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Review

A review of the ICTAC kinetics project, 2000
Part 2. Non-isothermal results

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ABSTRACT

The analysis of the ICTAC kinetics study, considered in Part 1, is extended to non-isothermal results. This time there are many analysis methods to be tested by writing our own computer programs. Again the results were compared with those obtained by the contributors using commercial or their own programs. Possible reasons for errors in the original study are suggested and recommendations made.

Contents

1. Introduction

The organisers of the original ICTAC study supplied non-isothermal data for calcite decomposition in vacuum and nitrogen. These samples were heated at rates of 1.8, 2.5, 3.5, 5.0, 6.2 and 10 K/min in nitrogen and 1.0, 3.0, 5.0, 7.5, 10, 15 and 25 K/min under vacuum. The simulated data from the study (two equally-weighted, parallel, first-order reactions) was also partially analysed by us.

The problems associated with analysing this data are somewhat different from those for isothermal data in Part 1 (previous paper).

Firstly, there are a larger number of different methods of analysis.

Secondly, there is the problem of evaluating the integral of the exponential term in the Arrhenius equation, usually represented by $p(x)$, where $x = E_a/RT$. The evaluation of this quantity for various values of T has traditionally been made by various approximating functions, summarised in Ref. [1]. In this paper the evaluation has been carried out mostly by Chebyshev polynomials described in Ref. [1]. These have already been shown to produce precise values,

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Table 1
Simulated non-isothermal data.

Method	Designation	E_a (kJ mol^{-1}) Mean	E_a (kJ mol^{-1}) Overall	ln (A/s)	Exponent $n' = 1/(1-p)$	min DEV in α
Non linear regression (NLR)						
Direct grid search, n'-dimensional Avrami–Erofeev equation	OI		130.000	29.934	1.9999	4.941×10^{-7}
Nelder–Mead((simplex)						
A. Standard Avrami–Erofeev equation, $n' = 2.0$	OI		129.999	29.933	(A2) (2.0)	8.119×10^{-8}
B. n'-dimensional Avrami–Erofeev equation	OI		129.999	29.933	2.0000	8.017×10^{-8}
C. Sestak–Berggren equation	OI		130.045	30.666	$n = 0.8035$ $m = 0.5066$	7.540×10^{-4}
Flynn & Wall	MI	129.992		29.933	(A2) (2.0)	5.881×10^{-4}
Ozawa	MI	130.980		30.637	(A2) (2.0)	0.16372
NPK (differential fit)						
A. Standard Avrami–Erofeev equation, $n' = 2.0$	OMD	130.009	130.027	29.942	(A2) (2.0)	5.29×10^{-4}
B. n'-Dimensional Avrami–Erofeev equation	OMD	(As *A*)	(As *A*)	29.941	1.9996	9.201×10^{-6}
C. Sestak–Berggren equation	OMD	(As *A*)	(As *A*)	29.969	$n = 0.8040$ $m = 0.5069$	7.544×10^{-4}
Friedman Isoconversional $n' = 2.0$	MI	130.062		30.004	(A2) (2.0)	1.969×10^{-5}
Li and Tang	MD	129.986		–	–	–
Coats and Redfern	MI	129.778		29.751	1st order	0.12326
Kissinger 5 points	OD		129.724	29.868	(A2) (2.0)	1.993×10^{-3}
Akahira and Sunose	MI	129.778		29.819	(A2) (2.0)	2.156×10^{-2}
Kofstad	OD		129.998	29.931		8.831×10^{-4}
Ingraham and Marrier	OD		126.344	23.718	(A2) (2.0)	–
Other methods not in the ICTAC paper						
NPK (integral fit)						
A. Standard Avrami–Erofeev equation, $n' = 2.0$	OMI	129.998	129.998	29.933	(A2) (2.0)	6.957×10^{-6}
B. n'-Dimensional Avrami–Erofeev equation	OMI	(As *A*)	(As *A*)	29.933	2.0000	1.384×10^{-7}
C. Sestak–Berggren equation	OMI	(As *A*)	(As *A*)	29.962	$n = 0.8036$ $m = 0.5068$	7.541×10^{-4}
Vyazovkin	MI	130.00		29.934	(A2) (2.0)	6.791×10^{-5}

Simulated from an Avrami–Erofeev equation (A2), using $E_a = 130.000$ kJ/mol, $A = 10^{13}$ s^{-1}, ($\ln(A) = 29.934$), $n' = 2.0$, analysed either as a general Avrami–Erofeev mechanism of dimension n' or assumed (A2) mechanism. Where no ln(*A*) was generated by the method, no value is quoted. The Ingraham and Marrier method only gives *A′*, the temperature coefficient of *A*. Designation column. O: single overall value of E_a. M: mean value of E_a from the set varying with α. I: integer method – original data used directly. D: differential method – original data has to be differentiated.

not an approximation, and may be evaluated up to the maximum precision of variables held in a computer program.

Thirdly, the temperature range covered is larger than for isothermal experiments and there is the likelihood of a change in E_a as α increases because temperature is rising at the same time.

In this paper an attempt is made to reproduce results from all of the methods listed in the original paper [2]. The results are compared to see if consistent best values of E_a and *A* can be established. Each method is considered using in turn the non-isothermal data for calcite decomposing under vacuum and nitrogen. To test the methods and to check on the performance of the computer programs, non-isothermal simulated data was made up using a value of E_a of 130.0 kJ/mol and *A* of 1.0×10^{13} s^{-1} and a single kinetic equation (A2) from Table 1, Part 1. Also, the simulated results for two reactions combined, provided for the ICTAC study in Ref. [2], were analysed.

In the tables of results, Tables 1–3, a designation of calculation type is shown. Designation 'O' means that a method yields only single overall values of E_a and A. Other methods, designated by 'M', produce a set of E_a and *A* values varying with the degree of decomposition α. The mean of these values is what is shown in the tables. Some methods may, of course yield both mean values and overall values, which are not necessarily the same. The ICTAC paper results [2] only gave single values, but it is essential to show the variation if possible. The variation in E_a is, however, shown in the follow-up paper by Vyazovkin [3], for some of the ICTAC data. The methods are further divided between 'I' for integral methods if the deviation of the integral plot of α versus temperature is matched against the theoretical plot, and 'D' for differential methods if $d\alpha/dt$ is matched. Differential methods mean that differentiation of the data is required at some point. Figs. 1 and 2 show the results of applying this to the two sets of data. The plots are very similar to Figs. 1 and 2 in Part 1 for isothermal results. The values of $d\alpha/dt$ have been rescaled to 0–1 separately for each heating rate because the value of $(d\alpha/dt)_{max}$ differs greatly between heating rates. The irregular shape of the gradient plots forecasts, similarly to the isothermal case, that the differential methods will not be very precise.

2. Methods of calculation

The various techniques are listed in the Tables 1–3 and illustrated in Figs. 3–9. The details of these calculations are given in Ref. [2] or may be found in the references given below.

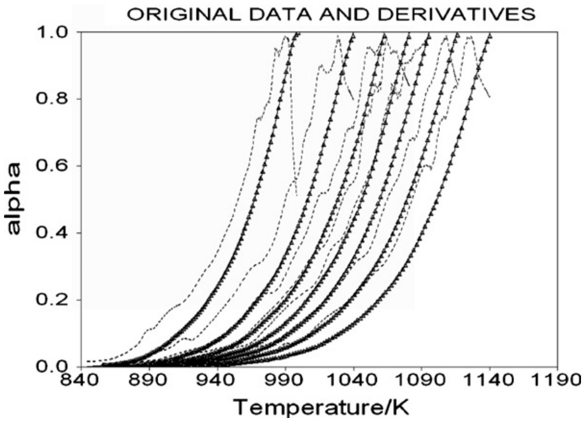

Fig. 1. Thermogravimetric plot together with differential plots for calcite decomposed under nitrogen at various heating rates (1.0, 3.0, 5.0, 7.5, 10.0, 15.0 and 25.0 K min^{-1}); (△) experimental points; (----) curve fitted to the experimental points; (....) differential plot. The differentials are re-scaled to appear as all the same peak height.

Table 2
Calcite decomposed non-isothermally under nitrogen.

Method	Designation	E_a (kJ mol^{-1}) Mean (all)	E_a (kJ mol^{-1}) Mean ($\alpha > 0.1$)	E_a (kJ mol^{-1}) Overall	ln(A/s)	Exponent n	Min DEV in α
Non linear regression (NLR)							
Direct grid search variable n	OI			194.309	15.838	0.1311	1.112×10^{-2}
Nelder–Mead(simplex)							
A. Standard zero order	OI			192.207	15.507	Zero order	1.907×10^{-2}
B. Near zero order (Fn)	OI			194.310	15.838	0.1311	1.112×10^{-2}
C. phase boundary (Rn)	OI			194.325	15.699	1.1510	1.112×10^{-2}
D. Sestak–Berggren equation	OI			193.893	15.872	$n = 0.1923$ $m = 0.0357$	1.076×10^{-2}
Flynn and Wall	MI	194.389	193.198		15.939	Zero order	7.388×10^{-2}
Ozawa	MI	200.329	199.511		17.301	Zero order	0.4902
NPK (differential fit) as by Sempere							
A. Zero order equation	OMI	192.962	193.397	192.894	15.760	Zero order	7.349×10^{-2}
B. n-Order equation	OMI	(As A)	(As A)	(As A)	15.663	0.1198	1.136×10^{-2}
C. Sestak–Berggren equation	OMI	(As A)	(As A)	(As A)	15.068	$n = 0.1928$ $m = 0.0409$	1.087×10^{-2}
Friedman Isoconversional	MD	193.091	193.481		16.071	Zero order	2.086×10^{-2}
Li and Tang	MD	190.938	191.140		–	–	–
Coats and Redfern	MI	194.467	193.280		16.824	1st order	0.1082
Kissinger 15 points	OD			193.182	15.754	Zero order	5.639×10^{-2}
Akahira and Sunose	MI	193.875	192.678		16.462	Zero order	0.4297
Kofstad	OD		187.052		14.973	Zero order	3.935×10^{-2}
Ingraham and Marrier	OD			176.268	4.756	Zero order	–
Other methods not in the ICTAC paper							
NPK (integral fit)							
A. Zero order equation	OMI	194.285	193.991	194.299	15.659	Zero order	4.025×10^{-2}
B. n-Order equation	OMI	(As A)	(As A)	(As A)	15.837	0.1311	1.112×10^{-2}
C. Sestak–Berggren equation	OMI	(As A)	(As A)	(As A)	15.225	$n = 0.1925$ $m = 0.0339$	1.078×10^{-2}
Vyazovkin	MI	194.580	193.284	–	16.727	Zero order	0.5898

Analysed either as a generalised order equation, phase boundary or an assumed 1st or zero order equation. Where no ln(A) was generated by the method, no value is quoted. The Ingraham & Marrier method only gives A', the temperature coefficient of A. Designation column. O: single overall value of E_a. M: mean value of E_a from the set varying with α. I: integer method – original data used directly. D: differential method – original data has to be differentiated.

Table 3
Calcite decomposed non-isothermally under vacuum.

Method	Desig-nation	E_a (kJ mol^{-1}) Mean (all)	E_a (kJ mol^{-1}) Overall	ln(A/s)	Exponent $n' = 1/(1-p)$	min DEV in α
Non linear regression (NLR)						
Direct grid search, n'-dimensional Avrami–Erofeev equation	OI		120.030	10.118	1.9614	1.844×10^{-2}
Nelder–Mead(simplex)						
A. Standard Avrami–Erofeev equation $n' = 2$.	OI		119.193	9.997	(A2) (2.0)	1.865×10^{-2}
B. n'-Dimensional Avrami–Erofeev equation	OI		120.042	10.120	1.9613	1.844×10^{-2}
C. Sestak–Berggren equation	OI		120.193	10.919	$n = 0.8776$ $m = 0.5181$	1.782×10^{-2}
Flynn and Wall	MI	124.003		11.139	(A2) (2.0)	0.1813
OzaO Ozawa	MI	130.682		12.569	(A2) (2.0)	0.3366
NPK (differential fit) as by Sempere						
A. Standard Avrami–Erofeev equation $n' = 2$	OMI	102.496	104.055	8.052	(A2) (2.0)	0.1461
B. n'-Dimensional Avrami-–Erofeev equation	OMI	(As A)	(As A)	7.865	2.2069	3.859×10^{-2}
C. Sestak–Berggren equation	OMI	(As A)	(As A)	7.932	$n = 0.8185$ $m = 0.5637$	3.843×10^{-2}
Friedman Isoconversional	MD	102.402		8.113	(A2) (2.0)	0.2816
Li & Tang	MD	111.184		–	–	–
Coats and Redfern	MI	124.030		11.768	1st order	0.1211
Kissinger 25 points	OD		124.010	10.628	(A2) (2.0)	4.026×10^{-2}
Akahira and Sunose	MI	123.299		13.089	(A2) (2.0)	0.6429
Kofstad	OD		100.590	7.999	(A2) (2.0)	0.3482
Ingraham and Marrier	OD		96.354	−1.636	(A2) (2.0)	–
Other methods not in the ICTAC paper						
NPK (integral fit)						
A. Standard Avrami–Erofeev equation $n' = 2$	OMI	123.686	124.594	10.609	(A2) (2.0)	8.171×10^{-2}
B. n'-Dimensional Avrami–Erofeev equation	OMI	(As A)	(As A)	10.733	1.8956	2.018×10^{-2}
C. Sestak–Berggren equation	OMI	(As A)	(As A)	10.852	$n = 0.8977$ $m = 0.5056$	1.948×10^{-2}
Vyazovkin	MI	123.979	–	13.594	(A2)(2.0)	0.6448

Analysed either as an assumed (A2) mechanism, a generalised Avrami–Erofeev equation (variable n'), or as a 1st order mechanism Where no ln(A) was generated by the method, no value is quoted. The Ingraham and Marrier method only gives A', the temperature coefficient of A. Designation column. O: single overall value of E_a. M: mean value of E_a from the set varying with α. I: integer method – original data used directly. D: differential method – original data has to be differentiated.

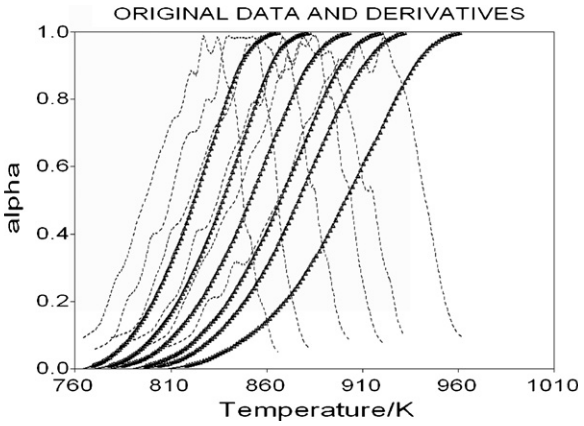

Fig. 2. Thermogravimetric plots together with differential plots for calcite decomposed under vacuum at various heating rates (1.8, 2.5, 3.5, 5.0, 6.2 and 10.0 K min^{-1}); (△) experimental points; (- - - -) curve fitted to the experimental points; (. . . .) differential plot. The differentials are re-scaled to appear as all the same peak height.

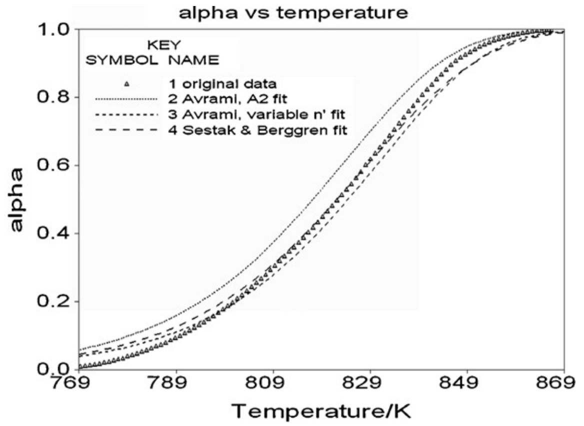

Fig. 3. Comparison of reconstructed curves with original data, using various kinetic equations. Sample: calcite decomposed in nitrogen. One heating rate only, 10 K/min. Plots 1, 4 and 5 are coincident over most of the range.

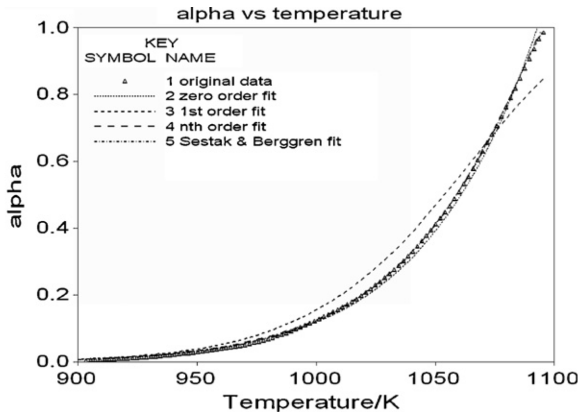

Fig. 4. Comparison of reconstructed curves with original data, using various kinetic equations. Sample: calcite decomposed under vacuum. One heating rate only, 1.5 K/min.

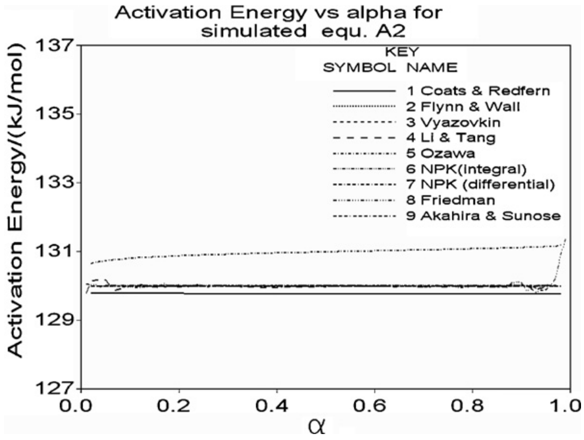

Fig. 5. Activation energy versus α for various calculation methods. Sample: data simulated for Avrami–Erofeev equation (A2) (extended ordinate scale). Several plots are near coincident.

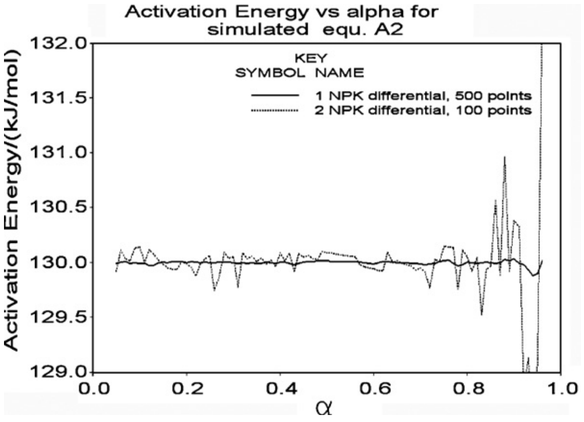

Fig. 6. Activation energy versus α from an analysis by the NPK differential method only. Sample: Data simulated for Avrami–Erofeev equation (A2) with sets of 100 and 500 points (extended ordinate scale).

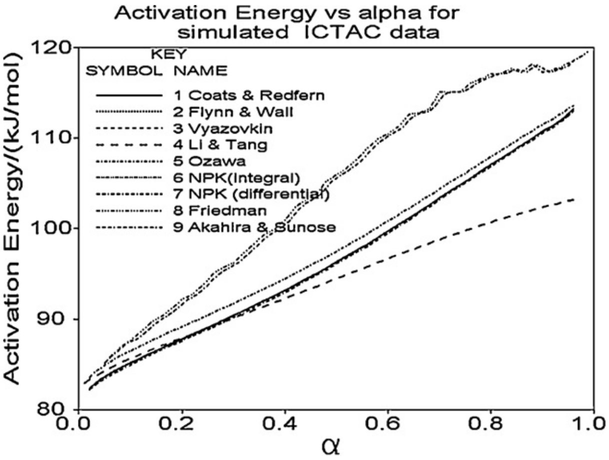

Fig. 7. Activation energy versus α for various calculation methods. Sample: Simulated data provided for the ICTAC report (two 1st order reactions combined). Plots 1, 2, 3 and 6 are coincident and appear as a single black line (expanded ordinate scale).

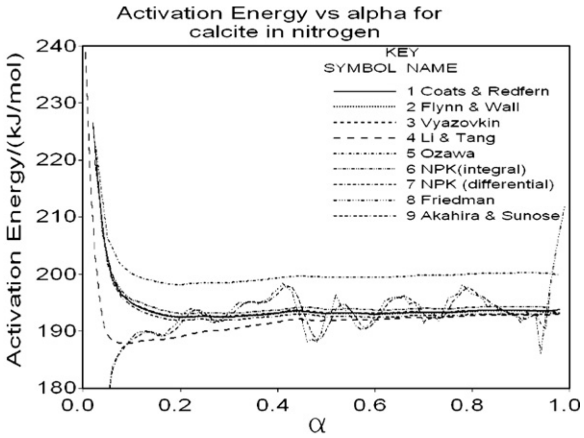

Fig. 8. Activation energy versus α for various calculation methods. Sample: Data calcite decomposed in nitrogen. Plots 1, 2 and 3 are coincident and appear as a single black line.

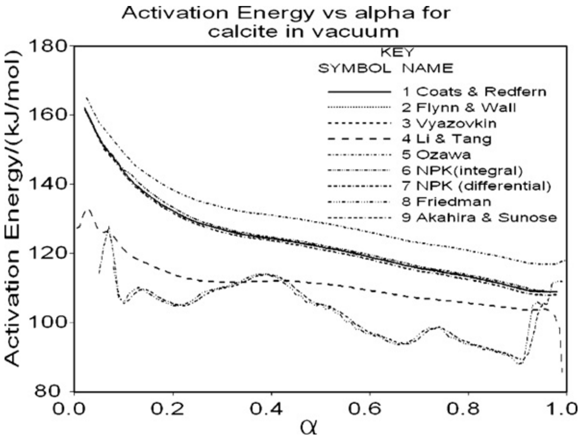

Fig. 9. Activation energy versus α for various calculation methods. Sample: Data calcite decomposed under vacuum. Plots 1, 2 and 3 are coincident and appear as a single black line.

Method	Ref.
Coats and Redfern	[4]
Ozawa	[5,6]
Flynn and Wall	[7]
Li and Tang	[8,9]
Akahira and Sunose	[10]
NPK	[11–13]
Friedman (Isoconversional)	[14]
(This result was obtained as part of the NPK calculation)	
Kofstad	[15]
Ingraham and Marrier	[16]
Kissinger	[17,18]
Freeman and Carroll	[19–22]
To these has been added a technique, not mentioned in Ref. [2], but has been referred to in Ref. [3]	
Vyazovkin	[23–26]

In the tables in Ref. [2] Desseyn refers to the Ozawa method, while others use the Flynn, Wall and Ozawa method. We have assumed that Desseyn means the original Ozawa method and the others mean the Flynn and Wall modification of the Ozawa method. We have therefore used separate calculations for the original Ozawa method and the Flynn and Wall methods. Similarly, the Akahira and Sunose method is a modification of the Kissinger method, but some workers appear to have used the original Kissinger method. For this reason we have used the two methods separately.

There are, of course, other methods available, but we have only used the ones in the original paper [2], plus Vyazovkin's method [23–26]. Two other methods, mentioned later, were tried and rejected.

The details of these methods are mostly given in Ref. [2]. The equation suggested by Akahira and Sunose [10] is:

$$\ln\left(\frac{\beta}{T^2}\right)=\ln\left(\frac{AE_a}{g(\alpha)R}\right)-\frac{E_a}{RT} \tag{1}$$

where β is heating rate.

This is an extension of the Kissinger method [17,18] applied through all of the range of α instead of only at the position of the peak in $d\alpha/dt$ versus T. For α constant, the plot of $\ln(\beta/T^2)$ versus $1/T$ is made from curves made at several heating rates. The gradient then gives the value of E_a and the intercept then gives A, if a function for $g(\alpha)$ assumed.

The Coats and Redfern method [4] was originally designed using two equations, one for 1st order and one for n order. In Ref. [2] the method used by Burnham is described as an extension of the Coats and Redfern method. This is for results from multiheating rate experiments. There is no mention of which order was used, but if Eq. (28) in Ref. [27] was meant to be the one used, that appears to be only for 1st order. Since the data for the experiments in vacuum appear to fit closely to an Avrami–Erofeev (A2) and the experiments in nitrogen are close to zero order, it is unlikely that this method will produce meaningful results. This may be seen in Table 1 for simulated data where E_a and $\ln(A)$ are not all that close to the values from other calculations.

The method of Vyazovkin [23–26] is an isoconversional one. He assumed that activation energy varies with α and wrote it as E_α. His 1st method involving various heating rates is:

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha,T_{\alpha,i})\beta_i}{I(E_\alpha,T_{\alpha,j})\beta_j}=\min \tag{2}$$

where I is the temperature integral:

$$I(E_\alpha,T_\alpha)=\int_0^{T_\alpha}\exp\left(\frac{-E_\alpha}{RT}\right)dT \tag{3}$$

Values of α were chosen and a set of data measured at various heating rates was interpolated to find the values of T where the conversion was α. For each α, Eq. (2) was applied. The term min implies that the minimum of the function had to be found. The value of E_a was adjusted to produce this minimum value. This was then repeated to find E_a at each α. The value of the integral in Eq. (3) had to be found from a series because the expression is not integrable. It was found from $E_a p(x)/R$ where $p(x)=\exp(-x)/x(x^2+10x+18)/(x^3+12x^2+36x+24)$. This was taken by Vyazovkin [23] from Senum and Yang [28]. There are later versions of Eq. (2) using arbitrary variation of temperature instead of linear rise [24]. Vyazovkin has also used numerical integration to find the temperature integral. We preferred to use Eq. (2) and to use Chebyshev polynomials to find the $I(E_a,T_a)$ values, being more precise [1]. The value of A was found by directly applying the equation:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{4}$$

where β is heating rate in $\mathrm{K\,s^{-1}}$

A 'general method' by Desseyn is described in the ICTAC report with an equation given as:

$$\ln\left(\frac{d\alpha}{dT}\right)=\ln\left(\frac{Af(\alpha)}{\beta}\right)-\frac{E_a}{RT} \tag{5}$$

There was no reference given, but it seems to appear in Ref. [29]. On page 129 of that paper Eq. (5) is given, together with other similar transpositions of Eqs. (4) and (5) is stated to be used with a single experiment. This is obviously wrong because a plot of the left-hand side of Eq. (5) against $1/T$ has the variable α in the so-called constant term. For this reason we have ignored the 'general method'.

3. Comparison of results from the various methods

As will shown later, E_a decreased as α increased for both samples. Strictly speaking, these are the only results that should be reported. However the original report [2] gave tables of single E_a values. These must be the means of the variable E_a values plus the results from methods that only produce single overall values. For the sake of comparison we have taken mean values to make up similar tables for comparison only. Some methods required a choice of mechanism before the analysis commenced, but in some cases n or n' could be found by curve fitting in the calculations. Analysis was carried out using all of the data available at all heating rates and E_a, $\ln(A)$ and m n or n' evaluated. The same definitions of m, n and n' were used as in Part 1. A reconstruction or simulation program, using these parameters, was always used to visually check how the fitted result matched the original. Rogue points or faults in the analysis method, distorting the fit, were also shown up by this means. This program was also used to evaluate DEV, the deviation of the reconstructed α values from the original data, for the methods that did not use DEV directly and therefore did not produce a value. Figs. 3 and 4 show how well the fitting matched. These figures are, for clarity, for one heating rate only and the method used was the NLR one. The figures show a slightly poorer fit if a fixed mechanism is assumed, but a closer fit if a variable n for Fig. 3 and n' for Fig. 4 is used.

The Šesták–Berggren equation also shows an even better fit over some of the α range. When this equation was used to analyse data simulated for an (A2) mechanism, the fit over the middle range of α was just as good as analysing using an (A2) mechanism. Discrepancies when plotting the original data and the fitted data only showed up at the extreme ends of the values of α. Some investigators in Ref. [2] tried to use 1st order as the mechanism for the decomposition in nitrogen. Fig. 3 shows this not to be a viable equation to use and zero order also to be not quite correct.

In Fig. 5, the result for the simulated data, most of the methods produce a horizontal line at $E_a = 130.0$ kJ/mol as expected. The Ozawa method gives a curve that lies too high. Probably this is because a very simple approximation for the value of $p(x)$ is being used (Doyle [30]). However, it has also been pointed out that the Ozawa method assumes that E_a is constant with respect to α [31,32], so that may be the reason for the discrepancy. The results produced by the Coats and Akahira methods appear as coincident and lie too low. The Li and Tang method also lies too low and shows a very strange result at low α. Several methods show minor fluctuations, but an expanded scale was used in this figure, so this may be unimportant. Several methods show wider fluctuations when α nears 1. These are the methods dependent upon differentiation of the data (NPK differential and Friedman), which shows that minor fluctuations in the data are amplified and exaggerated by the process of differentiation. In fact the simulated data for equation (A2), analysed in Fig. 5 contained 500 data points. The data for the two experimental results, supplied by ICTAC, contained only 100 points. The simulation of (A2) was repeated using only 100 points. This made little difference to most of the methods, but Fig. 6 shows the result for the NPK differential method alone for the two numbers of data points. The fluctuations are much more marked with only 100 points and this shows a general principle of interpolation and differentiation – the abscissa values must not be widely spaced or the effective fitted curves tend to dip between the experimental points producing erroneous readings. This is a good reason to avoid differential methods altogether. Sbirrazzuoli et al. [33] have produced a study using various calculation methods and testing the effect of varying numbers of data points. In fact 100 points was the lowest number that they tried. Varying the number of points had a marked effect upon the % error in E_a, the conclusion seems to be that 600–800 points are required for a reasonable result, so the data for the ICTAC project was deficient. Sbirrazzuoli and co-workers [34,35] also tested the effect of adding noise to simulated data. He presented results for the NLR method of calculation (the only one comparable with those used for the ICTAC report) with noise added to the simulated data ($n = 2$) with a standard deviation of 0.2. The resulting errors in the kinetic triplet were n: -3%; $\ln(A)$: -2%; E_a: -1.6%, which are quite considerable. If what is seen in Figs. 1 and 2 is regarded as noise, then the results obtained from that data must be considered also in error. Sbirrazzuoli [36] also tested the Friedman and Vyazovkin methods and decided that the Vyazovkin is the better.

The results for the simulated data from the ICTAC study are shown in Fig. 7 and may be compared with Fig. 3 in Ref. [3]. Vyazovkin plotted isothermal results in this figure as well as non-isothermal results. If only his non-isothermal results are used, the results are much the same as ours. Many of the methods coincide. However, the Ozawa results are slightly high. The Li and Tang curve crosses the other results, then lies too low. Roduit's Flynn and Wall result is slightly too low. The differential method results are much too high and show fluctuations.

Results for variation of E_a were produced by some of the methods (those listed in the tables as producing a mean result). For the two calcite samples this is shown in Figs. 8 and 9. The scale for E_a for these results spans about 50 kJ/mole whereas Figs. 5 and 6 cover only 2 kJ/mol. Thus minor fluctuations tend to be suppressed in Figs 8 and 9. Since the E_a values for both samples show a wide variation with α, there is probably no point in reporting single E_a values as a mean value, taken from the data in Figs. 8 and 9, or from the methods that yield only a single value. However the ICTAC report is based upon single values, so we have put these in our Tables 2 and 3 in order to show the consistency that should have been possible by the original researchers. In Figs. 8 and 9 several method approximately coincide and overprint in the plots. Criado and co-workers [37] and Starink [38] have pointed out that divergences in E_a values between methods can be due to inaccuracy in the calculation of the integral $p(x)$. Criado and co-workers [37] showed that Coats and Redfern's approximation for $p(x)$ could lead to E_a values that are as much as 4% low. However, we find that the Coats results appear to coincide with most of the other results. The Akahira results only lie slightly below the general result. The curves for the Ozawa method lie much too high, but Starink [38] has shown that this method is very poor in % error because of a very poor approximation for $p(x)$. He also produced results for a large number of equations as other approximations for $p(x)$. He also showed that the error in E_a determined varies with the value of x. His Fig. 2 shows that the % error is not good below $x = 40$ and becomes much larger as x decreases to 10. The values of x in the present experimental case range from 20.6–31.0 for the nitrogen sample and 13.8–25.2 for the vacuum sample. The use of Chebyshev polynomials produce a very low error down to at least $x = 5$ [1]. The Li and Tang results are distinctly too low. This method [8,9] uses differentiation of the original data, then takes functions of the data and integrates it. This seems to smooth out the fluctuations shown by other differential methods. However the result is values that rise with α while the other methods show falling values. The differential methods (NPK differential and Friedman) show widely fluctuating results because there are too few data points as explained above. This only shows the unsuitability of the data provided as shown in Figs. 1 and 2. The rest of the methods show close agreement in the position of the E_a curves.

Tables 1–3 show the numerical results for the simulation and the two samples. The mean results are, of course, the mean of the curves in Figs. 5, 8 and 9, but may also be compared with those methods that produce a single overall result. In Table 1 the mean results agree with the line at $E_a = 130$ kJ/mol in Fig. 5 for most methods. The Ozawa lies too high and Coats, Akahira and Li and Tang results are too low. Considering the methods yielding only a single overall result, these mostly provide close to the correct answer and this includes the Kofstad method. The results from the method of Ingraham and Marrier are distinctly too low.

In the cases of calcite in nitrogen and vacuum, Figs. 8 and 9 show a decrease in activation energy with increasing α. In the case in nitrogen the decrease is steep at low α, followed by an almost constant value during the rest of the decomposition. The calcite in vacuum shows a continuous decrease in E_a across the values of α. The values of E_a quoted in Tables 2 and 3 are either the means of the values seen in Figs. 8 and 9 or overall values found by various mathematical processes. There is no reason to suppose that these values should exactly agree when a decrease in individual values is shown in the values of E_a with α. This may be seen in the tables. In the tables, in the column labelled EXPONENT, if a mechanism is named then that mechanism was assumed and applied to the method, after trials with several mechanisms from Table 1 of Part 1. If only a figure is given for n or n' (or n and m for Šesták–Berggren) then that figure is a result derived from the method being applied.

Considering calcite in vacuum first, a reasonable conclusion from Table 3 is that the overall value of E_a is about 120 kJ/mol and ln(A) is around 10.0 to 11.0. The values, obtained as means, lie slightly higher at around 123 to 124 kJ/mol, with ln(A) around 11.0 to 13.0. The Ozawa result again lies too high. The results from NPK differential, Friedman, Li and Tang, Kofstad and Marrier are far too low and the differential methods fluctuate too greatly. Vyazovkin's method agrees well with other mean methods. In Ref. [2] some researchers have shown the variation in E_a by showing its value at $\alpha = 0.1$ and 0.9. We obtain, for the overlapping plots of Fig. 9, approximately 144 kJ/mol for E_a at $\alpha = 0.1$ and 110 kJ/mol for E_a at $\alpha = 0.9$. Sbirrazzuoli [36] has also shown that the Friedman method can have systematic errors when compared with other methods and recommends the Vyazovkin method [39].

In the case of the results in nitrogen, there is a difficulty in deciding on the mechanism. Attempts to fit various kinetic equations from Table 1 in Part 1 show that the kinetics are close to zero order with a slight deviation to a higher order, especially at higher α values. On the other hand, attempts to fit 1st order kinetics fail. In Ref. [2] the use of zero and 1st order has been made. In Table 2 attempts to use both of these orders have been made, together with fractional orders. The apparent value for E_a is around 193–194 kJ/mol and 15.5–15.9 for ln(A) and an order of around 0.13. In the nitrogen case, because only a few of E_a values at the early α values are high, the mean values are much the same as overall values. The Ozawa values are too high and the NPK differential and Friedman results are too low or fluctuating. However, the Friedman and NPK differential results fluctuate rather evenly on either side of the results by the other methods so the mean values are much the same. The Li and Tang results are too low as are those of Kofstad and Marrier, but the Vyazovkin method agrees well. This time the NPK integral results are very slightly high.

Sbirrazzuoli et al. [35] have analysed results using the Kissinger method both with and without noise added to simulated data. With noise of standard deviation of 0.2 added, the change in % error of the kinetic triplet values was around an order of magnitude. The Kissinger method depends upon finding the position of the peak in the dα/dT plot. The main problem is in fitting a curve to the differentiated experimental data. The problem is illustrated in Figs. 1 and 2. For the nitrogen data, Fig. 10 shows all seven peaks with only the region around the peaks plotted. Fig. 11 shows a similar plot for 6 peaks for the vacuum data. There is an obvious difficulty in fitting a curve to this data. This includes deciding how many points above and below the peak region to include in the fitted equation and which equation to use. Trial and error showed that the curves fitted the peaks best for about 20 points above and below for the vacuum data and about 15 points for the nitrogen data, with a cubic equation fitted for the vacuum data and a quadratic equation for the nitrogen data.

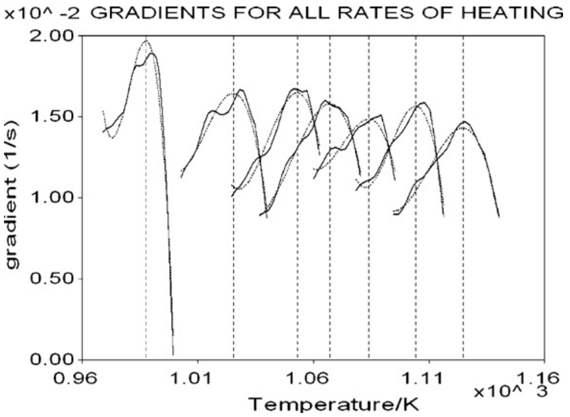

Fig. 10. Kissinger data plot. To show how the curves fitted the peaks of the differentiated data for calcite decomposed under nitrogen. Only the 15 points above and below the highest points have been fitted. Continuous line – experimental data. Dotted line – peak fitted to the line. Vertical dashed line – position of the peak used in the method.

Results from the other methods indicated that the nearest mechanism for the vacuum data was (A2), so this was applied in the analysis after the peaks had been located.

For the nitrogen data there is more doubt. The mechanism appeared to be near to zero order, but with a slight curve at the top end, producing a peak in dα/dT very close to the end of the data, shown in Fig. 1. This meant that for the higher heating rates there were fewer points available to be fitted to the equation on the upper side. If the mechanism was truly zero order there would be no peak at all, but it is not of the correct shape for 1st order. A way to deal with this would be to assume 1st order, then at least the values of α_m would be of no importance. If zero order was the true kinetic mechanism, then $f(\alpha) = 0$ and again α_m could be ignored. Thus 1st order could be assumed to agree with Ref. [2].

The best that can be said is that the data presented is unsuitable for this type of analysis, far more data points were required.

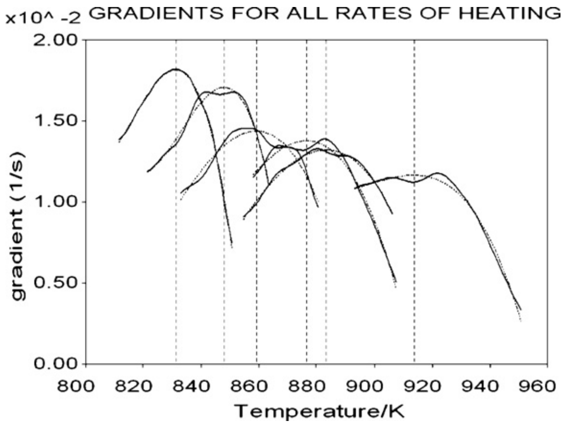

Fig. 11. Kissinger data plot to show the curves fitted the peaks of the differentiated data for calcite decomposed under vacuum. Only the 20 points above and below the highest points have been fitted. Continuous line – experimental data. Dotted line – peak fitted to the line. Vertical dashed line – position of the peak used in the method.

Considering all of the methods overall, the Ingraham and Marrier, Kofstad and Ozawa methods are too far out to be considered as valid. The Li and Tang, and Akahira and Sunose, methods produce results that are rather too low.

The Kissinger method depends too much on identifying the position of the peaks in $d\alpha/dT$, which is difficult if there are fluctuations, as in the vacuum results, so the method is not to be trusted. The differential NPK method also is badly affected by fluctuating data. In this study this is truer for the vacuum data than for the nitrogen data. The method can only be trusted if the data curves are relatively smooth. The rest of the methods have been shown to produce results that agree reasonably and have established sets of consensus results.

It should not be assumed that the results in the tables are necessarily the 'correct' answer or even fixed by the method. The methods often have choices to be made in the procedure, which affects the result. For instance the differential methods are not very precise at the ends of the range of α, because there are only data points on one side of the analysis position, so $d\alpha/dT$ is in error in these regions. This may be seen in Figs. 8 and 9. To find meaningful mean values for the tables, these end points were examined visually on the plots and removed. The NPK method has many choices in calculation:

A. Which equation to choose for interpolation and differentiation along each experimental curve – e.g. quadratic, cubic, other polynomial? We found the quadratic equation to be the most suitable.
B. What size to choose for the submatrices [13]? (Size of temperature steps across the submatrix and the number of these steps. Also number of α steps down the submatrix). This varied between samples for us.
C. How much to overlap the submatrices? Sempere and co-workers [11,12] used a single line overlap; we used a large overlap, leaving only one line not overlapped [13].
D. What equation to choose for interpolation across a matrix ie across the experimental curves. – e.g. linear or quadratic. We used a linear equation.
E. How is the value of the intercept to be corrected to obtain $\ln(A)$ – Correction Method 1 or 2 [13]. We used method 1 here.
F. Should the data be differentiated and fitted to a differential theory or should the original integral data be fitted to integrated theory equations? We favour the latter for smoother resulting plots.

These factors had to be determined by trial and error to produce meaningful E_a plots and agreement between methods.

Each of these variations produces slightly different results from the same data, so this must be allowed for in comparisons with other workers' results.

4. Comments on the Freeman and Carroll method

The original method [19] was only applied to the order type equations i.e. $da/dt = A/\beta e^{-E_a/RT}(1-a)^n$. The plot was made of

$$\frac{\Delta\ln(d\alpha/dt)}{\Delta\ln(1-\alpha)} \text{ against } \frac{\Delta(1/T)}{\Delta\ln(1-\alpha)} \tag{6}$$

The intercept gave the value of n, E_a was calculated from –gradient x R. Once n was known the equation:

$$\ln\left(\frac{d\alpha}{dt}\right) - n\ln(1-\alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT} \tag{7}$$

was applied and the intercept gave A/β and hence the value of A.

The method was extended by Heide et al. [20,21] and by Boy and Böhme [22] to other kinetic equations, for instance, to test an Avrami–Erofeev equation, data was plotted as:

$$\frac{\Delta\ln\left(d\alpha/dT\right) - \Delta\ln(1-\alpha)}{\Delta\ln[-\ln(1-\alpha)]} \text{ versus } \frac{\Delta(1/T)}{\Delta\ln[-\ln(1-\alpha)]} \tag{8}$$

The intercept was then the value of p in the original Avrami–Erofeev equation ($p = (n'-1)/n'$ from the definition in Part 1). Simulated data was produced for a zero order and (A2). When the data was analysed by the correct type of plot for that data, the expected values of E_a, A were obtained and the intercept corresponded to either n, n' for the Avrami–Erofeev equations. Similar testing was carried out for the rest of the possible kinetic models. However, there was a great deal of ambiguity. If the kinetics being obeyed are unknown, it is necessary to make all of the plots and to choose which is the best fit. Even with perfect simulated data several plots appeared, by eye, to fit perfectly. Looking at the numerical statistics of the fitting it was very often not possible to decide between several equations. For instance, simulated data generated for an Avrami–Erofeev Eq. (14) (A2) equally fitted the Avrami–Erofeev plot and an Order plot and Eqs. (5), (11) and (12). Although very close to perfect lines, these plots gave incorrect, widely varying values of E_a, A and intercept. Thus the method cannot unambiguously determine the kinetic equation and the kinetic constants. Vyazovkin [40] has commented on the difficulty in discriminating in selecting between models in general. Criticisms of the Freeman–Carroll method have appeared before [41–43], generally because of lack of discrimination between mechanisms and sensitivity to noise. If the kinetic mechanism is known from other sources, eg one of the other methods, then E_a and A could be found correctly. Simulated data for the (A2) mechanism and one heating rate, 1 K/s, was produced assuming an Avrami–Erofeev mechanism. The resulting plot is shown in Fig. 12. A perfect line is shown and the gradient gives an E_a of 130 kJ/mol and an $\ln(A)$ of 29.9336 and a p exponent of 0.5 ($n' = 2$), which were exactly the starting values for the simulation. It should be noted that a scale was chosen to spread the points across the plot, but this involved large offsets for the starting values of abscissa and ordinate. This means that a long extrapolation has to be used to get the intercept. In the case of real, experimental data, with even minor fluctuations due to experimental noise or variation in the sample due to impurities, grain size or temperature gradients, it would become impossible to decide between four or five possible mechanisms.

The numerical differentiation used did not work correctly at high values of α, because the steps of α were very small. Instead, use was made of the relationship: $d\alpha/dT = (1-\alpha)\,d(-\ln(1-\alpha))/dt$. Thus

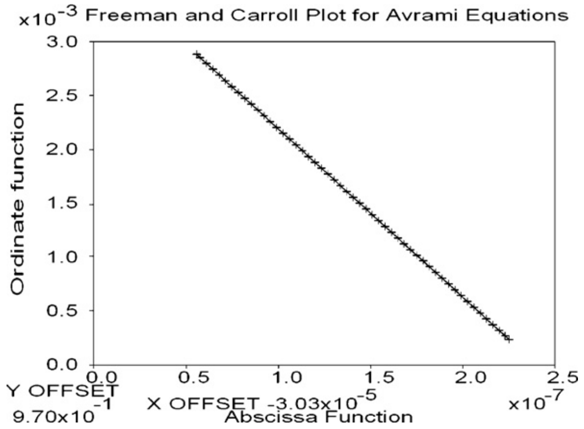

Fig. 12. Freeman and Carroll plot for simulated data for an Avrami–Erofeev (A2) equation. Plot axes are for general Avrami–Erofeev equations. Abscissa: $\Delta(1/T)/\Delta(\ln(-\ln(1-\alpha)))$. Ordinate: $\Delta(\ln(d\alpha/dT - d(\ln(1-\alpha)))/\Delta(\ln(-\ln(1-\alpha))$. (+) points; (- - -) best fitted line.

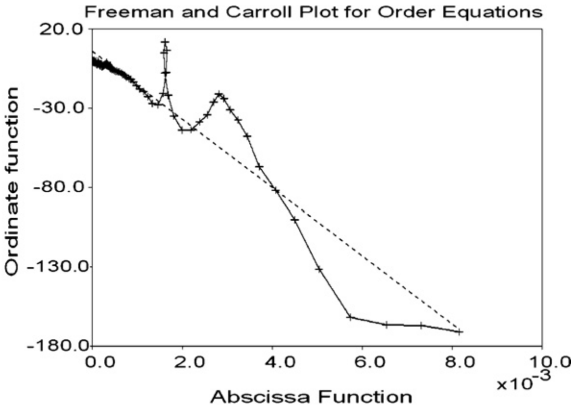

Fig. 13. Freeman and Carroll plot for data for calcite decomposed in nitrogen. Plot axes are for general order equations. Abscissa: $\Delta(1/T)/\Delta(\ln(1-\alpha))$. Ordinate: $\Delta(\ln(\mathrm{d}\alpha/\mathrm{d}T))$. (+) Experimental points; (- - -) best fitted line.

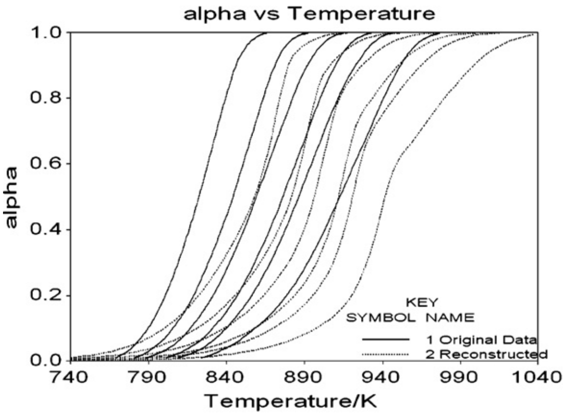

Fig. 15. Reconstruction of the experimental data under vacuum by simulation by two simultaneous kinetic equations using Roduit's parameters from Table 5 in Ref. [29].

$\ln(1-\alpha)$ was actually differentiated, which has large numerical intervals and Fig. 12 is almost a perfect straight line.

The method involves a double differentiation, and if there are fluctuations in the data, as mentioned above, this produces extreme fluctuations in the final plot. The plot for the decomposition in nitrogen is shown in Fig. 13 and the plot for vacuum in Fig. 14 (the lowest heating rates only in both cases). The nitrogen result shows a great deal of fluctuation. The value of the intercept is very sensitive to changes in the slope of the plot and cannot be reliably determined from this. The vacuum conditions cause even more fluctuation, including doubling back of the plot, so no reliance at all may be placed on the results. This is because the abscissa contains α which does not increase regularly with temperature. Sbirrazzuoli [34] mention the errors introduced by noise added to data in a Freeman–Carroll analysis, but the errors in the present case must be enormous by comparison with his.

Reference [2] quotes the original theory of the method only and not the development of the other plots made by Heide et al. [20–22]. It is not mentioned which type of plot was made, so it must be assumed that only the one type of plot was made. There is no mention of the value of the intercept n or p in the results in paper [2]. However the plot could be correct for the nitrogen data because the kinetics appear, from the other methods, to be near zero order or at least a low value of n. The results under vacuum seem to follow an Avrami–Erofeev mechanism with a p value of about 0.5. Thus plotting the data as an order type equation would be incorrect. It has already been pointed out that these types of plot in a Freeman and Carroll analysis equally well fit data from either mechanism. The results obtained for the two sets of data analysed here were:

In N2 $E_a = 156.126$ kJ/mol $\ln(A) = 28.2533$ $n = 2.0322$
In vacuum $E_a = 55.642$ kJ/mol $\ln(A) = 6.9350$ $p = 0.5189$

However, this must be counted as completely unreliable because of the nature of the plot in Fig. 13 and an even worse one for the vacuum data in Fig. 14. For these reasons the results were not put into Tables 1 and 2 because they are not

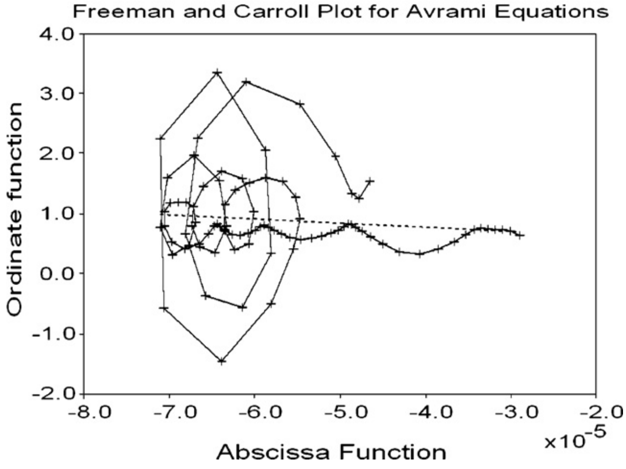

Fig. 14. Freeman and Carroll plot for data for calcite decomposed under vacuum. Plot axes are for general Avrami–Erofeev equations. Abscissa: $\Delta(1/T)/\Delta(\ln(-\ln(1-\alpha)))$. Ordinate: $\Delta(\ln(\mathrm{d}\alpha/\mathrm{d}T-\mathrm{d}(\ln(1-\alpha)))/\Delta(\ln(-\ln(1-\alpha)))$. (+) Experimental points. (- - -) best fitted line.

5. Comparison with the results in Ref. [2]

5.1. *Calcite in vacuum results in Table 1 of Ref. [2]*

There is a great deal of scatter in the results, some being double the values that we obtained. Where researchers have split their results between high and low α, then many of their results compare reasonably well with our values at $\alpha = 0.1$ and 0.9. The experimental data, when plotted, fits a sigmoid shape, which cannot be produced by a simple order mechanism or any acceleratory process. The results seen could be produced by overlapping acceleratory and order mechanisms, but in fact fit quite well to an Avrami–Erofeev mechanism type (A2). Results in the ICTAC report using order mechanisms produce particularly poor results. Unexpectedly Anderson does produce a reasonable answer for order 0.5 fitted overall. The results of Burnham using a 1st order expression are poor. Desseyn's results are all too high or too low, his Ozawa calculation giving high results due to inaccurate values of $p(x)$. Nomen and Sempere's NPK differential method results are very close to ours, but our NPK integral results are likely to be more reliable and are closer to those of our other methods. Opfermann's results also are too high or too low and his values of n for the Avrami–Erofeev equation do not seem to be quite correct. Li and Tang's results are too low or too high and they seem to have ignored variation of E_a with α.

Roduit has also suggested, in a follow-up paper, Ref. [44], that the experimental curves may be better represented by two parallel reactions with different sets of parameters: E_{a1}, A_1, n_1 and E_{a2}, A_2, n_2. The α values are added together with different weightings, w_1 and w_2. These values are listed in his Table 5. We have used his parameters to simulate the resulting curves and compare them with the experimental data in Fig. 15. The curves are a poor fit, lying too high along the temperature scale and with a kink near to the end. If the parameters are used to form plots of the separate

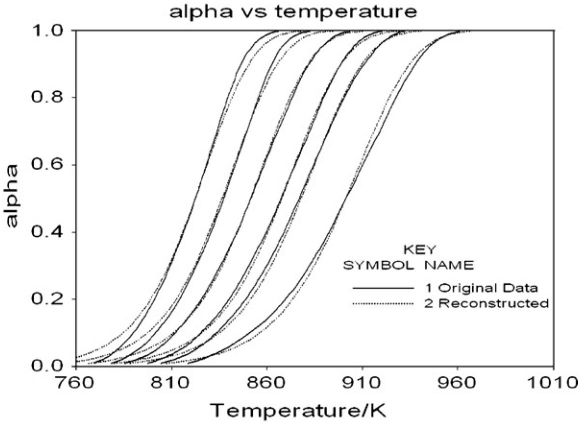

Fig. 16. Reconstruction of the experimental data under vacuum by simulation of the kinetic equation using our parameters for the NLR or NPK method from our Table 3.

reactions, the curves lie far too far to the right of the experimental curves. If the data from the two equations are to be added to fit the experimental result, then they must be much closer to the experimental curves. Probably one needs to be to the right and one to the left of the experimental result. To further investigate this model we changed the NLR (simplex) program to use the seven parameters described above ($w_2 = 1 - w_1$) for two parallel reactions. Roduit [44] mentions that there is a danger of 'overfitting' the experimental data by introducing too many adjustable parameters. In this case the optimisation is trying to find a good minimum or 'valley' in multidimensional space. With seven variables there are likely to be many false 'valleys' for the optimisation to fall down. This may be what has happened with Roduit's parameters. It is said that two to three, perhaps four, is the maximum number of parameters that should be employed in this type of optimisation. In our case, using several starting points for the seven parameters produced different final points, which confirms the existence of false minima. It was also noticed that, whatever the starting point, one set of parameters settled with values very near to the values for a single mechanism for the n'-dimensional Avrami–Erofeev equation, as listed in our Table 3. The weighting w_1 for this was very near to unity, i.e. the reaction appeared to be almost entirely a simple single step. The second reaction had a w_2 value that was very close to zero (typically 0.000001). The values of E_{a2}, A_2 and n_2 were meaningless because this reaction is contributing nothing to the overall results. Whatever the starting point, the optimisation seemed to reject the hypothesis of two reactions and confirmed a simple single reaction. It would probably be better to consider the reaction as approximating to an Avrami–Erofeev equation (A2) but with deviations at several places due to extraneous factors such as inhomogeneity of the sample or heat flow variations. Thus the main reaction step is accounted for with a single set of parameters, and minor fluctuations are ignored.

Considering all of the results in Table 3, the best fitting parameters, produced by us, was for the NLR and NPK (integral) (Šesták and Berggren equation), the direct grid search being close as well. The resulting reconstruction is shown in Fig. 16, which is far better than Fig. 15.

If compared with our results, Desseyn's results are the worst and Roduit's are the best.

5.2. Calcite in nitrogen results in Table 2 of Ref.[2]

The spread of results in this case is much less and many results agree with ours. The Ozawa method results of Desseyn are again too high due to inaccurate values for $p(x)$ and the Flynn and Wall results are to be preferred. Where values are shown separately for low and high α, the results again bear out the change with α shown in Fig. 8. However, the variation of E_a with α, found in Ref. [2], was generally greater than in our case, and Roduit found an increase with α instead of a decrease when he used the Friedman and Flynn, Wall and Ozawa methods. Roduit's results for the Multivariate-NLR method follow those for the isothermal case. In Table 2 in Ref. [2] and the follow-up paper [44], he describes using both Fn and Rn mechanisms. These again produce identical E_a values, slightly different ln(A) values but a value of n very different from the n_R value. The values from the two mechanisms are connected by the Eq. (13) of Part 1, as are our results in Table 2.

Li and Tang again ignored the variation in E_a, although two of their results were close. Desseyn's results were again the worst, with Anderson, Burnham and Roduit producing the most consistent results.

5.3. Connection between Fn and Rn equations

This connection was explained in Part 1, Section 1.2. The same connection applies in non-isothermal experiments. In this case, Roduit's Table 4 shows: $n + (1/n_R) + 0.177 + 1/1.215 = 1.00005$ (should be 1.0) and $15.67 + \ln(1.215) = 15.86$ (should be 15.86).

Our Table 2 shows: $n + (1/n_R) = 0.1311 + 1/1.151 = 0.99991$ (should be 1.0) and $15.699 + \ln(1.151) = 15.840$ (should be 15.838) which are approximately the correct values to prove the connection.

5.4. Freeman and Carroll method

The results of E_a in Ref [2] produced by Desseyn for both decomposition in nitrogen and vacuum are nowhere near the apparently correct results by other methods shown in our Tables 2 and 3 and by other researchers in Ref [2]. The results for ln(A) are shown as negative, which is impossibly low, so the analysis must have been incorrect.

6. Other methods

The methods of Stander and van Vuuren [45] and also Loglog plots of Hancock and Sharp [46] were applied to this data. Although the methods worked well enough for perfect, simulated data, they did not work at all well for these experimental data. The plots were not good enough to pick out which kinetic equation was being obeyed. The results were not worth reporting and have been left out.

7. Recommendations

Many of the following points have been made previously by other researchers, but are reiterated here for emphasis.

1. Avoid the use differential methods when the experimental curve is fluctuating. If a differential method must be used, do not use a number of data points as low as 100. At least 500 points would be best.
2. Do not use the double differential Freeman and Carroll method.
3. Determine the mechanism followed, or the nearest one, if possible.
4. Use methods that allow the determination of variable values of n or n'.
5. Use a reconstruction program to see how good the final fit is.
6. Do not use the Ozawa, Li and Tang, Coats and Redfern, Akahira, Kofstad or Ingraham and Marrier methods, these being too imprecise.
7. The best methods seem to be NLR, NPK (integral), both with variable parameters n or n' (or m and n for Šesták–Berggren), and

Flynn and Wall.The Kissinger method could be used, provided the position of the peaks in dα/dt can be determined accurately.

8. If $p(x)$ is required, use the Chebyshev polynomial method of calculation [1]
9. Report the variation of E_a against α.

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References

[1] G.R. Heal, Thermochim. Acta 340–341 (1999) 69–76.
[2] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kremmler, R. Keuleers, J. Janssens, H.O. Desseyn, Chao-Rui Li, B. Tong, B. Tang, J. Roduit, T. Malek, Mitsuhashi, Thermochim. Acta 355 (2000) 125–143.
[3] S. Vyazovkin, Thermochim. Acta 355 (2000) 155–163.
[4] A.W. Coats, J.P. Redfern, Nature (London) 201 (1969) 68–69.
[5] T. Ozawa, Bull. Chem. Soc. Jpn. 39 (1965) 1881–1886.
[6] T. Ozawa, J. Thermal Anal. 2 (1970) 301–324.
[7] J.H. Flynn, L.A. Wall, J Res. Nat. Bur. Stand. 70A (1966) 487–523.
[8] C.-R. Li, T.B. Tang, J. Thermal Anal. 49 (1997) 1243–1248.
[9] C.-R. Li, T.B. Tang, Thermochim. Acta 325 (1999) 43–46.
[10] T. Akahira, T. Sunose, Res. Report Chiba Inst. Sci. Technol. 16 (1971) 22–31.
[11] R. Serra, R. Nomen, J. Sempere, J. Thermal Anal. 52 (1998) 933–943.
[12] R. Serra, R. Nomen, J. Sempere, J. Thermal Anal. 56 (1999) 843–849.
[13] G.R. Heal, Thermochim. Acta 426 (2005) 15–21, 23–31.
[14] H. Friedman, J. Polym. Sci. Part C 6 (1964) 183–195.
[15] P. Kofstad, Nature 179 (1957) 1362–1363.
[16] T.R. Ingraham, P. Marrier, Can. J. Chem. Eng. 42 (1964) 161.
[17] H.E. Kissinger, J. Res. Nat. Bur. Stand. 57 (1956) 217–221.
[18] H.E. Kissinger, Anal. Chem. 29 (1957) 1702–1706.
[19] E.S. Freeman, B. Carroll, J. Phys. Chem. 62 (1958) 394–397.
[20] K. Heide, W. Höland, H. Gölker, K. Seyfarth, M. Müller, R. Sauer, Thermochim. Acta 13 (1975) 365–378.
[21] K. Heide, W. Höland, Thermochim. Acta 23 (1978) 183–184.
[22] S. Boy, K. Böhme, Thermochim. Acta 20 (1977) 195–209.
[23] S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comput. Sci. 36 (1996) 42–45.
[24] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393–402.
[25] S. Vyazovkin, J. Therm. Anal. Cal. 83 (2006) 45–51.
[26] S. Vyazovkin, Int. J. Chem. Kinet. 34 (2002) 418–420.
[27] A.K. Burnham, R.L. Braun, Energy Fuels 13 (1999) 1–22.
[28] G.I. Senum, R.T. Yang, J. Therm. Anal. 11 (1979) 445–447.
[29] R.R. Keuleers, J.F. Jansens, H.O. Desseyn, Thermochim. Acta 385 (2002) 127–142.
[30] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639–642.
[31] J.M. Criado, P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, J. Therm. Anal. Cal. 92 (1) (2008) 199–203.
[32] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178–183.
[33] N. Sbirrazzuoli, Y. Girault, L. Elégant, Thermochim. Acta 260 (1995) 147–164.
[34] N. Sbirrazzuoli, Thermochim. Acta 273 (1996) 169–184.
[35] N. Sbirrazzuoli, Y. Girault, L. Elégant, Thermochim. Acta 293 (1997) 25–37.
[36] N. Sbirrazzuoli, Macromol. Chem. Phys. 208 (2007) 1592–1597.
[37] L.A. Pérez-Maqueda, P.E. Sánchez-Jiménez, J.M. Criado, Polymer 46 (2005) 2950–2954.
[38] M.J. Starink, Thermochim. Acta 404 (2003) 163–176.
[39] N. Sbirrazzuoli, L. Vincent, A. Mija, N. Guigo, Chemom. Intell. Lab. Syst. 90 (2009) 219–226.
[40] S.V. Vyazovkin, I.S. Romanovsky, A.I. Lesnikovich, J. Thermal Anal. 34 (1988) 239–247.
[41] J.M. Criado, D. Dollimore, G.R. Heal, Thermochim. Acta 54 (1982) 159–165.
[42] A. Ortega, Int. J. Chem. Kinet. 34 (2002) 193–208.
[43] N.A. Liu, W.C. Fan, Thermochim. Acta 338 (1999) 85–94.
[44] B. Roduit, Thermochim. Acta 355 (2000) 171–180.
[45] P.P. Stander, C.P.J. van Vuuren, J. Thermal Anal. 41 (1994) 493–509.
[46] J.D. Hancock, J.H. Sharp, J. Amer. Ceram. Soc. 55 (2) (1972) 74–77.