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Review

A review of the ICTAC Kinetics Project, 2000
Part 1. Isothermal results

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ABSTRACT

The ICTAC Kinetics Project is reviewed comparing the isothermal results of the various contributors, pointing out the various discrepancies seen. Instead of using the commercially available computer programs, which differed between contributors, our own computer programs are written to repeat the calculations for the methods given in the paper. The results of our methods agree very well with each other, but differ very much from the original paper. Reasons for this are suggested and recommendations are made to try to get consistent results in future.

Contents

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1. Introduction

Following the Kinetics Workshop, held during the 11th International Congress on Thermal Analysis and Calorimetry (ICTAC) in Philadelphia, USA, in August 1996 the ICTAC Kinetics Project was set up [1,2]. Several sets of test data were made available and a number of volunteer participants passed the data through the kinetic analysis methods and computer programs that they normally used. The results were reported in detail [3] by the group and further analysed by individual organisers and participants [4–7]. Experimental data was provided and used by all of the participants so that there could be no bias caused by the experiments themselves. The purpose was to test the procedures of various workers, using different computational methods, varying computer programs and perhaps different computers. If they had all obtained near identical results that would have been perfect. If one or two workers seemed to produce results way out from the rest, then they could have been invited to correct their errors. In practice the results were very scattered. In a later paper [8], Brown and Galwey pointed out the scatter of results and plotted the values of activation energy E_a obtained against ln(A), the log of the pre-exponential factor, from the results presented by the study. These showed very roughly a compensation plot. They then challenged the participants to explain their results and the scatter shown. In the absence of any reply to this challenge, this present review has been undertaken to attempt to find out what went wrong with the study and to suggest what the truth is regarding the kinetic triplet values (E_a, ln(A) and parameter n of the kinetic equation). It will also point out which participants seem to be most at error in their results. The computer programs used by the participants were not available to the present authors. They are often delivered bundled with the apparatus. Presumably if we had run them they would have produced results identical to those in the paper [3] unless there had been operator error. The detail of the programming was not available because the programs are often commercially produced and listings are not made available because of confidentiality. For this reason we wrote our own programs in Fortran 77 or used the Microsoft Excel Spreadsheet program. As far as possible all of the methods of calculation for both isothermal and non-isothermal data were used, the latter to be reported in Part 2. Not all of the sets of data available for the original study [3] have been used. Because of the time and work involved in analysis, several sets are left out. The decomposition of ammonium perchlorate was deemed to be too complex, involving overlapping reactions, so this was left out. To test if the analysis programs work or not, really requires sets of simulated data. The original study used simulated data, but was for two overlapping reactions. It was decided that for this paper, because of the complication of overlapping reactions and the extra work involved, it would be better to use data for a single reaction. If a participant could not even reproduce the starting parameters for the simulation, then that person could have been requested to withdraw from the study pending correction of some faulty computer programming being used. For this reason the simulated data from the original study has not been examined in any detail but replaced by data for a single reaction mechanism. The data from the ICTAC study used is therefore that for calcite decomposition in vacuum and nitrogen, isothermal (and non-isothermal in Part 2) conditions, with some reference to the ICTAC simulated data. Our simulated data was for isothermal (and non-isothermal also in Part 2) using a mechanism chosen to be close to that found for the experimental results.

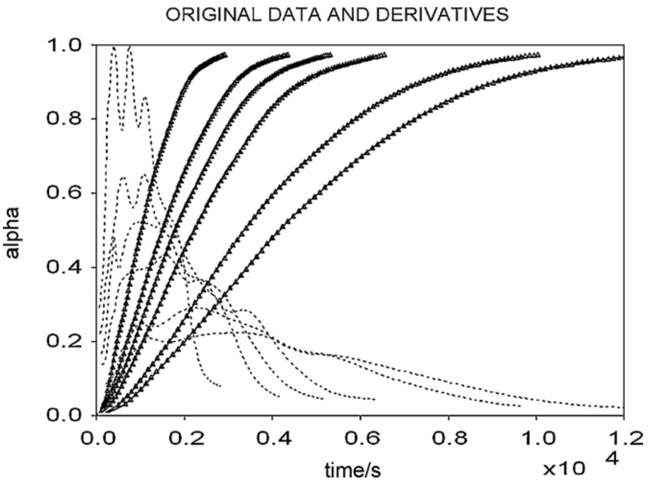

Fig. 1. Thermogravimetric plots together with differential plots for calcite under vacuum at various temperatures (550, 540, 535, 530, 520, 515 °C). (△) experimental points; (—) curve fitted to the experimental points; (. . .) differential plot. The differentials are re-scaled to the peak of the largest one (at 550 °C).

The data made available to the participants in this project, and to the present authors, was unfortunately not well chosen. Each set consists of 100 points only. Modern instruments are capable of logging many more than this during the run of an experiment and computer program can easily deal with these larger data sets. It appears that the data was edited to suppress many points, to reduce the result to 100 points only. This will cause difficulties when a method of calculation requires differentiation of the data. Observation of Figs. 1 and 2 show that the decomposition reaction is actually complex and seems to show many overlapping reactions. It is possible that these are just instrumental noise, but the peaks seem to be too large for this. Also, comparing separate runs shows small peaks at roughly similar i.e. repeatable, positions, so noise is unlikely. Thus the decomposition of calcite is not a simple reaction and is still not well understood. Better choices could have been made. The results produced in this paper are not to be taken as a 'correct' answer for the decomposition of calcite, but as the best that may be obtained from the poor data used. They will, however, show up where agreement between methods of calculation appear and the discrepancies of the results of many participants.

1.1. Possible errors

The scatter of results in the tables in Ref. [3] shows that many mistakes must have been made. These might be caused as follows:

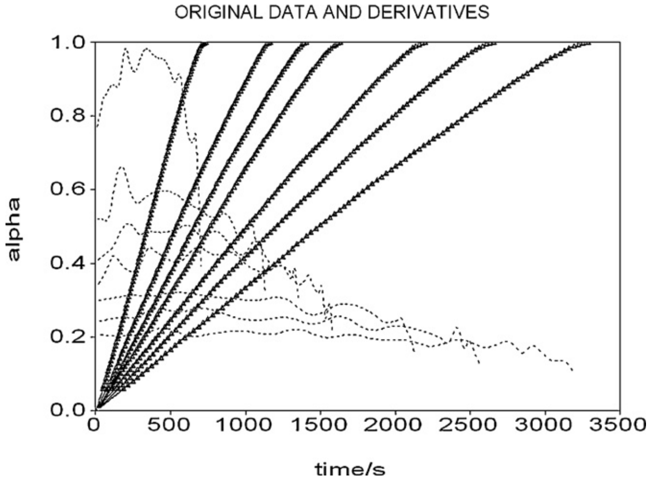

Fig. 2. Thermogravimetric plots together with differential plots for calcite under nitrogen at various temperatures (773, 750, 740, 732, 719, 710 and 700 °C). (△) experimental points; (—) curve fitted to the experimental points; (. . .) differential plot. The differentials are re-scaled to the peak of the largest one (at 773 °C).

A. Since $\ln(A\,\mathrm{s}^{-1})$ is reported in the tables it must be made certain that the value of A output by the computer programs is in s^{-1} and not min^{-1}, especially when the supplied data is in min^{-1} for the experimental results but in s^{-1} for the simulated data. This will not affect the E values but would cause $\ln(A)$ to differ by $\ln(60) = 4.094$.

B. It is the log of A that is shown in the tables, but a program might have output A and the log taken before insertion into the report. It might be that the wrong log was taken, i.e. it should be $\log_e$ not $\log_{10}$. This will again cause $\ln(A)$ values to differ.

C. If an optimisation procedure is used:
   1. is it suitable for the type of results being optimised?
   2. are the ‘stopping’ criteria set too high so that the optimisation stops too soon?

D. Is a mechanism chosen to be the nearest to fit the data the correct one? For instance there seems to be disagreement amongst the participants between Avrami–Erofeev and order equations being the best fit.

E. What is the definition of the exponents used in the equations? The original paper seems to confuse the definition of the letter n. In the text the Šesták–Berggren equation is used as a general function to show all of the types of the α functions that might be included in the rate equation.

$$\frac{d\alpha}{dt} = k(\alpha)^m (1-\alpha)^n [-\ln(1-\alpha)]^p \tag{1}$$

These terms may be used together or singly. If $m = 0$ and $p = 0$ then n is correctly interpreted as the order of reaction. In an Avrami–Erofeev type equation $m = 0$, $n = 1$ and p has various values. Unfortunately, in the tables in Ref. [3] and in general literature, n is also used to define the Avrami–Erofeev equation instead of p, and is referred to as the dimension of the Avrami–Erofeev equation. The value of p is connected to n by $p = (n-1)/n$.

Table 3 in Ref. [3] contains n with both meanings. In this paper, to distinguish the two values of n, the n in Eq. (1) is retained so “order” equations become:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

or in integral form:

$$1-(1-\alpha)^{(1-n)} = (1-n)kt \tag{3}$$

but, if the equation is 1st order, $n = 1$ then

$$-\ln(1-\alpha) = kt \tag{4}$$

In the case of Avrami–Erofeev equations the quantity n (dimension) has been changed to n' so that $p = (n'-1)/n'$.

F. Is the kinetic equation of the correct form?

There are two methods of defining the kinetic equations. If the fundamental equation is taken to be the differential form i.e. if the rate of decomposition is the basic process, then for an Avrami–Erofeev equation.

Definition 1.

$$\begin{aligned}\frac{d\alpha}{dt} &= k(1-\alpha)[-\ln(1-\alpha)]^{(n'-1)/n'}\\ &= Ae^{-E_a/RT}(1-\alpha)[-\ln(1-\alpha)]^{(n'-1)/n'}\end{aligned} \tag{5}$$

The derived integrated equation is then:

$$n'[-\ln(1-\alpha)]^{1/n'} = kt \quad \text{or} \quad [-\ln(1-\alpha)]^{1/n'} = \frac{1}{n'}Ae^{-E_a/RT} \tag{6}$$

Table 1

Kinetic equations used for isothermal and non-isothermal analysis.

No.	Code	$g(\alpha)$	$F(\alpha)$	Name of equation
Diffusion equations				
1	D1	α^2	$1/(2\alpha)$	One dimension (parabolic)
2	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-1/\ln(1-\alpha)$	Two dimension (Valensi–Barrer)
3	D3	$[1-(1-\alpha)^{1/3}]^2$	$1.5(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	Three dimension (Jander)
4	D4	$[1-2/3\alpha-(1-\alpha)^{2/3}]$	$1.5/[(1-\alpha)^{-1/3}-1]$	(Ginstling–Brounshtein)
5	D5	$[1/(1-\alpha)^{1/3}-1]^2$	$1.5(1-\alpha)^{4/3}/[1/(1-\alpha)^{1/3}-1]$	(Zhuravlev)
6	D6	$[(1+\alpha)^{1/3}-1]^2$	$1.5(1+\alpha)^{2/3}/[(1+\alpha)^{1/3}-1]$	(Anti-Jander)
7	D7	$[1-(1-\alpha)^{1/3})]^2 = \log(t)$	$\{1.5(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]\}/t$	(Kroger–Ziegler)
8	D8	$[1-(1-\alpha)^{1/2})]^2$	$(1-\alpha)^{1/2}/[1-(1-\alpha)^{1/2}]$	Two dimension (Jander)
9	D9	$[(1+\alpha)^{1/2}-1]^2$	$(1+\alpha)^{1/2}/[(1+\alpha)^{1/2}-1]$	Two dimension (Anti-Jander)
10	D10	$[1/(1-\alpha)^{1/3}-1]$	$3(1-\alpha)^{4/3}$	Interfacial transfer
11	D11	$1/(1-\alpha)^{1/3-}-1+1/3\ln(1-\alpha)$	$3/[(1-\alpha)^{-4/3}-(1-\alpha)^{-1}]$	Transfer and diffusion
12	D12	$1/5(1-\alpha)^{-5/3}-1/4(1-\alpha)^{-4/3}+1/20$	$3/[(1-\alpha)^{-8/3}-(1-\alpha)^{-7/3}]$	Two direction diffusion
Avrami–Erofeev (JMA) neucleation and growth				
13	A1	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	(Avrami–Erofeev)
14	A2	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	(Avrami–Erofeev)
15	A3	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	(Avrami–Erofeev)
16	A4	$[-\ln(1-\alpha)]^{3/4}$	$4/3(1-\alpha)[-\ln(1-\alpha)]^{1/4}$	(Avrami–Erofeev)
17	A5	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	(Avrami–Erofeev)
Order/interface				
18	F0	α	Constant	Zero order
19	F1	$-\ln(1-\alpha)$	$(1-\alpha)$	1st order
20	F2	$1/(1-\alpha)-1$	$(1-\alpha)^2$	2nd order
21	R2	$[1-(1-\alpha)^{1/2}]$	$2(1-\alpha)^{1/2}$	Contracting area
22	R3	$[1-(1-\alpha)^{1/3}]$	$3(1-\alpha)^{2/3}$	Contracting volume
23	R4	$[1-(1-\alpha)^{2/3}]$	$3/2(1-\alpha)^{1/3}$	Contracting interface
Power/exponential				
24	P2	$\alpha^{1/2}$	$2\alpha^{1/2}$	Power law (half)
25	P3	$\alpha^{1/3}$	$3\alpha^{2/3}$	Power law (third)
26	P4	$\alpha^{1/4}$	$4\alpha^{3/4}$	Power law (quarter)
27	E1	$\ln(\alpha)$	α	Exponential

α is fraction decomposed, t is time, k is rate constant. Integral equation $g(\alpha) = kt$. Differential equation $d\alpha/dt = kf(\alpha)$.

Definition 2. If the integral equation is taken to be fundamental:

$$[-\ln(1-\alpha)]^{1/n'} = kt = Ae^{-E_a/RT}t \tag{7}$$

The derived differential equation is then:

$$\begin{aligned}\frac{d\alpha}{dt} &= n'k(1-\alpha)[-\ln(1-\alpha)]^{(n'-1)/n'} \\ &= n'Ae^{-E_a/RT}(1-\alpha)[-\ln(1-\alpha)]^{(n'-1)/n'}\end{aligned} \tag{8}$$

Typical values of n' are 3/2, 4/3, 2, 3 and 4.

Thus if $n' = 3/2$ was used and Definition 1 was adhered to, then a differential analysis would return the correct value of A. If integral analysis was used, then not A but $(1/n')A$ or $2/3A$ would be obtained. This may well be allowed for in the output from the analysing programs used in the report. If Definition 2 was used, then an integral method would return the correct A value, but a differential method would produce $n'A$ or $3/2A$. Again this might have been allowed for in the analysing program. In the paper [3] there seems to be a mixture of Definition 1 and Definition 2. For instance on page 138 of Ref. [3] the Johnson–Mehl–Avrami equation is defined by Eq. (5) above, but essentially the same Avrami–Erofeev equation is defined by Eq. (8) above. The researchers who used fitting of the Avrami–Erofeev equation (Opfermann and Roduit) are said, in the paper, to use the Definition 2, so there should be no difficulty. Other methods, described in equation form, seem to use Definition 1 and be differential in type of analysis so the A values will be unambiguous. However, the Avrami–Erofeev equations seem to be by Definition 2 The values of $\ln(A)$ then will be in error by $\ln(3/2)$, or 0.4055 if differential analysis is used. Since the actual value of n' found (see Table 3) was around 1.5587, the actual correction was 0.4434. Recent literature shows both definitions used. An examination of all the possible kinetic equations in Table 1 show that about seven of them do not generate constants in front of A, but the rest all do so.

The situation for order type equations is that Definition 1 gives Eqs. (2) and (3), but the alternative equation definition of the integral form is:

$$1-(1-\alpha)^{(1-n)} = kt \tag{9}$$

so that the differential form is:

$$\frac{d\alpha}{dt} = \frac{1}{1-n}k(1-\alpha)^n \tag{10}$$

There is no correction factor for 1st order kinetics, but for 0.5 order the correction to $\ln(A)$ will be $\ln(2) = 0.6931$.

Either definition is valid, but it should be made clear which is being used if results from various laboratories and computer programs are to be compared. The question arises: were the participants asked about the form of their equations used or at least corrected as above?

In this paper Definition 2 is always used, only because it seems from literature about the commercial computer programs that they all use Definition 2 and must have produced many of the results in Ref. [3]. Originally we used Definition 1 and this was changed to Definition 2 between the publication about the NPK method [20] and this paper. The programs generating simulated data and the analysing program were both changed, so there is no difference in those results. However, the results for calcite decomposition were used in both publications so those in Ref. [20] and this paper do not exactly agree. The same consideration is also true for the non-isothermal data in Part 2 of this series.

1.2. Connection between Fn and Rn equations

Roduit, in Table 4 of Ref. [3] and in his follow up paper [6] in Table 4, reported that the data for decomposition in nitrogen followed an nth order or a contracting geometry mechanism. The kinetic equations are F1, F2 and R2 to R4 in Table 1. The generalised forms are:

$$\text{Fn}: \quad \frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^n \tag{11}$$

$$\text{Rn}: \quad \frac{d\alpha}{dt} = A_R e^{-E/RT} n_R (1-\alpha)^{(1-1/n_R)} \tag{12}$$

They are similar in type in that they all contain $(1-\alpha)$ raised to a power but are derived differently, either from an order mechanism for the Fn reactions or from a moving interface for the Rn reactions. The ‘n’ quantity is not the same in the two cases, so we have called the Eq. (11) quantity n_R. Similarly the A values will differ, so for the Rn equation we have used A_R. If the same data is to fit the two equations equally well, then the $d\alpha/dt$ values must be the same at the same α points i.e.

$$A_R n_R (1-\alpha)^{(1-1/n_R)} = A(1-\alpha)^n \tag{13}$$

For this to be true, two parts of these equations must be equal.

$$\begin{aligned}&1-\frac{1}{n_R} = n \quad \text{or} \quad n+\frac{1}{n_R} = 1 \quad \text{and} \quad A_R n_R = A \quad \text{or} \\ &\ln(A_R)+\ln(n_R) = \ln(A)\end{aligned} \tag{14}$$

Examination of the results of Roduit in Table 4 in Ref. [6], for isothermal reaction, show this to be true:

$$\begin{aligned}&n+\frac{1}{n_R} = 0.092+\frac{1}{1.101} = 1.00026 \quad \text{and} \\ &14.28+\ln(1.101) = 14.38\end{aligned}$$

The results shown by us in our Table 4 show a similar relationship:

$$\begin{aligned}&n+\frac{1}{n_R} = 0.0639+\frac{1}{1.0683} = 0.99997 \quad \text{and} \\ &13.295+\ln(1.0683) = 13.3611\end{aligned}$$

Thus the two equation types Fn and Rn are not really independent but are effectively the same.

2. Analysis of experimental and simulated data

The programs written were intended to duplicate the results in Ref. [3] to try to find any errors in the original work. Also, some extra methods of calculation were added for comparison and confirmation. All of the programs were checked for correctness and precision by analysing simulated data derived from Eq. (6) using $n' = 3/2$ (the equivalent of $p = 1/3$) which is the nearest form of the Avrami–Erofeev equation to that found in Table 3 of Ref. [3]. The other parameters used were $E_a = 130$ kJ/mol and $A = 10^{13}$ s^{-1} ($\ln(A) = 29.9336$). Temperatures used were 475, 476, 477, 478, 479 and 480 K. All of the methods tried should return these parameters accurately if they are to be passed as fit for use.

Table 1 contains a list of all the mechanisms that were available to be tested and these were built into the programs written.

The participants in the study reported on the fit of only some of the equations from Table 1. Presumably all possible equations available were tried and rejected by some process and only the nearest reported. A later paper will deal with aspects of multiple simultaneous kinetic processes and will show that, for this particular decomposition, it is impossible to determine the kinetic triplet for the whole decomposition. It is only possible for the initial phase, where only a single kinetic process is operating. However, we had to first examine the original ICTAC calculations, to try to find the reasons for so many errors and variation and to be sure if a single kinetic process was possible.

Regarding the application of statistics to the fitting of various kinetic mechanisms. If strict statistical rules were applied, then

Table 2
Simulated isothermal data.

Method	Designation	E_a (kJ mol^{-1}) Mean	E_a (kJ mol^{-1}) Overall	ln(A s^{-1})	Exponent $n' = 1/(1-p)$	Min DEV in alpha
Non linear regression (NLR) methods						
Direct grid search (OPT)	OI		130.000	29.934	1.5000	2.079×10^{-6}
Powell from point 1	OI		128.395	29.532	1.4991	2.300×10^{-3}
Fletcher–Powell	OI		130.077	29.953	1.5008	1.080×10^{-4}
Nelder–Mead (simplex) integral fit	OI		130.000	29.934	1.5000	2.079×10^{-6}
Excel (SOLVER)	OI		130.000	29.934	1.5000	2.079×10^{-6}
Other kinetic equation, optimised by Nelder–Mead method only						
Sestak–Berggren, $p = 0.0$ (as by Burnham) integral fit	OI		126.855	29.587	$n = 0.8782$ $m = 0.3433$	5.617×10^{-3}
Sestak–Berggren, $p = 0.0$ (as by Burnham) differential fit	OD		129.552	30.252	$n = 0.8726$ $m = 0.3420$	6.634×10^{-4}
Friedman Isoconversional analysis, integral fit (Avrami–Erofeev)						
Using all data	MI		130.030	29.942	A5 (1.5)	1.331×10^{-5}
Other methods of analysis						
NPK differential method	OMD	130.011	129.801	31.758	A5 (1.5)	0.4006
NPK integral method	OMI	130.003	130.001	29.938	A5 (1.5)	6.310×10^{-2}

Data from a simulated Avrami–Erofeev A5 equation using $E = 130.000$ kJ/mol, $A = 1 \times 10^{13}$ s^{-1} (ln(A) = 29.9336), analysed as a general Avrami–Erofeev mechanism of dimension n' or assumed to be an A5 mechanism ($n' = 1.5$). A model was assumed to obtain ln(A) from the Friedman plot – see text. 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.

it would be necessary to plot residuals resulting from the preferred equation against the measured value. The plot ought to show a random scatter of points, either side of zero, with no portion of the plot showing a trend. If this is carried out with the present data and any of the suggested equations, there are large peaks in the plots or sinusoidal progressions. Thus the equation is statistically invalid because there is no random scatter of the residuals.

2.1. Data sets used and methods used

Three calculation methods were applied, following the original paper [3]. These were non-linear regression (NLR), non parametric kinetics (NPK) and Friedman (Isoconversional). The first two were model fitting methods. The Friedman method should be model-free. However, the first plot of ln(dα/dt) versus $1/T$ produced model-free values of E_a, but the determination of ln(A) requires a

Table 3
Calcite decomposed isothermally under vacuum.

Method	Designation	E_a (kJ mol^{-1}) Mean	E_a (kJ mol^{-1}) Overall	ln(A s^{-1})	Exponent $n' = 1/(1-p)$	Min DEV in alpha
Non linear regression (NLR) methods						
n'-Dimensional Avrami–Erofeev equation, various optimisation methods						
Direct grid search(OPT)	OI		221.830	25.277	1.5587	9.008×10^{-3}
Powell from point 1	OI		224.068	25.612	1.5170	9.100×10^{-3}
Powell from point A	OI		217.304	24.602	1.5218	9.817×10^{-3}
Fletcher–Powell	OI		221.623	25.276	1.5587	1.192×10^{-2}
Nelder–Mead (simplex)	OI		221.830	25.277	1.5587	9.011×10^{-3}
Excel (SOLVER)	OI		221.830	25.277	1.5587	9.011×10^{-3}
Other kinetic equation, Sestak–Berggren (as used by Burnham)						
Nelder and Mead ($p = 0.0$) integral fit	OI		221.888	25.701	$n = 0.8210$ $m = 0.3462$	5.809×10^{-3}
Nelder and Mead ($p = 0.0$) differential fit	OD		221.810	25.661	$n = 0.8009$ $m = 0.3282$	7.834×10^{-3}
Nelder and Mead ($p = 0.0$), n held at 1.0, integral fit	OI		221.708	25.903	$n = 1.0$ $m = 0.4256$	1.107×10^{-2}
Nelder and Mead ($p = 0.0$), n held at 1.0, differential fit	OD		221.423	25.850	$n = 1.0$ $m = 0.4372$	1.712×10^{-2}
Other kinetic equations, (as by Anderson, Burnham and Desseyn). Using NLR method with Nelder and Mead (simplex) optimization					n	
Reaction order 0.5, all α	OI		221.814	25.306	Order 0.5	3.527×10^{-2}
Reaction order 1.0, all α	OI		222.426	25.102	1st order (1.0)	7.586×10^{-2}
Reaction order 0.5, $\alpha < 0.5$	OI		221.038	24.732	Order 0.5	3.447×10^{-2}
Reaction order 0.5, $\alpha > 0.5$	OI		223.136	25.241	Order 0.5	1.364×10^{-2}
Reaction order 1.0, $\alpha < 0.5$	OI		221.467	24.888	1st order (1.0)	4.138×10^{-2}
Reaction order 1.0, $\alpha > 0.5$	OI		223.584	25.688	1st order (1.0)	4.708×10^{-2}
Variable reaction order n, all α	OI		222.432	24.999	0.3238	3.018×10^{-2}
Friedman Isoconversional analysis, integral fit (order equations)					n	
Reaction Order 1, all α (as by Burnham)	OI		221.763	25.371	1st order	9.097×10^{-2}
Reaction Order 0.5, all α	OI		221.763	26.342	Order 0.5	0.1974
Avrami-Erofeev equation, $n' = 1.5$	OI		221.675	25.445	A5 (1.5)	7.221×10^{-2}
Other methods of analysis						
NPK differential fit, $n' = 1.5$	OMD	225.564	222.816	26.647	A5 (1.5)	0.3376
NPK integral fit, $n' = 1.5$	OMI	221.213	223.640	25.547	A5 (1.5)	9.150×10^{-3}

Analysed either as a general Avrami–Erofeev equation of dimension n', an assumed A5 mechanism, an order equation or a Sestak–Berggren equation. A model was assumed to obtain ln(A) from the Friedman plot – see text. 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 4
Calcite decomposed isothermally under nitrogen.

Method	Designation	E_a (kJ mol^{-1}) Mean	E_a (kJ mol^{-1}) Overall	ln(A s^{-1})	Exponent n	Min DEV in alpha
Non linear regression (NLR) methods						
n-Order (Fn), various optimisation methods						
Direct grid search (OPT)	OI		172.808	13.361	0.0646	8.601×10^{-3}
Powell from point 1	OI		181.709	14.446	0.0973	1.627×10^{-2}
Powell from point A	OI		163.327	12.245	0.0963	1.684×10^{-2}
Fletcher–Powell	OI		172.808	13.361	0.0639	8.600×10^{-3}
Nelder–Mead (simplex)	OI		172.809	13.361	0.0639	8.600×10^{-3}
NPK differential method, assumes zero order	OMD	175.729	175.366	13.495	Zero order	7.641×10^{-2}
Other kinetic equations, optimised by Nelder–Mead method only						
Nelder–Mead (simplex) using phase boundary model (Rn)	OI		172.809	13.295	$n_R = 1.0683$	8.549×10^{-3}
Sestak–Berggren ($p = 0$) integral fit	OI		172.739	13.478	$n = 0.1451$ $m = 0.0585$	7.147×10^{-3}
Sestak–Berggren ($p = 0$) differential fit	OD		177.384	14.134	$n = 0.1943$ $m = 0.1236$	1.659×10^{-2}
Other kinetic equations (as by Anderson) NLR method					n	
Reaction order 0.0, all α	OI		172.794	13.323	Zero order	1.152×10^{-2}
Reaction order 0.0, $\alpha < 0.5$	OI		166.464	12.575	Zero order	4.569×10^{-3}
Friedman Isoconversional analysis, integral fit						
Zero order, all α	MI	168.273		12.993	Zero order	0.1529
Other method of analysis not in the ICTAC paper						
NPK integral method, assumes zero order	OMI	168.429	172.994	13.301	Zero order	2.780×10^{-2}

Analysed either as a general order mechanism, phase boundary or assumed zero order mechanism. A model was assumed to obtain ln(A) from the Friedman plot – see text. 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.

plot of the intercepts from the first plots against α to give a new intercept of ln(A). The fluctuation in these plots was extreme, so that it was impossible to plot a line. The most that can be said was that ln(A) for the nitrogen sample was ~12 and for the vacuum sample it was ~24. This shows again the unsuitability of the chosen sample. The strategy adopted was, like Burnham in the original report, to choose a model so that ln($f(\alpha)$) could be calculated and included in the plot. Then the intercept became simply ln(A). Sometimes the model for all the methods had to be pre-chosen (to agree with the ICTAC results), but in other results, the parameters (n', n or m) were allowed to vary and were determined by the method applied.

The data for calcite decomposed under vacuum and nitrogen was used, together with our simulated data.

Table 3 in Ref. [3] shows a considerable scatter in the values of both E_a and ln(A). The commonest equation applied was an Avrami–Erofeev type with a variable exponent n'. The analysis technique used was most often NLR (non linear regression). Data for decomposition at several temperatures was supplied. The analysis program used arbitrarily-chosen starting values for E_a, ln(A) and n which were then optimised. For each temperature separate rate constants k were calculated and Eq. (6) transposed to provide a theoretical α' at each time t. The deviation of the theoretical from the experimental line was found as a measure of fit by:

$$\mathrm{DEV} = \sqrt{\frac{\left(\sum_{j=1}^{s} \left\{ \sum_{k=1}^{q} (\alpha_{j,k} - \alpha'_{j,k})^2 \right\} /q \right)}{s}} \tag{15}$$

where j is the index number of a set of results at one temperature, running from 1 to s, and k is the index number of a set of data points at one temperature running from 1 to q. DEV is thus averaged over the number of data points and experimental temperatures to make an easier comparison between data sets with different numbers of s and q. Thus DEV is the root mean square deviation of a calculated α' point from an experimental α. The values of E_a, ln(A) and n' (or n) were then optimised to reduce DEV to the lowest possible value.

The experimental data is not likely to fit exactly any equation as is shown by Figs. 1 and 2. The differential of the data clearly shows fluctuations, which probably means that a simple single reaction is not taking place. However, for the purposes of this paper this is ignored. That is, equations are be fitted to the data regardless of the fact that the decomposition process may be more complex. Since DEV reflects fitting a set of such curves, the results must be a compromise. If other criteria are used in alternative methods then there is no reason to expect the same set of E_a, ln(A) and n' (or n) to be reproduced exactly by all methods.

The first task was to find the optimum values of the parameters using this definition of DEV, but by a non-optimising method. Quicker optimising methods could then tried to get closer to the optimum values. To carry this out the method of direct grid search was used. Wide ranges of E_a, ln(A) and n' were chosen (for calcite in nitrogen, where an order equation was used, n' was replaced by n). The ranges of E_a and ln(A) were divided into 500 steps and all possible values of E_a and ln(A) used to get values of DEV. If the range of the parameter n' were to be similarly divided, the calculation would have been very long. However, it was quickly found that n' only made a small change in DEV, so a simple search across n' values was made for each of the E_a and ln(A) values. Once the minimum in the table of DEV values was found, the range of E_a and ln(A) value was narrowed and the calculation was repeated. This procedure was repeated until values of E_a and ln(A) were found for the optimum fit point to a precision of 2×10^{-3} kJ/mol in E_a, 5×10^{-5} in ln(A) and 10^{-3} in n'. The results in Tables 2–4 are actually quoted to a lower precision than this. The direct grid search results are shown in Tables 2–4 as values of E_a, ln(A) and n' (or n) together with the value of DEV at that point, to show how well the theory had fitted.

Some of the methods of analysis used the value of DEV in their calculation, but others did not. Also one method used deviation in the time direction, instead of the alpha direction. To make all DEV values comparable, a separate simulation or reconstruction program was used. Whatever the method of analysis, the values of E_a, A and n (or n') were read into the simulation program and compared with the experimental data to generate an independent value of DEV. A graphical output was also generated to see visually how close the fit was. The simulation was also carried out using the parameters quoted in Ref. [3], which showed quickly how badly wrong some of the results were.

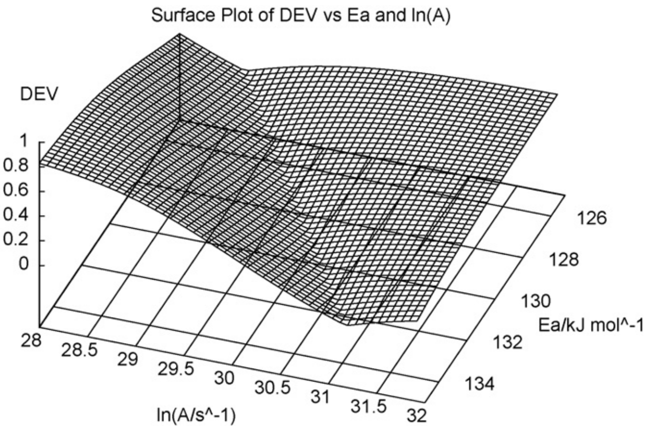

Fig. 3. Surface plot for DEV against E_a and ln(A) for the data simulated using an Avrami–Erofeev equation with $n' = 1.5$, fitted to an Avrami–Erofeev equation with variable n'.

As expected Table 2 shows that the values of the parameters for the simulated data are retrieved accurately. The value of DEV is very small, probably only reflecting the precision of the calculation or precision of transfer of the data figures from simulation program to the search program. The other tables showed reasonably small values of DEV and any attempt to refine the values of E_a and ln(A) by smaller ranges produced no lowering in DEV.

A by-product of the direct grid search program, when using a wide range of E_a and ln(A), were tables of DEV output into a file for each E_a and ln(A) value (500 × 500 points). The value of n' could be ignored because it had been optimised for each E_a and ln(A) value. A three-dimensional plot was then made from the table using the GNUPLOT package [9]. This was chosen because of the ease of rotating a plot on a computer and because contour line levels for plotting could be explicitly set. The plots are shown in Figs. 3–5.

These plots, together with the contour plots shown below, are only for the particular NLR method applied and the Avrami–Erofeev equation with variable parameter n', but are taken as the standard and compared with other methods and equations. The reason that the plots are valley shaped is that points on a line running down the base of the valley are almost equally good at producing lowest DEV values and, in fact, these lines are a type of compensation plot. They are the equivalent of figures given in Ref. [8].

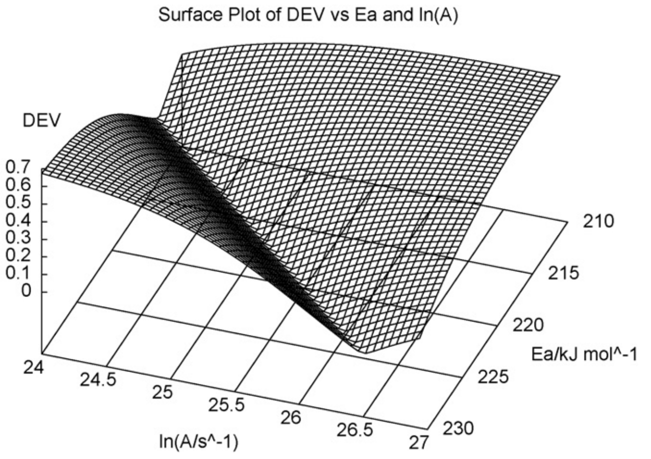

Fig. 4. Surface plot for DEV against E_a and ln(A) for the decomposition of calcite under vacuum using an Avrami–Erofeev equation, with variable n'.

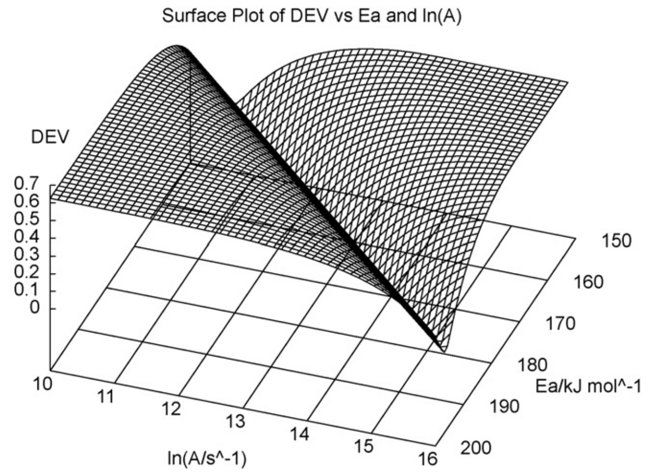

Fig. 5. Surface plot for DEV against E_a and ln(A) for the decomposition of calcite under nitrogen using an n order equation.

The correspondence is as follows:

Figure numbers In this paper	Figure numbers In Ref [8]	Data from tables In Ref. [3]
Fig. 6	Fig. 2	Table 3
Fig. 7	Fig. 3	Table 4

Lines that are the equivalent of those drawn in Ref. [8], for the variation of E_a with ln(A), were drawn down the base of the valleys. The results are more precise here because they are derived from the original data and are not the scattered results from several investigators. The equations of these lines are given in our Table 5 and are equivalent to the slopes and intercepts shown in Table 1 in Ref. [8].

From Figs. 4 and 5, contour plots were derived and are shown in Figs. 6 and 7. Higher level contours were deliberately left out because only the positions of the valleys were of interest. The points plotted and labelled correspond to the results reported by the various investigators. The ranges of E_a and ln(A) for the plots may be seen in Figs. 4 and 5 to be arbitrarily chosen, but are not too widely set, so that the experimental points are spread enough to easily distinguish them. Some of the data in Tables 3 and 4 in Ref. [3] are outside of these ranges and so are not shown. If the ranges had been enlarged to accommodate them, the central part would have been too compressed to observe. It is assumed that these missing points are too widely off to be considered to be viable results.

2.2. Optimisation methods

A number of algorithms are available for optimisation (minimisation of DEV by varying E_a, ln(A) and n). Many of these depend on determining a direction of steepest descent, following that direction until DEV begins to rise again and then recalculating a new direction. Some of the early work was carried out by Rosenbrock [10]. Further developments were made by Powell [11], Fletcher and Powell [12] and by Fletcher and Reeve [13]. The improvements were usually in making sure that the routine could turn in direction when

Table 5
Gradient and intercept values for the lines running down the valley bases (kinetic compensation effect parameters) for plots of E_a in kJ mol^{-1} versus ln(A), derived from the data used to plot the valleys.

Taken from the data used for the plots in figures	Gradient (kJ mol^{-1})	Intercept (kJ mol^{-1})	R^2
Simulated Fig. 9	3.992	10.495	1.0
Calcite in vacuum Fig. 10A	6.686	52.824	0.999991
Calcite in nitrogen Fig. 10B	8.399	61.357	0.999987

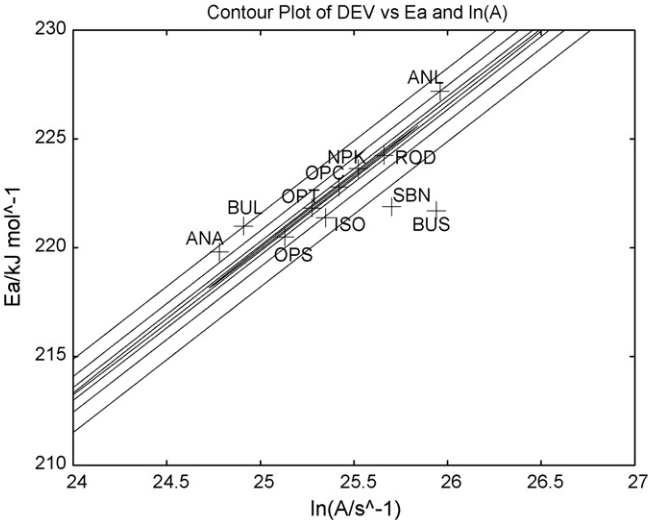

Fig. 6. Contour plot for DEV versus E_a and ln(A) for calcite in vacuum. Contours of DEV are plotted in pairs at 0.1, 0.05, 0.02, 0.01, 0.007, reading from outside inwards. Key to the points plotted: (A) OPT – optimum point from direct grid search by the present authors. (B) Results in Table 1 in Ref. [3], which were derived by an NLR method and Avrami–Erofeev n'-dimensional equation. OPC – Opfermann corrected – see text. OPS – Opferman sets 1 + 3, low α. ROD – Roduit. (C) Results in Table 1 in Ref. [3] which were derived by other methods and equations. ANA – Anderson, $n = 0.5$, all data. ANL – Anderson $n = 0.5$, lower data. BUS – Burnham, Šesták–Berggren equation, $m = 0.495$, $n = 1.0$. BUL – Burnham Friedman equation $n = 1$, low α. Burnham Friedman equation $n = 1$, high α – too far off to show. (D) Results obtained by the present authors by other methods – see text. SBN – Šesták–Berggren equation, Nelder–Mead optimisation, $m = 0.3462$, $n = 0.8210$. NPK – non-parametric kinetics. Integral method, see Ref. [20]. ISO – Isoconversional method. (Friedman) output from the NPK method.

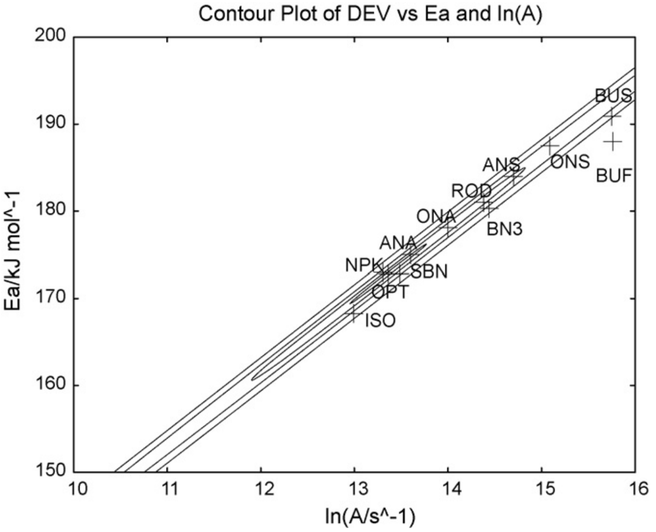

Fig. 7. Contour plot for DEV versus E_a and ln(A) for calcite in nitrogen. Contours of DEV are plotted in pairs at 0.1, 0.05, 0.02, 0.01, reading from the outside inwards. Key to the points plotted: (A) OPT – optimum point from direct grid search by the present authors. (B) Results in Table 4 in Ref. [3] derived by NLR method and n order equation. ONA – Opfermann n order, all data. ONS – Opfermann n order, sets 2 + 4. ROD – Roduit. (C) Results in Table 4 in Ref. [3] derived by other methods and equations. ANA – Anderson equation $n = 0.0$, all data. ANS – Anderson equation $n = 0.0$, sets 2 + 4. BU3 – Burnham (773, 732 and 700 K only) Šesták–Berggren equation, $m = 0.087$, $n = 0.155$. BUF – Burnham sets 2 + 4 Friedman equation, $n = 1$. BUS – Burnham sets 2 + 4 Šesták–Berggren equation. (D) Results obtained by the present authors by other methods – see text. SBN – Sestak–Berggren equation, present authors, Nelder–Mead optimisation, $m = 0.0577$, $n = 0.143$. NPK – non-parametric kinetics. Integral, method see Ref. [20]. ISO – Isoconversional method (Friedman) output from the NPK method.

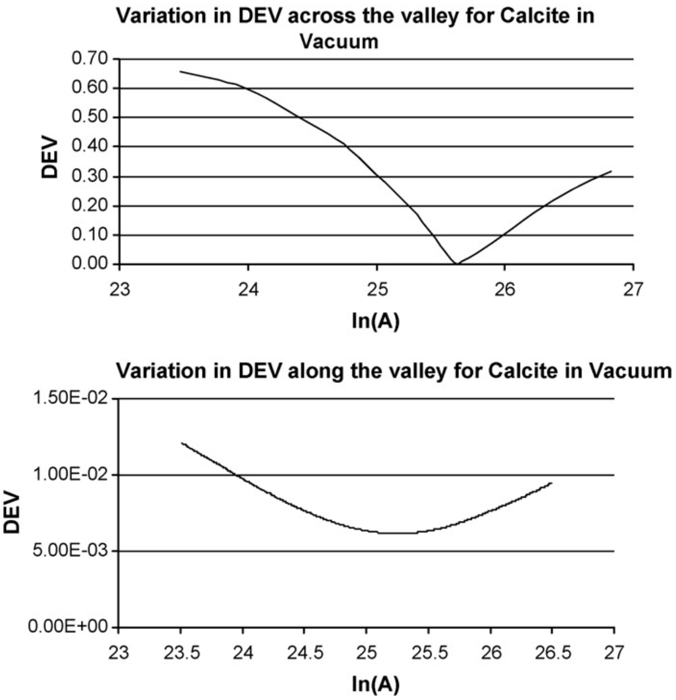

Fig. 8. Variation of DEV across the valley and along the valley for calcite in vacuum, measured at the optimum point. Note the very different vertical scales.

some difficult function was being minimised and not to get stuck at some false minimum. A completely different technique was promoted by Nelder and Mead [14]. This uses a simplex, which is a multidimensional shaped object in space, delineated by the axes of the variables of the problem. In this case there are three variables (E_a, ln(A) and n') and the simplex has four vertices and four faces. Replacing one vertex at a time controls the movement of the simplex along the valley, plus some contraction or expansion as required. When near the optimum point the simplex no longer moves and then only contracts onto the final position. Thus it is very unlikely that the simplex would stick at a false optimum point.

Subroutines in Fortran are available on the Internet for some of these methods, for instance: Powell [15], Fletcher–Powell [16], Nelder–Mead [17]. These were adapted in programs to minimise DEV. It is worth testing all of these various methods on the present problem, because if they fail, that may be the reason that some of the reported results are a long way out. The valley plots in Figs. 3–5 show that the valleys are relatively narrow and steep sided for the calcite samples, but are rather broader for the simulated data. If the views are rotated to look at the base of the valleys, the line appears to be horizontal with no minimum. However, a minimum is present, but not seen visually. DEV was calculated along a line running down the base of the valleys and another set of results measured across the valleys at right angles to the line down the valleys. The cross-valley position could have been chosen at any point but was in fact placed at the optimum points. These DEV results were plotted against ln(A) as a parameter. Fig. 8 shows the results for the calcite under vacuum. The minimum is now clearly visible, but a comparison of the scales of DEV shows that the variation of DEV is very small along the valley but large across the valley. The results for calcite under nitrogen and the simulated data showed a similar pattern. When the optimising routines mentioned above are used there is a danger that they may be over-influenced by the steep sides and miss the gradient down the valley. If this happens the routine will end up stopping at the wrong point or oscillating from side to side of a valley, being incapable of rotating 90° to continue correctly.

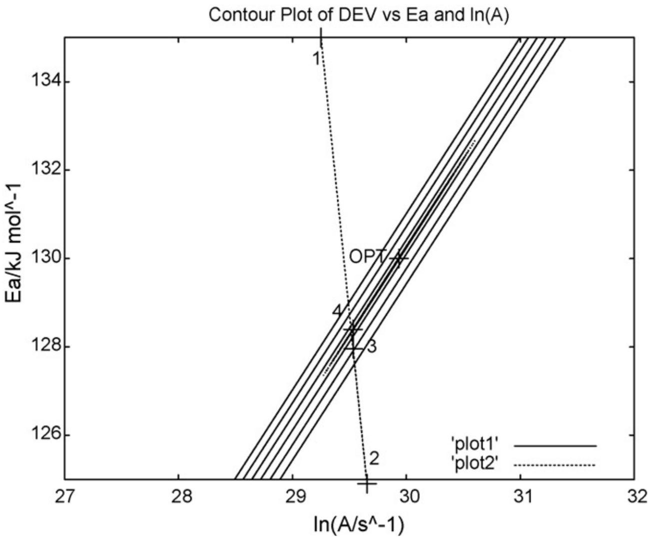

Fig. 9. Contour plot of the base of the valley for simulated data using an Avrami–Erofeev equation with $n' = 3/2$, showing the path taken by the Powell optimisation method. Plot 1 contour lines. Plot 2 path taken by optimisation. The points run from 1 to 4. The point at 2 is caused by overshoot, followed by a return to 3 and 4. Does not reach the optimum point.

Similar results were obtained in the EXCEL spreadsheet using the SOLVER function. This uses an optimiser routine devised by Lasdon et al. [18].

2.3. Simulated data for Avrami–Erofeev equation with $n' = 1.5$

Table 2 shows that the optimum point for this data, OPT reproduces the starting data used by the simulation program. The Powell optimisation fails even for this ‘perfect’ data as shown in Fig. 9. The other optimisation methods succeed in reaching the optimum point as do the isoconversional and NPK methods. No graphical results are presented because they would only consist of a set of contours with one point marked for OPT and the result for optimisation. The only exception is shown in Fig. 9. The values of the minimum DEV in the table vary a great deal between the methods. This is because the correct value of DEV should be zero, but the optimum point is not reached with equal precision in all cases so DEV is always slightly above zero. In fact, the Nelder–Mead method seems to end rather nearer to the starting parameters than the direct grid search method.

2.4. Calcite under vacuum – analysis of the results shown in Ref. [3]

It must be emphasised that the plots of the valleys were produced only from a calculation of DEV from an n'-dimensional Avrami–Erofeev equation. Other kinetic equations cannot be expected to fit the data in the same way so are not strictly relevant to the valley plots. However, it is of interest to see how close results by order or Šesták–Berggren equations are to the valley. GNUPLOT was used to make contour plots instead of the three-dimensional plots. On the same plots the ICTAC study results are shown as crosses. Fig. 6 shows the vacuum data results taken from Ref. [3], plus some results produced by the present authors. Some of the points are obviously erroneous. In Table 3 in Ref. [3], the results from Malek and Mitsuhashi are far too low and they do not supply a value of ln(A), so this result has been ignored. Also Anderson’s result for $n = 1$ is too far out to fit. Desseyn et al. gave results varying with α, but it was decided only to consider single or mean values in these plots.

The result produced by Opfermann for vacuum, using the total data, is $E_a = 222.8$ kJ/mol, $\ln(A) = 11.04$ and $n = 1.5543$. If these figures are put into a simulation program they are obviously wrong. The resulting absurd α values run from 10^{-9} to 10^{-11}! If it is assumed that mistake B described above has been made, then the antilog$_{10}$ of 11.04 may be taken to obtain 1.09647×10^{11} for A. The correct log$_e$ of this gives 25.42, a much more reasonable value. This produces a point in Fig. 6, which is in fact the closest to the optimum point along the base of the valley. The optimisation had almost reached the optimum point. Opfermann’s result, using only two of the data sets, produced a point only a little too far down the valley. Roduit’s value is too far up the valley and slightly up the wall of the valley as well. It looks as if this optimisation stopped prematurely. Results using an order equation (Anderson and Burnham {low α}) are at least near to the valley. Burnham’s use of the Šesták–Berggren equation gives a result a long way from the valley.

None of the results examined appear to show the fault from Section 1.1: possible error A (see above) in ln(A). That is no error is large enough to be explained by mixing up s^{-1} with $\min^{-1}$.

If the wrong definition of kinetic equation has been used then A must be corrected as suggested in Section 1.1 possible error F. The original paper suggested that Opfermann and Roduit both used the correct definition of the kinetic equation for Avrami–Erofeev with variable n'. Any attempt to move their points on Fig. 6 to the right by 0.443 in ln(A) took them well outside of the valley and is obviously a wrong move. The 1st order points do not require moving. The 0.5 order points require ln(A) moving by $\ln(2) = 0.693$ to the left, which also took them away from the valley and the optimum point. It looks as if the correct form of the equations was used for Avrami–Erofeev, 1st order and 0.5 order.

2.4.1. Optimisation using vacuum data

2.4.1.1. Avrami–Erofeev equation use. The optimising routines were applied to the three sets of data and the final points found are shown in Tables 2–4.

Figs. 9–12 show some of the steps in the progress of the optimising routines. The optimisation passed through many steps but only some are indicated on these plots. These were where there was a sharp change in direction, plus the starting and finishing points. In Fig. 10 the original Powell calculation obviously does not work correctly. Starting from two separate points labelled 1 and A and following the labelled points, shows that the valley is reached and the direction of movement turns down the valley. The optimisation then stops, and a detailed examination of the end point shows that the calculation is zigzagging from side to side, then stops.

Stopping criteria were examined and the precision increased, but the result was no better. The method did not even work for simulated data as shown in Fig. 9. The Fletcher–Powell calculations improved on the Powell method as shown visually in Fig. 11A. However, Tables 3 and 4 show that the optimum points are not always reached precisely enough. The last method by Nelder and Mead shows in Fig. 12A that OPT is reached and in Table 3, the exact optimum values are presented. The speed of optimisation for Nelder and Mead was also much greater. Examination of the minimum DEV values produced shows that much the same value was produced by several optimisation methods. This would mean that choosing the method by the lowest DEV produced would be very difficult. The difficulties in selecting a model have been discussed by Vyazovkin and Lesnikovich [19,20]

2.4.1.2. 1st and 0.5 order calculations. Attempts were made to replicate the results of Anderson, Burnham and Desseyn who applied order equations to the vacuum data. Neither type of equation got anywhere near fitting the data. Because the order may not be exactly 0.5 or 1, a variable order was tried. The nearest fit is shown in Fig. 13, but is not very convincing. The shape of the data curves is obviously

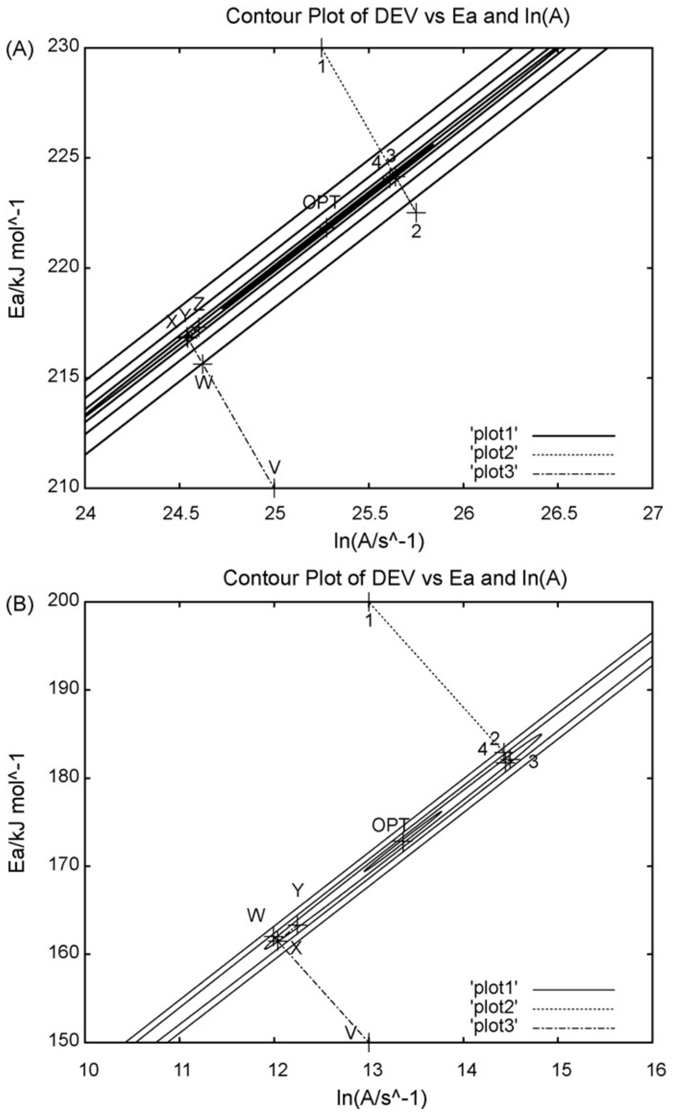

Fig. 10. Contour plot of the base of the valleys for: (A) calcite in vacuum, (B) calcite in nitrogen, showing the paths taken by the Powell optimisation method. Plot 1 contour lines. Plot 2 and Plot 3 paths taken by optimisations. The points and lines marked from 1 to 4 and V to Z (V to Y for diagram B) are attempts reach the optimum point, OPT from two starting points. They do not reach the optimum point.

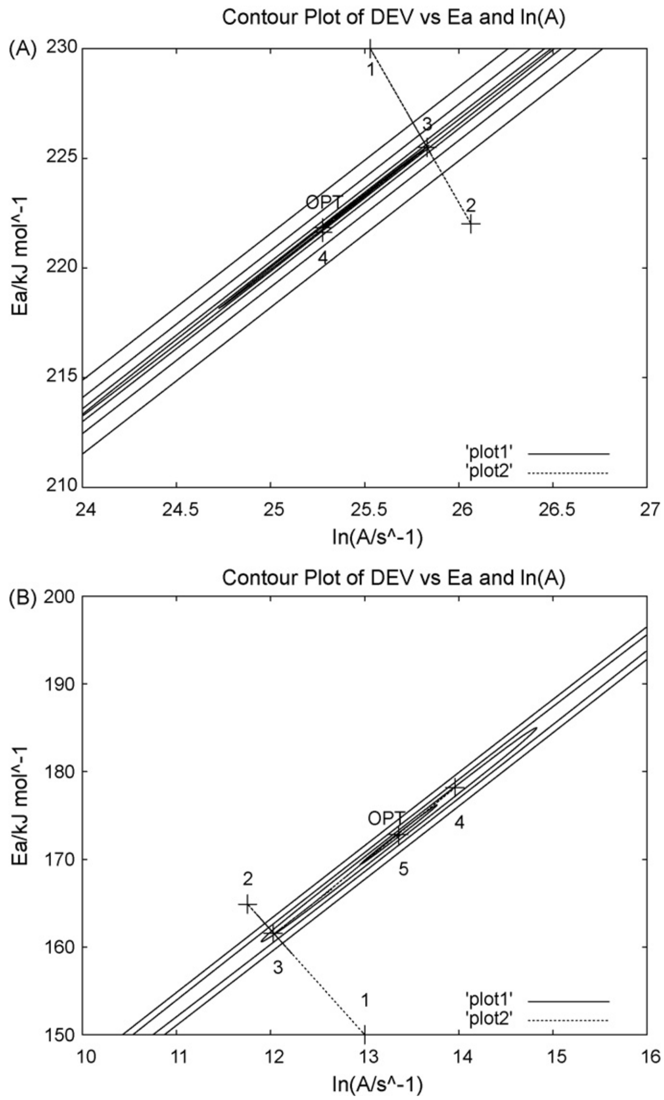

Fig. 11. Contour plots of the base of the valleys for: (A) calcite in vacuum, (B) calcite in nitrogen, showing the path taken by the Fletcher–Powell optimisation method. Plot 1 contour lines. Plot 2 path taken by optimisation. (A) The points run from 1 to 4 with overshoot at point 2. Point 4 and OPT nearly coincide. (B) The points run from 1 to 5 with overshoot at 2 and 4. Point 5 and OPT coincide.

nothing like 0.5 or 1st order because there is an accelerating portion of the curve at low α. The order type equations all have to pass through $\alpha = 0$ at time = 0 and the best fitting lines do not. It is just possible that this may be due to an induction period, where the main mechanism is not followed for a period of time, during which the sample had not reached the final decomposition temperature. A correction of the time scale was carried out assuming that the reaction actually started at a time t_0 after the start of data collection. The delay was different for each data set temperature. Each set of data was first separately optimised by NLR, including t_0 as an extra factor to be determined by the Nelder–Mead procedure. The whole data sets were then optimised for E_a and ln(A), holding the individual t_0 values constant. The results for a 1st order plot were no better than Fig. 13, but for a 0.5 order there was a slightly better fit, but this was by no means perfect. What would really be required would be to include the six individual values of t_0 as parameters for the optimisation, together with E_a, A and n. However nine parameters is beyond the capabilities of all of the optimisation methods which only work well for three to four parameters. Following Anderson, the optimisation was repeated for order 0.5, only in the lower α ranges and for 1st order in the upper range, assuming a mechanism change around $\alpha = 0.5$. Again the fit was only slightly better than in Fig. 13. The plots for these results are not shown, but the numerical results obtained are shown in Table 3. The minimum values of DEV are not as good as for the Avrami–Erofeev equation. The upper experimental curve is of the right shape for $n = 1.0$ and $\alpha > 0.5$, but order 0.5 does not appear to be a good fit for the lower half. The fit of the Avrami–Erofeev equation with $n = 1.5587$ is shown in Fig. 14 and, taken with the low value of DEV in Table 3, must be the more likely mechanism.

2.4.1.3. Šesták–Berggren equation [21]. The idea seems to have grown, more recently, that if p, in Eq. (1), is equated to zero, the resulting equation,

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{16}$$

has a validity of its own.

This is now seems to be known as the Šesták–Berggren equation and attempts have been made to fit it to experimental curves of various shapes. Recently Criado and co-workers [22] have suggested

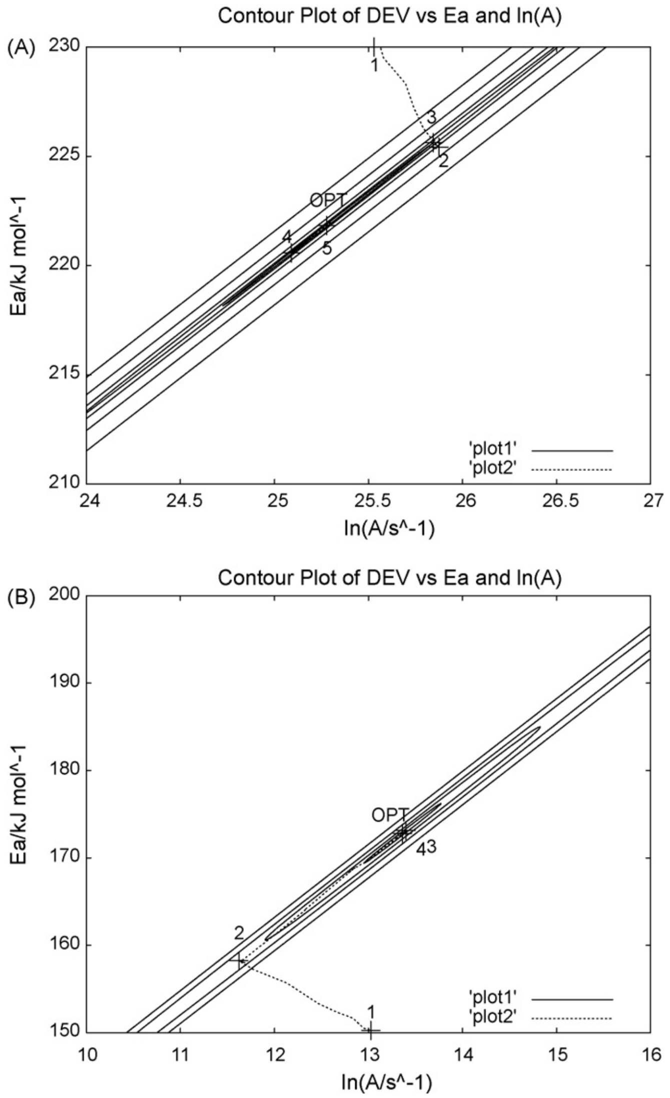

Fig. 12. Contour plots of the base of the valleys for: (A) calcite in vacuum, (B) calcite in nitrogen, showing the paths taken by the Nelder–Mead optimisation method. Plot 1 contour lines. Plot 2 path taken by optimisation. (A) The points run from 1 to 5 with overshoot at 2 and 4. Point 5 coincides with OPT. (B) The points run from 1 to 4 with overshoot at 3. Point 4 coincides with OPT.

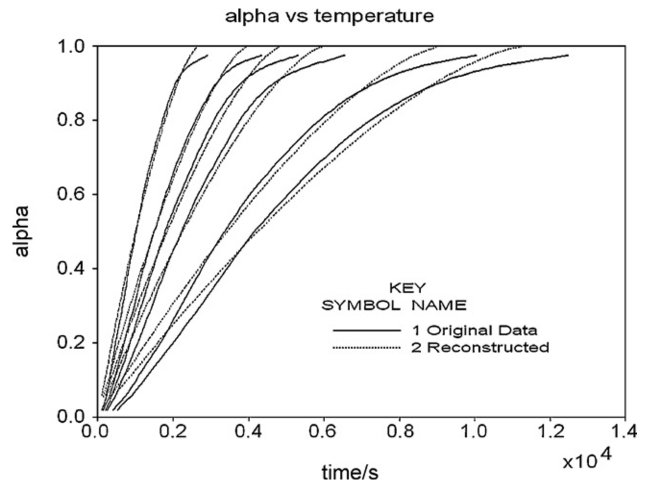

Fig. 13. Attempt to fit an n order equation to the vacuum data by NLR method (Nelder–Mead), with $n = 0.3238$.

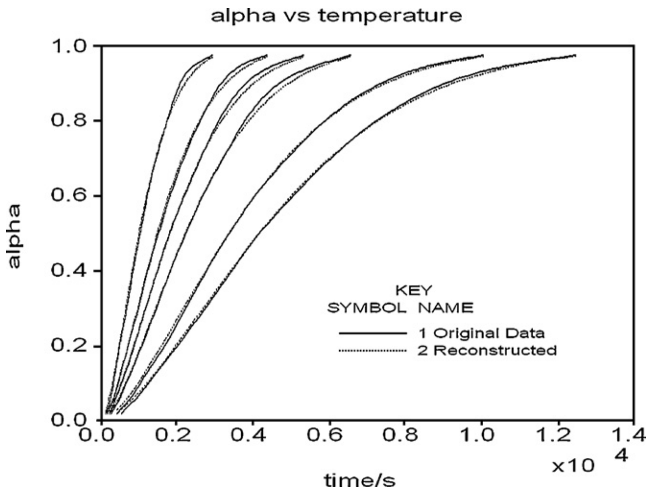

Fig. 14. Attempt to fit an Avrami–Erofeev equation to the vacuum data by NLR method (Nelder–Mead), with $n' = 1.5587$.

a new version of this equation with an extra variable c:

$$\frac{d\alpha}{dt} = kc\alpha^m(1-\alpha)^n \tag{17}$$

Because equation Eq. (16) was used in the original study, we decided use that and not Eq. (17) to make comparisons easier. The meaning of Eq. (16) and the use of Eq. (17) will be covered in a later paper.

Burnham has suggested this equation as a fit to the data. It is not stated how this was done, considering that the equation does not integrate. It is possible to apply numerical differentiation of the original data and to fit the theoretical $d\alpha/dt$ to the experimental values. In view of the fluctuations shown in Figs. 1 and 2, this is not likely to be very precise. For Nelder–Mead optimisation in a Fortran77 program, numerical integration could be used for the Šesták–Berggren equation. This was carried out by the Clenshaw–Curtis method, in a routine called intcc, found at a website provided by Ooura [23]. This should give more precise results than the differential method as is shown in Table 3. Compare differential and integral results under the headings:-‘other kinetic equation, Šesták–Berggren’ and ‘other methods of analysis’ at the bottom. Slightly different parameters to those of Burnham were obtained. The fit of the theoretical curve to the original data is shown in Fig. 15 and is marginally better than the fit for the Avrami–Erofeev equation in Fig. 14. Observation of the diagrams

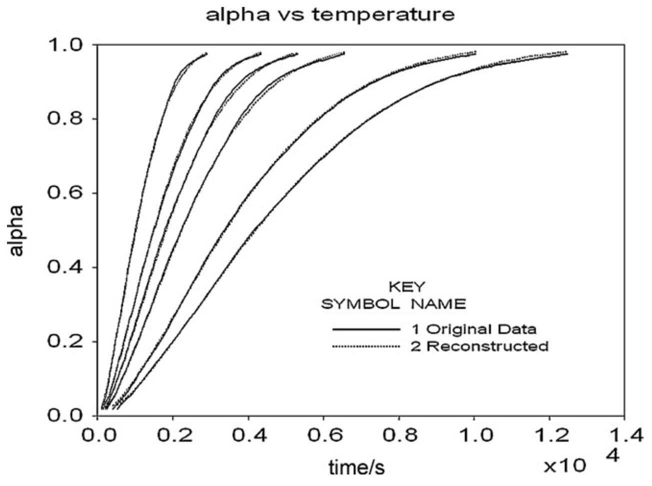

Fig. 15. Attempt to fit a Šesták–Berggren equation to the vacuum data by NLR method (Nelder–Mead), with $n = 0.8210$ and $m = 0.3462$.

of the fitting of the equation, Figs. 14 and 15, showed that sometimes the fit is better at the top of the data and sometimes at the bottom, so there is no unique answer.

When Burnham's result (BUS) and the result from Nelder and Mead's (SBN) optimisation were plotted on Fig. 6 the points were well away from the valley. It might be that if Criado's new equation, Eq. (17), had been applied then the Šesták–Berggren results in Fig. 6 might have been closer to the optimum point. It was assumed that the valley would be in a different place if produced for the Šesták–Berggren equation instead of for Avrami–Erofeev.

2.4.2. Other calculations with the vacuum data

The NPK (non-parametric kinetics) method uses SVD (singular value decomposition) and has been described for isothermal data analysed by an integral and a differential method [24]. It was shown that the integral analysis was the most efficient, so this has been applied to the present data and the results entered into Table 3. The figures obtained are close to the optimum values even though the calculation depends upon a different principle (decomposition of a matrix) and not upon DEV. Although DEV is not calculated during the NPK method, it was determined using the simulation program as a measure of fitting of the theory and is marked as NPK in Fig. 6. It was convenient to include in the NPK program a calculation by an isoconversional or Friedman method. This produced values of E_a and $\ln(A)$ at pre-chosen values of α. Here α was in steps of 0.05. A plot of E_a versus α was usually near a horizontal straight line except for a few figures at low α. The rest of the E_a and $\ln(A)$ values were averaged to produce the figures given in Tables 1 and 2. Since the NPK method has to assume a kinetic equation the Avrami–Erofeev with $n' = 1.5$ was used, with the 1st order equation used by Burnham as an alternative. It may be seen from Table 1 that the results are not very close to OPT, but they are from a different method of calculation to that used in the determination of the valley and OPT. For this reason no attempt has been made to calculate the minimum in DEV, except for the Avrami–Erofeev equation with $n' = 1.5$ because this is very close to the value when n is allowed to vary, when it comes out as about 1.5587.

2.5. Calcite under nitrogen – analysis of the results in Ref. [3]

The direct grid search method was again used for this data to produce the OPT result for comparison with other methods and the Ref. [3] results.

The tables in Ref. [3] showed results not quite as scattered as for those under vacuum. The results produced by Malek and co-workers were left out for the same reasons as above. Several Ref. [3] results lie in the valley, but too far up. This again suggests that optimisation has stopped prematurely with little or no progression down the valley. It could be that the wrong form of the kinetic equation was used (as explained above in Section 1.1: possible error F). From Eq. (9), the correction to $\ln(A)$ would be $\ln(1/(1-n))$. Since n was about 0.0639, the correction would be 0.0660. Examination of Fig. 7 showed that such a small correction makes practically no difference to the points but only takes them away from the valley. For the other types of equations there is no correction for 1st order or for zero order.

2.5.1. Optimisation using nitrogen data

Fig. 16 shows an attempt to fit various orders to this data. It shows that the data plot is only slightly curved and lies somewhere between a 0.5 order and zero order curves. For this reason using an order type plot with variable value for n seems to be the best solution, so Eq. (3) was used in the optimisations. Fig. 10B shows that the Powell method does not work for the nitrogen data either. Reasonable results are produced by Fletcher–Powell and Nelder–Mead methods. The OPT point is reached in each case. Table 4 shows the precision produced, and Fig. 17 shows the closeness of the fit. The result obtained by the Nelder–Mead method is very close to the optimum value. The result from Anderson [3] is surprisingly close to the optimum value considering that he assumed zero order. Observation of the plot in Fig. 16 shows a gentle curve, not a straight line. A 1st order plot is also not feasible, as shown in Fig. 16. This time the original plot seems to start at the origin and the curvature is always in the same direction. Therefore, adjusting a value of zero time, $t_{0,}$ does not help. Table 4 contains the results for the fitting of a zero order equation. The minimum deviation is, as expected, much higher than for the other methods. Anderson did not quote a range of α for his fitting so at first the whole range was used for one analysis. As an alternative, data for $\alpha < 0.5$ only was used. The fit then seemed much better. The value of DEV, shown in Table 4, then appeared to be lower than for many other methods. This could mean that the first part of the decomposition follows zero order but slows slightly when $\alpha > 0.5$ to a new mechanism, with n of about 0.0639.

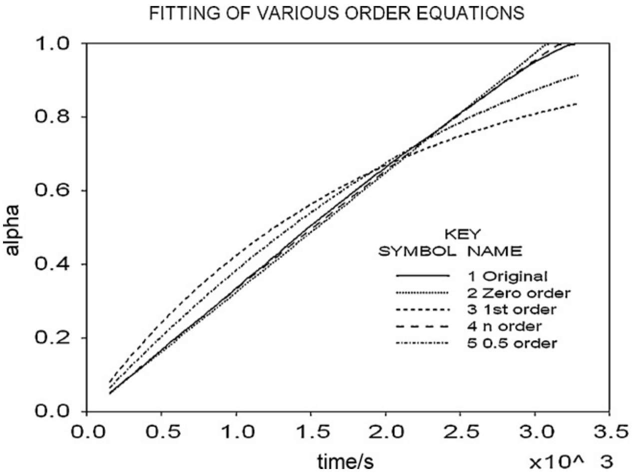

Fig. 16. Plot of the nitrogen data at 700 °C only. Attempts to fit equations for zero, 0.5, 1st and *n*th ($n = 0.0996$, differs from the result for multiple temperatures) order by NLR method (Nelder–Mead).

An attempt to use the Avrami–Erofeev equation to fit this data was, as expected, a complete failure because the experimental data does not have the sigmoid shape that would be required.

The Šesták–Berggren equation was a further complication, in this case by having two determinable parameters, n and m. The values of the parameters determined by us again differed slightly from those of Burnham. The plot of the fitting of the data in Fig. 18 is

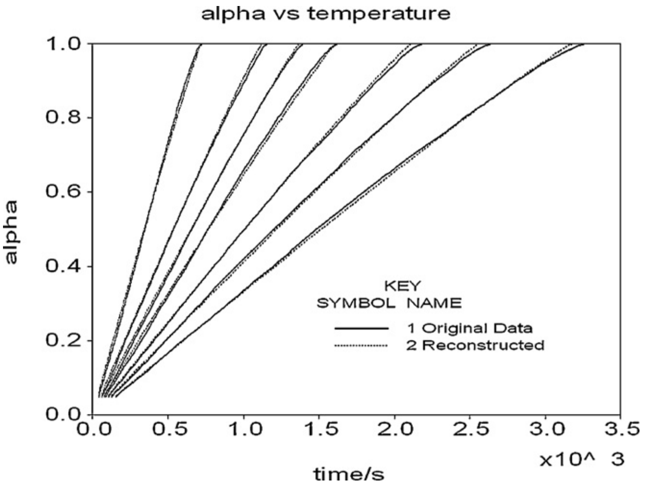

Fig. 17. Attempt to fit an order equation to all of the nitrogen data, with $n = 0.0639$.

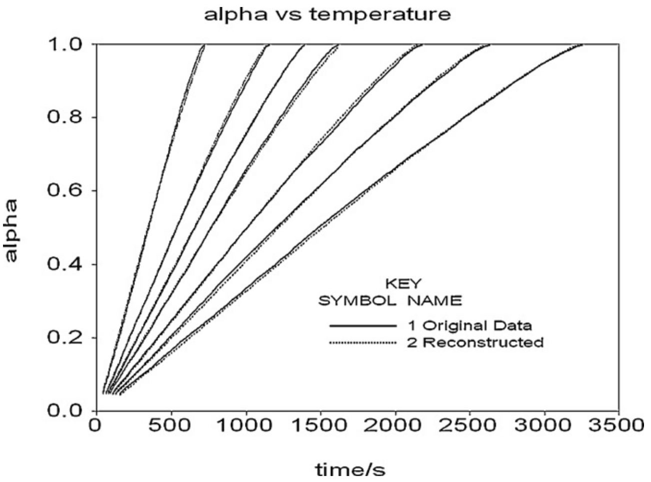

Fig. 18. Attempt to fit a Šesták–Berggren equation to all of the nitrogen data, with $n = 0.1451$, $m = 0.0585$.

almost indistinguishable from the n order method in Fig. 17. However, at the top end of the plots, above $\alpha = 0.9$, the line curves to the right to a greater extent and the Šesták–Breggren function follows this better. The value of DEV, shown in Table 4, is actually slightly better than for the n order equation. Strictly speaking a new valley and OPT point should be drawn up using the Šesták–Berggren equation to compare with the value produced by optimisation. However, the results from the two equations are very close and the point in Fig. 7, corresponding to the use of the Šesták–Berggren equation, lies in the valley produced for the Avrami–Erofeev equation, close to OPT.

2.5.2. *Other calculation for nitrogen data*

The NPK method may not be satisfactory in this case because it has to assume a function for a chosen mechanism. The nearest possible mechanism, in this case, is zero order. The result is in Table 4 and shows values of E and A close to the optimum values, but DEV is not as low as for the other methods.

3. Variation in E_a with alpha

The NPK method allows the calculation of one value of E_a from an overall matrix of all of the data (reported in Tables 2–4) and as separate E_a values from the matrices for sets of individual steps of five data points at a time. These are from the interpolated sets of data, not the original experimental sets. For an explanation, see Ref. [24]. The values of E_a are plotted in Fig. 19 for the vacuum sample and the nitrogen sample, using integral data i.e. the original data. The mean of these values is shown in the tables, as well the overall figures from the total matrix calculation. Fig. 20 is a similar plot, but uses a differential method i.e. the original data has to be differentiated first. The Isoconversional or Friedman method also gives the variation of E_a and is shown for comparison. It is obvious from Fig. 20 that the differential methods are not suitable for these samples and should not be used. The fluctuations are considerable and reflect the differentiated results shown in Figs. 1 and 2. Considering the integrated data only, the vacuum result showed only slight variation across the range with a standard deviation of 3.0 kJ/mol, while the nitrogen result showed a slight continuous rise with a standard deviation of 5.5 kJ/mol. These results are useful for comparison with the non-isothermal results in Part 2.

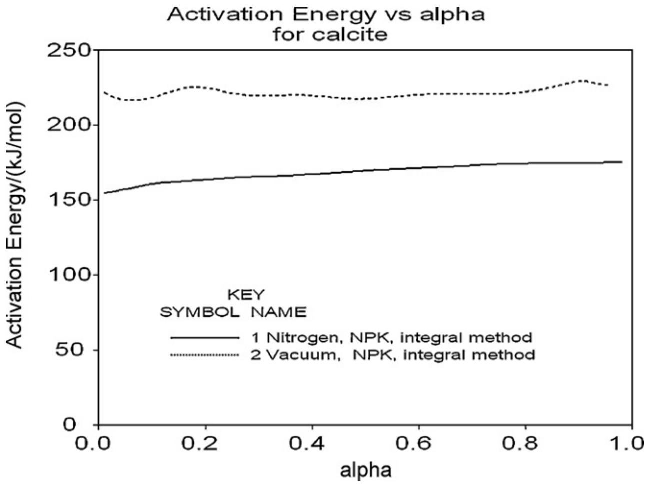

Fig. 19. Variation of E_a with α for the vacuum and nitrogen samples calculated by the NPK method using integral data.

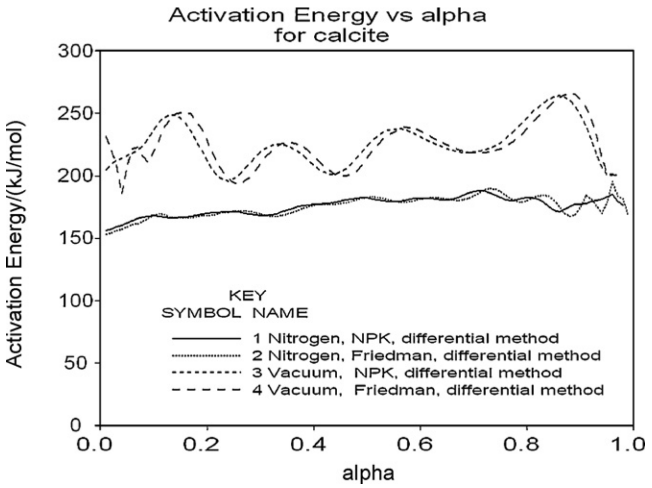

Fig. 20. Variation of E_a with α for the vacuum and nitrogen samples calculated by the NPK and Friedman methods using differentiated data.

4. Conclusions

The experimental data used in the ICTAC study and in this report is almost certainly not suitable to produce firm conclusions about the kinetic triplet values or the mechanism followed. However the original study was to compare results from several laboratories, so in some ways the actual values of parameters obtained are less important than the comparisons between laboratories and instruments. Therefor readers should not take these results as definitive, precise results for the decomposition of calcite. There seem to be several reactions taking place together, so the results just indicate general values, averaging out the figures for the set of reactions taking place.

In their paper [8], Brown and Galwey remarked “Who is to decide and for what reason that some results are to be identified as ‘faulty’?” This is true in the sense that it is possible to argue that one kinetic equation or another is the best fit to the data, and which optimisation method should be used. It is especially true if the argument is over the fit in one range of α being better than another. Vyazovkin and Lesnikovich [25] have clearly shown that the incorrect function will lead to errors in the Arrhenius parameters. However in this paper the Avrami–Erofeev equation with variable n' was adopted because it was the equation used by the majority of investigators; thus everyone should be able to reproduce the parameters E_a, $\ln(A)$ and n'. As for a correct answer, we believe that this is the optimum point obtained by Direct Grid search, but it is a time consuming method. The points plotted as OPT lie on the base of their valleys and at the minimum point according to the contour plots in Figs. 6 and 7 and at the minimum indicated in Fig. 8.

The first conclusion from the result tables in Ref. [3] and the plots, Figs. 6 and 7, is that there is no agreement at all. Brown and Galwey [8] have commented on this at length. Figs. 9–12 show that some optimisation methods fail or are less satisfactory, but a method such as that of Nelder and Mead always reaches the point OPT. The second conclusion is that there must be faults in the programming of the analysis systems used by many of the contributors. Brown and Galwey [8] have invited the contributors to look again at their programming to find out why they cannot agree. They may have used the wrong optimisation technique or have set the precision for the stopping of optimisation to be too high. It was shown in Fig. 8 that the slope along the valleys is low, so it is easy to stop short of the optimum point. We now invite them to show why they do not get the optimum points described here. If they do not respond to this, then the results from these programs, including some commercial products supplied with equipment, must be regarded as suspect. The programs need to show that they can at least accurately retrieve the parameters for a single kinetic equation such as the simulated one described above.

It was not in the remit of the study to examine the mechanism of the decomposition suggested by the equations. However, since a decision is required between several possible mechanisms it is helpful to consider this. The value of n' suggested by the Avrami–Erofeev equation fit is about 1.5587. This is close to the value of 1.5, which is the standard value for one of the versions of the Avrami–Erofeev equation. This has been stated by Hulbert [26] to be derived from diffusion controlled mechanism in either, needles with a constant rate of nucleation, or in spheres with a zero rate of nucleation. The present results do not quite fit this mechanism, but this may be due to several extra factors e.g. unequal particle sizes, inhomogeneous temperature, strain in some crystals or impurities or a more complex mechanism. However, it looks as if the major part of the decomposition is by this mechanism. Alternative mechanisms suggested were 0.5 or 1.0 order. To obtain a reasonable fit the time scale had to be changed and/or the range had to be split at $\alpha = 0.5$. This is possibly correct but gives the impression of straining the theory to try to force a fit. Burnham has suggested the use of the Šesták–Berggren equation. In their original paper [21] these authors looked at a series of mechanisms which produced a series of functions of α and they commented that they fell into three types. They then put these together in a single, generalised Eq. (1). They did not seem to mean that the parameters m, n and p could have a wide range of numerical values but only the standard values that appeared earlier in their paper (from the generally recognised equations at the time, or devised later, provided there was some underlying mechanism to suggest them). They pointed out that there was no known mechanism which produced values for m, n and p simultaneously. It is a mistake then to try to fit this equation to any chosen data and to allow the parameters to have any value that seems to give a good fit, when there is no mechanism from which this is devised. The process is the same as saying that a polynomial equation can be fitted exactly to any data provided sufficient number of terms is included and there is not a theoretical meaning to the result.

In the case of the nitrogen results, an order equation seems to fit with an n value of about 0.0639. The meaning of this is unclear. As stated above, it may mean that the mechanism is mainly zero order with some deviation away as more of the calcite is used up. The Šesták–Berggren equation has an extra parameter added because m was allowed to vary. This is a further, unnecessary complication, because there is no mechanism suggested to explain the values of n and m found.

The NLR method is only valid if careful checks are made to ensure that the true minimum or optimum point is reached. The results in Ref. [3] do not achieve this. A mechanism should be identified from the results. Often several seem to be equally valid, but there is no point in choosing an equation which has no theoretical basis (other than a suggestion that it may be autocatalytic [27]). Equally, fitting equations to only part of the range, just to produce a low value of DEV is only valid if there is good evidence for a change of mechanism. In the present study for vacuum data the Avrami–Erofeev equation seems to be the best fit with $n' = 1.5587$. This seems to indicate that really $n' = 1.5$, but there are minor fluctuations from a simple mechanism causing the experimental value found. In the case of the nitrogen data, the nearest mechanism seems to be zero order, but as part of the sample is used up, the rate reduces steadily, causing an apparent order of $n = 0.0639$.

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