperature results but in general, in the early stages of the reaction, the product gas concentration is rising, thus impeding the progress of the decomposition, while in the latter stages it is declining, thus favouring faster decomposition. The net effect should be a decrease in apparent reaction order. Again, more efficient product gas removal will reduce this effect thus the observed trend is consistent with this theory. This explanation relies upon the pressure of product gas having sufficient influence to distort the way in which the reaction rate changes as a function of extent of reaction but not as a function of temperature. This last point must be true as the measured activation of energies are not greatly distorted by changing experimental conditions [1]. This may be possible as, from Eq. (42), it can be inferred that the product gas pressure can have a significant but not profound effect except when it is close to the equilibrium pressure, whereas the reaction rate has an exponential dependence on temperature.

There is potentially a second, more subtle, effect that could contribute to an explanation of the observed trends. It is commonly assumed that solid state decomposition reactions proceed through the advancement of an interface that is effectively a two dimensional object that consumes the surface of a decomposing particle then proceed geometrically to the core. However, it is known that carbon dioxide can diffuse within calcium carbonate [14] thus it is possible that a carbonate ion removed from the surface that the interface traditionally represents, could decompose and then the product gas could diffuse to an adjacent surface giving access to the external environment. Under this supposition the interface could be considered to have a certain thickness and this thickness could be significant with respect to the diameter of a decomposing particle. Further, this means that initially the interface could be very convoluted, perhaps fractal in nature, and this would mean that the initial rate of reaction would be very high. As the particle is consumed the very high initial surface area would decline rapidly. This could give rise to high apparent reaction orders. This type of effect would be reduced as the pressure of product gas increases because the ability of carbon dioxide to diffuse from the bulk to the surface in reduced. This phenomenon could not only contribute to an explanation of the observed increases in reaction order with decreasing product gas pressure, but also to the high ultimate reaction order of 1.5 using CRTA. A prediction of this theory would be that lower pressures would give rise to higher specific surface areas especially during the early stages of the reaction.

Notwithstanding the above arguments, the discrepancy between the reaction order obtained using the 10 mg samples and those obtained with the 100 mg samples indicates that even CRTA results ara prone to error. The explanation might lie in temperature gradients through the sample bed that are simply a consequence of the proximity of the exterior of the sample to the furnace wall. This source of error is particularly acute in vacuum systems. Confirmation of the theories proposed above and the elucidation of the true alpha function for this reaction will have to be consigned to future work.

Overall conclusions

If we consider Table 1 the following points are now apparent. In Category a) the experimental results that have been obtained following our recommended criteria for good experimental practice are collected. They are all in good agreement amongst themselves and with the values obtained by us [1]. It is our contention that these values are close to the true value for the activation energy for this reaction within the context of the well known energy barrier model for chemical kinetics. In Category b) the results obtained under significant pressures of carbon dioxide are collected. They give very high values for E. From the results presented in the first section of this article it can be seen that this fact is in complete agreement with what would be expected based on traditional kinetic arguments. In Category c) the values obtained by analysis of a single rising temperature experiment are collected. The results show this to be an unreliable method that may or may not give the right answer. The remaining results are assembled in Category d). These are all isothermal experiments using large samples. They are, with one exception, rather low, which is exactly what would be expected from the self cooling effects that large samples generate. The single exception uses very large samples indeed (500-2000 mg), thus the results may be affected by a build up of carbon dioxide in the reaction chamber. Overall, the results reveal no surprises. Where good experimental practice has been followed, coupled to reliable methods of data analysis, consistent reproducible activation energies are obtained. When high pressures of product gas are introduced into sample environment, very high activation energies are observed and this is completely consistent with conventional kinetic theory. Analysis of single rising temperature experiments are unreliable and may or may not lead to a correct for E. Large samples tend to produce low values of E due to self cooling effects, this is also entirely consistent with conventional kinetic theory and what is known of the effects of experimental errors in these types of experiment. Thus, we can see that the 'significant deviations' referred to in the opening paragraph of the Introduction of this paper arise from an uncritical acceptance of the literature. When only reliable results are considered, based on the dictates of conventional kinetic theory and good experimental practice, then good agreement is found for activation energies.

When the alpha function and the value of A are considered the picture is less clear. Our results suggest this can be significantly affected by the partial pressure of product gas in the sample environment and the way in which it changes with the progress of the reaction. They imply that nucleation or diffusion are not the rate controlling factors in this reaction, but that it is best described by an order expression. However, the apparent order changes with experimental conditions. We propose above an explanation of why this may occur and present a new theory of how the reaction interface in these types of reaction may proceed through small sample particles and how it might change with product gas pressure. There may, in fact, be no 'true' alpha function. It is entirely possible that it is a function of product gas pressure. All of this indicates that it is most important to control the pressure of product gas in order to observe the kinetics of these types of reaction, thus CRTA remains the best method of studying them. It is hoped that future work will either confirm or disprove the ideas presented here.

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Zusammenfassung — Im Anschluß an vorangehende Arbeiten zur Messung sinnvoller Aktivierungsenergien und zur Anwendung von CRTA bei der Bestimmung kinetischer Parameter untersuchen wir hier weitere Fehlerquellen bei der Bestimmung der Aktivierungsenergien und stellen Überlegungen zur Form der Alpha-Funktion bzw. zum Wert von A an. Ausgehend von theoretischen Argumenten, die auf der Theorie des Übergangszustandes basieren, schlossen wir darauf, daß es unter Berücksichtigung bedeutender Drücke der in der Reaktionsumgebung auftretenden gasförmigen Produkte zu sehr hohen Werten für die scheinbaren Aktivierungsenergien kommt. Es sei bemerkt, daß, obwohl dies in der Praxis für Calciumkarbonat beobachtet werden kann, es in keiner Weise die Anwendung der Arrheniusschen Gleichung bei Feststoff-Zersetzungsreaktionen in Frage stellt, vorausgesetzt, man vermeidet diese Art von Beeinflussung der Versuchsergebnisse. Für die Zersetzung von Calciumkarbonat versuchten wir, die Alpha-Funktion unter Anwendung von Daten zu bestimmen, die einer Reihe verschiedener Temperaturprogramme und Reaktionsbedingungen entstammen. Man fand, daß die scheinbare Alpha-Funktion von der angewendeten Methode und den Versuchsbedingungen abhängt. Es wird eine Erklärung dafür vorgeschlagen und vorläufig eine neue Betrachtungsweise für derartige Reaktionen eingeführt. Bei einer Durchsicht der Literatur konnte darauf geschlossen werden, daß zwar sehr viele Varianten für die Aktivierungsenergie von Calciumkarbonat existieren, daß aber eine kritische Einschätzung zu einer guten Übereinstimmung derjenigen Werte führt, denen gute Versuchspraktiken und eine zuverlässige Datenverdichtung zugrunde liegen. Die scheinbaren Unterschiede der Ergebnisse können unter Berücksichtigung der vorgebrachten theoretischen Argumente und leicht verständlicher experimenteller Fehlerquellen erklärt werden.