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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA COMPUTER PROGRAM TGA--ETC(U)
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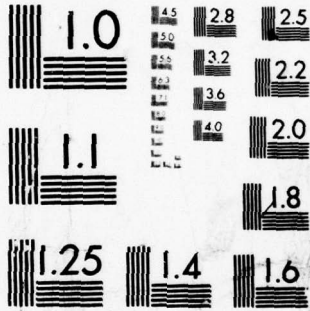
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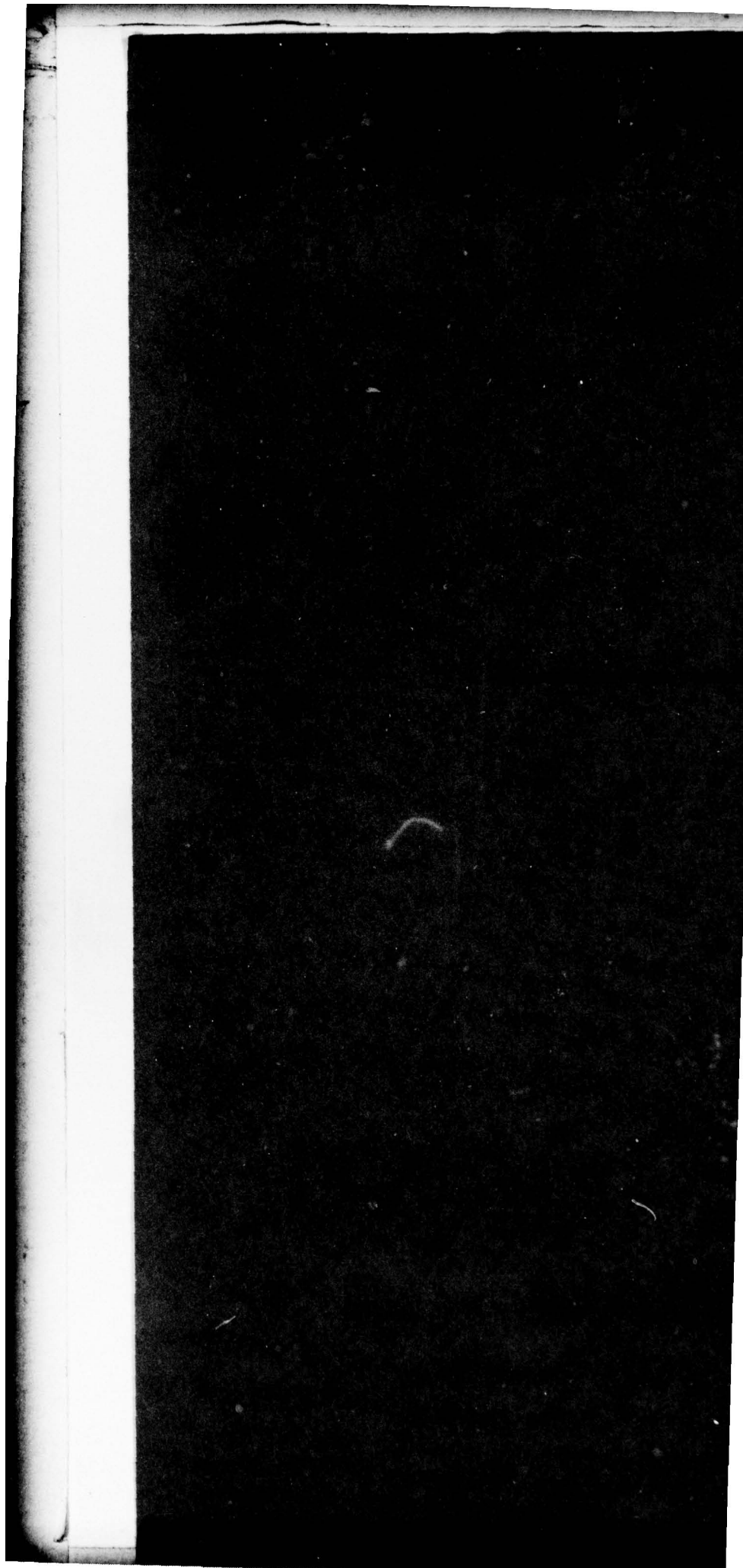
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AWRE REPORT NO. 056/78 ✓

6 Kinetic Analysis of Thermogravimetric Data
Computer Program TGA2

10 H. Briscall

11 Apr 79

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Recommended for issue by

A Catherall, Superintendent

Approved by

D Deverell, Senior Superintendent

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CONTENTS

	<u>Page</u>
SUMMARY	3
1. INTRODUCTION	3
2. THE DOYLE/ZSAKO METHOD	4
2.1 The outline of the method	4
2.2 Modifications of Doyle/Zsako method for TGA2	6
3. DESCRIPTION OF THE PROGRAM TGA2	7
3.1 Input	7
3.2 Program TGA2	8
3.3 Output	9
4. DESCRIPTION OF THE CURVE	9
4.1 Preparation of four standard curves	10
4.2 The effect of limiting the range of $(1 - \alpha)$ by truncating the ends of the curve	10
4.3 The effect of limiting the number of uniformly spaced $(1 - \alpha)$ values in the range 0.05 to 0.95	10
4.4 The effect of progressive removal of the ends of the curve	12
4.5 The relative importance of the different parts of the $(1 - \alpha)/T$ curve	12
5. DISCUSSION	13
REFERENCES	17
APPENDIX A: PROGRAM TGA2	18
FIGURES 1 - 5	21

SUMMARY

Zsako has modified a curve fitting method reported by Doyle and in this report the method is further simplified to allow the use of a digital computer. The best description of the thermogram step was found to be given by 19 equally spaced co-ordinates between the $(1 - \alpha)$ limits of 0.05 to 0.95.

These co-ordinates, together with the heating rate, are used to calculate E and log Z, by an iterative process which minimises the standard deviation of the $\log g(\alpha) - \log p(x)$ values.

The standard deviation allows a comparative assessment of the validity of the kinetic equations chosen to represent the mechanism of the reaction. A further simplification involved the use of an approximate equation for $-\log p(x)$ in place of tabulated values.

The TGA2 method of calculation was shown to be valid by re-calculating E and log Z for standard curves which were generated from tables of $-\log p(x)$.

Published data by Doyle and Zsako were re-calculated and the answers were in good agreement with the original results.

1. INTRODUCTION

The thermal decomposition of solids may be described by the equation $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$.

This is a simplified statement of a complex process in which many different steps may be proceeding simultaneously. These include physical processes such as diffusion of heat and diffusion of gaseous products, as well as breaking of chemical bonds.

Thus, the kinetics of thermal decomposition reactions depend upon experimental conditions as well as the chemical nature of the solid [1,2].

Many efforts have been made to obtain kinetic parameters from isothermal and dynamic thermograms and these have been reviewed [3,4].

Utilising a single weight loss/temperature curve has an obvious advantage over isothermal weight loss/time curves produced at several different temperatures. Graphical comparison methods have been used [5] but if TGA data can be prepared in a suitable form, the computer can remove most of the tedium and cost of the calculation.

A suitable method for this kind of treatment was a curve fitting method reported by Doyle [6] and later simplified by Zsako [7]. This report describes how the method was further simplified to allow the required parameters to be extracted quickly while retaining the accuracy of the original method.

The usual notations were used, ie:-

α = fractional weight loss,

E = activation energy in kcal/mole,

Z = pre-exponential factor,

b = order of reaction,

R = gas constant,

S^\ddagger = activation entropy,

h = Planck's constant,

k = Boltzmann's constant,

$T_{1/2}$ = temperature of half weight loss,

u = E/RT ,

x = the value of u at the sample temperature.

2. THE DOYLE/ZSAKO METHOD

2.1 The outline of the method

The equation to a thermogram is

$$g(\alpha) = \frac{ZE}{Rq} p(x), \quad \dots(1)$$

where the form of $g(\alpha)$ depends upon the nature of the process and

$$p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du. \quad \dots(2)$$

Doyle prepared a table of $-\log p(x)$ from $x = 10$ to $x = 50$. A first approximation of E was calculated assuming the reaction order to be unity, and this approximation was improved by trial and error curve fitting techniques. Zsako simplified this process as follows. Taking logs and rearranging, equation (1) becomes

$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log p(x) = B, \quad \dots(3)$$

where B is dependent upon the nature of the compound and the heating rate but not upon the temperature.

The value of $g(\alpha)$ can be found for a given temperature if the particular function of α is known, and $-\log p(x)$ can be obtained from Doyle's tables if E is known.

Then, if E is known and used to calculate B at several temperatures, the constancy of B will indicate the validity of the particular kinetic equation selected to calculate g(α). Conversely, if the kinetic equation representing the reaction is known, the constancy of B will indicate the validity of a chosen E value. The constancy of B can be quantified by means of the standard deviation,

$$\text{SIGMA} = \sqrt{\frac{\sum B^2 - \frac{(\sum B)^2}{N}}{N - 1}}, \quad \dots(4)$$

where N is the number of B values. (SIGMA)_{min} will indicate which of two E values (or which of two kinetic equations) best fits the reaction.

Taking the form of the kinetic equation as $f(\alpha) = (1 - \alpha)^b$, Zsako assumed, in turn, reaction orders of 0, 1/3, 1/2, 2/3, 1 and 2 and found a value for E, in each case, which gave a minimum standard deviation of B values. Comparing the (SIGMA)_{min} values corresponding to the six E values, the overall (SIGMA)_{min} value indicated which of the six kinetic equations best fitted the reaction.

The six kinetic equations are listed in table 1.

TABLE 1

Kinetic Equations Based on $f(\alpha) = (1 - \alpha)^b$ [7]

b	Form of g(α)
0	(α)
$\frac{1}{3}$	$\frac{3}{2} \left[1 - \sqrt[3]{(1 - \alpha)^2} \right]$
$\frac{1}{2}$	$2 \left[1 - \sqrt{(1 - \alpha)} \right]$
$\frac{2}{3}$	$3 \left[1 - \sqrt[3]{(1 - \alpha)} \right]$
1	$-\ln(1 - \alpha)$
2	$\frac{\alpha}{1 - \alpha}$

If the selected (SIGMA)_{min} value is small enough, \bar{B} can be used to calculate Z from equation (3).

Then $\bar{B} = \log ZE/Rq$ and

$$\log Z = \bar{B} + \log Rq - \log E, \quad \dots(5)$$

also the apparent activation entropy

$$S^\ddagger = 2.303R \log \frac{ZH}{kT_1}. \quad \dots(6)$$

In order to extend Doyle's tabulated $-\log p(x)$ values when $x > 50$ Zsako used the approximation

$$p(x) = e^{-x} \left(\frac{1}{x^2} - \frac{2}{x^3} \right) \quad \dots(7)$$

and intermediate values of $-\log p(x)$ were found by interpolation.

2.2 Modification of the Doyle/Zsako method for TGA2

2.2.1 Calculation of $-\log p(x)$

Comparing the approximation equation (7) with values for x obtained from standard tables of e^{-x} and the integral

$$\int_x^\infty \frac{e^{-u}}{u} du,$$

it was shown (table 2) that the approximation is sufficiently close down to $x = 4.0$. Then, instead of using tables of $-\log p(x)$, equation (7) was used throughout this work. In practice x is rarely less than 4.0, but in the event, a diagnostic message was printed by the computer program to indicate that E was inaccurate.

TABLE 2

A Test of the Approximation Equation (7)
over the Range $x = 2$ to 50

x	A - Log p(x) from Integral (Tabulated Values) [8]	B - Log p(x) from Approximation Equation (7)	Ratio B/A
50	25.129	25.125865	0.99988
40	20.597	20.594464	0.99988
30	16.010	16.010155	1.0000
20	11.328	11.331665	1.0003
10	6.415666	6.438694	1.00359
9	5.896899	5.925212	1.00480
8	5.368888	5.404500	1.00663
7	4.829246	4.875506	1.00958
6	4.274602	4.337379	1.01469
5	3.699839	3.790578	1.02453
4	3.096592	3.241743	1.04687
3	2.449659	2.733754	1.11597
2	1.726291	16.882666	9.780

3. DESCRIPTION OF THE PROGRAM TGA2

TGA2 is written in FORTRAN and has been successfully used for several years, and recently on the IBM 370/168. It is described under the headings Input, Program and Output, in sections 3.1 to 3.3. A thermogram may consist of one or more steps which represent different reactions and these steps must be treated separately. The data for a weight loss step were plotted as active weight fractions $(1 - \alpha)$, as a function of temperature and a smooth curve was drawn using a flex rule. It was the position on the temperature scale and the shape of this smoothed curve which was used as a basis for the calculation of kinetic parameters. Values of temperature were taken from the smoothed curve corresponding to equal increments of $(1 - \alpha)$ and an example is given in figure 1 where 19 co-ordinates were taken corresponding to $(1 - \alpha)$ values from 0.05 to 0.95 in equal increments of 0.05. The extremes of the curve, ie, $(1 - \alpha) = 1.0$ and 0.0 were not used because of the inaccuracy of estimating temperature at small slopes.

3.1 Input

<u>Line Number</u>	<u>Format</u>	<u>Symbol</u>	<u>Explanation</u>
1	I2	NDA	The number of pairs of co-ordinates describing the smoothed curve
2	F6.3	HDIF	Increments of $(1 - \alpha)$
3	6A4	ORDER(J)	Titles for the different kinetic equations
4 to (NDA + 4)	F7.4	H(I)	Active weight fractions $(1 - \alpha)$
NDA + 5	I8	RUN	Run identity number
	A8	STEP	Step identity number
	A8	RANGE	Temperature limits of step in °C
	F8.3	QM	Heating rate °C/min
NDA + 6 to (2 NDA + 6)	F7.1	TC(I)	Temperature in °C corresponding to the active weight fractions on line 4 onwards
Last line	-	-	Blank

Note that several sets of data may be calculated in one computer run, additional sets corresponding to lines (NDA + 5) to (2NDA + 6) being stacked together without spaces. In all cases the last line of the complete data input must be blank. All data sets applied at one time must be compatible with the lines 1 to (NDA + 4) which are not repeated.

3.2 Program TGA2

A flow chart showing the logic of TGA2 is shown in figure 5 and a full print-out of the FORTRAN statements is reproduced in appendix A. The main calculations embodied in TGA2 are explained in sections 3.2.1 to 3.2.3.

3.2.1 Minimum of SIGMA (equation (4))

At a constant heating rate, SIGMA is a function dependent on activation energy. Then, for a given rate equation, $g(\alpha)$, SIGMA may be minimised by finding the appropriate value for E. Subroutine VD01A [9] finds the minimum of a function of a single variable by an iterative process. In this case the variable is E and the function is

$$\sqrt{\frac{\Sigma B^2 - \frac{(\Sigma B)^2}{N}}{N - 1}}$$

The subroutine requires a starting approximation of E and this is provided by

$$E_{(\text{approx})} = \frac{-RT^2}{-\ln(1-\alpha)} \cdot \frac{d(1-\alpha)}{dT} \quad (\text{cf, reference [10], equation 21}) \quad \dots(8)$$

The iterative process continued until E is precise to within 25 cal/mole.

3.2.2 Calculation of $\frac{d(1-\alpha)}{dT}$

Subroutine SLOPE calculates the slope of a curve from a list of co-ordinates using the Newton-Stirling [11] formula for central differences when the argument changes by a fixed amount (HDIF in this subroutine). The slope at $(1-\alpha) = 0.8$ is used in equation (8) to calculate $E_{(\text{approx})}$.

3.2.3 Diagnostics

If E/RT is allowed to assume a value ≤ 2.0 , the program will stop at Statement 117 having tried to find the log of a negative number. To avoid this during the iterative process, a barrier has been inserted (Statement 109) so that, if $E/RT \leq 2.1$, SIGMA is put to 1000.0 to change the direction of search for SIGMA_{min}.

If E/RT is < 4.0 for SIGMA_{min}, table 2 shows that E will be inaccurate and in the event a statement is printed to that effect.

If the number of evaluations of SIGMA exceeds the limit stated when VD01A is called (100 in TGA2) then a diagnostic is printed - "MAXFUN TOO SMALL".

A diagnostic message will be printed if ROUNDING ERRORS prevent the calculation of E to the desired precision.

3.3 Output

The output from TGA2 is in the form of a table and an example is given in figure 2. This table lists $SIGMA_{min}$ and the corresponding calculated values for activation energy, $\log Z$, Z and activation entropy (S^\ddagger). Each line represents a different $g(\alpha)$ function and the best values are those in line with the minimum $SIGMA_{min}$ (sic) value.

Points to note are:-

(a) The calculation will indicate the best fit to the data of the $g(\alpha)$ functions included in the program. If the correct $g(\alpha)$ function is not included, a misleading answer will be given.

(b) $\log Z$ and S are calculated in all cases, but these are valid only if $SIGMA_{min}$ is sufficiently small.

4. DESCRIPTION OF THE CURVE

The basis for the calculation of kinetic parameters by TGA2 was a description of the smoothed thermogram step in terms of the co-ordinates $(1 - \alpha)$ and T . There were possible variations in this description, such as range and number of co-ordinates, which would possibly affect the results of the calculation. These variations were investigated as follows:-

(a) The effect of limiting the range of $(1 - \alpha)$ by truncating both ends of the curve simultaneously (section 4.2).

(b) The effect of limiting the number of co-ordinates, uniformly spaced with respect to $(1 - \alpha)$ (section 4.3).

(c) The effect of truncating the ends of the curve separately (section 4.4).

(d) With a $(1 - \alpha)$ spacing of 0.05 (19 co-ordinates) the effect of taking the top 7, middle 7 and bottom 7 co-ordinates in turn (section 4.5).

In order to make a quantitative assessment of the various treatments discussed in sections 4.2 to 4.5, standard thermograms were required with known kinetic parameters. These were calculated from assumed values of the relevant kinetic parameters and the equation to the thermogram (equation (1)). They covered the range of activation energies which were likely to be encountered in thermal degradation reactions, ie, from 10 to 66 kcal/mole (section 4.1).

It can be seen from the results of the investigations into the description of the curves in tables 5, 6 and 7 that the values of E and log Z are not greatly affected by the variations applied and, therefore, a different quantitative assessment was devised depending upon the SIGMA values. It may be said that the choice of best SIGMA is easier and probably more reliable if it is much smaller than the next best value of SIGMA, or, in other words, if the ratio (next best SIGMA/best SIGMA) is large. The value of this ratio has been used throughout this work as a criterion when judging between the different treatments applied to the standard curves.

4.1 Preparation of four standard curves

TABLE 3

Assumed Kinetic Parameters for the Standard Thermograms

E, kcal/mole	Log Z	Reaction Order (b)	Heating Rate, q, °C/min
10.0	2.4	1	10
30.0	10.0	1	10
50.0	15.0	1	10
66.0	19.0	1	10

The values shown in table 3 were substituted in a rearranged equation (1) when $g(\alpha) = (1 - \alpha)^b$, ie,

$$(1 - \alpha)^b = \frac{ZE}{Rq} p(x),$$

and using Zsako's tables for $-\log p(x)$ at different temperatures, several $(1 - \alpha)$ and T co-ordinates were calculated and used as a basis for four standard curves. The curves were smoothed and initially described by 33 co-ordinates with a range of $(1 - \alpha)$ from 0.02 to 0.98 in equal steps of 0.03. These are reproduced in table 4.

TABLE 4

Co-ordinates Taken from Four Smoothed Standard Curves

- (a) E = 10.0 log Z = 2.4 (b) E = 30.0 log Z = 10.0
 (c) E = 50.0 log Z = 15.0 (d) E = 66.0 log Z = 19.0

(1 - α)	Temperature, °C			
	(a) 10/10 ^{2.4}	(b) 30/10 ¹⁰	(c) 50/10 ¹⁵	(d) 66/10 ¹⁹
0.98	80.0*	208.5	314.2	367.0
0.95	100.0	221.6	327.3	377.9
0.92	112.3	229.3	334.4	384.0
0.89	121.3	234.5	339.1	388.2
0.86	128.5	238.8	342.6	391.4
0.83	134.3	242.5	345.6	394.0
0.80	139.4	245.5	348.2	396.5
0.77	144.3	248.2	350.4	398.6
0.74	148.6	250.5	352.5	400.4
0.71	152.7	252.4	354.4	402.1
0.68	156.3	254.3	356.2	403.6
0.65	159.6	256.1	357.8	405.1
0.62	162.9	257.9	359.5	406.5
0.59	166.2	259.7	360.8	407.9
0.56	169.4	261.5	362.1	409.3
0.53	172.5	263.2	363.6	410.5
0.50	175.5	264.7	365.1	411.7
0.47	178.6	266.2	366.5	412.9
0.44	181.5	267.8	367.8	414.0
0.41	184.4	269.3	369.0	415.0
0.38	187.4	270.9	370.3	416.2
0.35	190.3	272.4	371.5	417.3
0.32	193.2	273.9	372.6	418.5
0.29	196.2	275.3	373.8	419.7
0.26	199.4	276.8	375.1	420.9
0.23	202.7	278.5	376.5	422.3
0.20	206.2	280.2	378.0	423.5
0.17	210.0	282.0	379.7	424.9
0.14	214.1	284.1	381.5	426.4
0.11	219.0	286.5	383.5	427.8
0.08	224.5	289.2	385.7	429.5
0.05	231.4*	292.5	388.3	431.6*
0.02	245.2*	298.0	392.8	435.3*

*Calculated from $p(x) = e^{-x}(\frac{1}{x^2} - \frac{2}{x^3})$.

4.2 The effect of limiting the range of $(1 - \alpha)$ by truncating the ends of the curve

Table 5 shows that the re-calculated values for E and log Z are altered little by this treatment of the standard curves, and they are at worst within a few per cent of those assumed. The lowest range, 0.2/0.8, shows a low value for the ratio (next best/best SIGMA) in all four cases and this shows that the ends of the curve beyond 0.2/0.8 are necessary if the correct or minimum SIGMA value is to be distinguished easily. On balance the range 0.05/0.95 is to be preferred with two instances of the highest ratio favouring this range.

TABLE 5

The Effect of Limiting the Range of $(1 - \alpha)$ Values Using Co-ordinates from the Standard Thermograms

E/Log Z	Range	NDA* ^a	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.02/0.98	33	10.1	2.5	0.00580	0.0355	6.12
	0.05/0.95	31	10.0	2.4	0.00187	0.0224	11.98
	0.08/0.92	29	10.0	2.4	0.00167	0.0176	10.54
	0.20/0.80	21	10.1	2.4	0.00152	0.00693	4.56
30/10.0	0.02/0.98	33	30.1	10.0	0.00525	0.0353	6.72
	0.05/0.95	31	30.0	10.0	0.00452	0.0244	5.4
	0.08/0.92	29	30.0	10.0	0.00446	0.0194	4.35
	0.20/0.80	21	30.1	10.1	0.00429	0.00947	2.21
50/15.0	0.02/0.98	33	50.2	15.1	0.00624	0.0320	5.13
	0.05/0.95	31	50.4	15.1	0.00468	0.0250	5.34
	0.08/0.92	29	50.6	15.2	0.00419	0.0198	4.73
	0.20/0.80	21	50.7	15.2	0.00355	0.00624	1.76
66/19.0	0.02/0.98	33	66.0	19.0	0.00633	0.0312	4.93
	0.05/0.95	31	65.7	18.9	0.00486	0.0222	4.57
	0.08/0.92	29	65.5	18.8	0.00356	0.0182	5.11
	0.20/0.80	21	65.2	18.7	0.00248	0.00829	3.34

Note: In all cases the best fit was given with $b = 1$.

*Number of co-ordinates.

4.3 The effect of limiting the number of uniformly spaced $(1 - \alpha)$ values in the range 0.05 to 0.95

Again the recalculated E and log Z values vary little with the different treatments.

Comparing the recalculated values of E and log Z in table 6 with the assumed values, the smallest NDATA is marginally favoured. The ratio (next best/best SIGMA) suggests that the best distinction is obtained at either NDATA = 7 or 19.

TABLE 6

The Effect of Limiting the Number* of Uniformly Spaced (1 - α) Values

E/Log Z	(1 - α) Limits	(NDATA)*	(1 - α) Spacing (HDIF)	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.05/0.95	31	0.03	10.0	2.4	0.00187	0.0224	12.0
		19	0.05	10.0	2.4	0.00219	0.0243	11.1
		7	0.15	10.0	2.4	0.00165	0.0329	19.9
30/10.0	0.05/0.95	31	0.03	30.0	10.0	0.00452	0.0244	5.4
		19	0.05	29.9	10.0	0.00375	0.0259	6.91
		7	0.15	29.9	10.0	0.00521	0.0353	6.78
50/15.0	0.05/0.95	31	0.03	50.4	15.1	0.00468	0.0250	5.3
		19	0.05	50.4	15.1	0.00278	0.0254	9.1
		7	0.15	50.3	15.1	0.00309	0.0335	10.8
66/19.0	0.05/0.95	31	0.03	65.7	18.9	0.00486	0.0222	4.4
		19	0.05	65.8	18.9	0.00520	0.0240	4.6
		7	0.15	66.1	19.0	0.00676	0.0306	4.5

*Number of co-ordinates.

4.4 The effect of progressive removal of the ends of the curve

Figures 3 and 4 show a similar effect and there is a downward trend in the ratio (next best/best SIGMA) as the end of the curve is reduced. The maximum at 0.05 and 0.95 in some cases suggests that the co-ordinates at the extremes of the curve, ie, 0.02 and 0.98, are not always reliable. Limits of 0.05 and 0.95 are favoured on balance.

4.5 The relative importance of the different parts of the (1 - α)/T curve

Taking a curve represented by 19 co-ordinates with a (1 - α) spacing of 0.05, the re-calculated results from the whole curve is compared in table 7 with the re-calculated values from the top, middle and bottom parts of the curve respectively. Surprisingly, the E and log Z values do not vary much, except in the case of the bottom part of the 66/19.0 curve. The list of ratios (next best/best SIGMA) shows that, as far as distinguishing one SIGMA from another, the middle and the top parts of the curve were poor, with an improvement shown from the bottom part of the curve which was, therefore, judged to be the most important part for this purpose.

TABLE 7

The Relative Importance of the Different Parts of the $(1 - \alpha)/T$ Curve
with all $(1 - \alpha)$ Spacings of 0.05

E/Log Z	$(1 - \alpha)$ Limits	Part of Curve	Order	E	Log Z	Best SIGMA	Next Best SIGMA	Ratio Next Best SIGMA/Best
10/2.4	0.05/0.95	Whole	1	10.0	2.4	0.00219	0.0243	11.1
		Bottom	1	10.1	2.5	0.00138	0.00594	4.3
		Middle	1	10.0	2.4	0.000475	0.00193	4.1
		Top	2/3	9.7	2.2	0.00253	0.00261	1.0
30/10.0	0.05/0.95	Whole	1	29.9	10.0	0.00375	0.0259	6.9
		Bottom	1	29.8	9.9	0.00197	0.00726	3.7
		Middle	1	29.9	9.7	0.00115	0.00142	1.2
		Top	1/2	28.7	9.4	0.00188	0.00208	1.1
50/15.0	0.05/0.95	Whole	1	50.4	15.1	0.00278	0.0254	9.1
		Bottom	1	50.2	15.1	0.00254	0.00740	2.9
		Middle	1	50.2	15.1	0.00238	0.00331	1.4
		Top	2/3	48.8	14.5	0.00171	0.00240	1.4
66/19.0	0.05/0.95	Whole	1	65.8	18.9	0.00520	0.0240	4.6
		Bottom	2/3	48.7	13.3	0.00126	0.00383	3.0
		Middle	2/3	57.6	16.2	0.00158	0.00189	1.2
		Top	1	66.2	19.1	0.00216	0.00323	1.5

5. DISCUSSION

The aim in writing TGA2 was to provide the means of calculating kinetic parameters from dynamic thermogravimetric data, and to do it easily and quickly, and for the results to be at least as reliable as other available methods.

Doyle [6] has provided adequate thermogravimetric data on octamethylcyclotetrasiloxane (OMCTS) and polytetrafluoroethylene (PTFE). The relevant numbers (19 temperatures and 1 heating rate for each run) were abstracted from the paper and applied to the computer with program TGA2. The process for both sets took approximately 30 min plus a few seconds computer time. A comparison of the results is shown in table 8.

TABLE 8

A Comparison of Results from Reference [6] and TGA2

Method	OMCTS		PTFE	
	Activation Energy, kcal/mole	Order	Activation Energy, kcal/mole	Order
Ref [6]	11.65	0	66-68	1
TGA2	11.44	0	60.45	2/3

Zsako has published data [7] from the thermal decomposition of (I) Co(dimethylglyoxime)₂(p.ethylaniline)₂NCS and (II) Co(dimethylglyoxime)₂(γ-picoline)₂NCS. He has calculated kinetic parameters for the decomposition of these compounds using the Horowitz and Metzger method, the Freeman and Carroll method, as well as the modified Doyle method. These results are compared with TGA2 in table 9.

TABLE 9

A Comparison of Kinetic Parameters Calculated for Cobalt Complexes I and II by Different Methods

Method	Compound I				Compound II			
	E	Reaction Order	Z	S [‡]	E	Reaction Order	Z	S [‡]
Horowitz and Metzger	42	2	-	-	33	1	-	+ 1
Zsako	28.9	1	11.71	- 5.84	28.3	1	11.45	- 7.06
Freeman and Carroll	29.2	1.16	-	-	28.7	0.82	-	-
TGA2	27.7	1	10.77	- 10.16	28.5	1	11.12	- 8.54

Both tables 8 and 9 indicate that the TGA2 results are comparable with the original results of Doyle, Zsako and with those of Freeman and Carroll. All of these give a lower value for activation energy than the Horowitz and Metzger method.

A word of warning is probably necessary at this stage.

The method of using TGA2 is so simple that there is a temptation to do the calculations and quote values for kinetic parameters which are meaningless, and it is especially important to remember the limitations of the method; the important ones are listed as follows:-

(a) The weight loss step which is considered must be directly related to a simple reaction and not compounded from several different processes.

(b) The results will only be as good as the original TGA experimental results allow.

For instance, care must be taken to minimise diffusion effects which arise from the use of samples with a large particle size, or a high heating rate. Particular attention should be paid to the lower 1/3 or "tail" of the curve which has been shown to be distinctive. Also in this area, a build-up of non-volatile catalysts as the weight loss proceeds may cause spurious results, eg, impure carbon burning in air.

(c) The third important consideration is to decide which mechanism best describes the solid state reaction. Zsako has used the six relatively simple equations listed in table 1, but many others have been developed and they are designed to accommodate different rate controlling processes. Examples are given in table 10.

TABLE 10

Kinetic Equations Based on Various Solid State Mechanisms [8]

<u>Function</u>	<u>Equation</u>	<u>Rate-Controlling Process</u>
D ₁	$\alpha^2 = kt$	One-dimensional diffusion
D ₂	$(1 - \alpha) \ln (1 - \alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D ₃	$[1 - 3\sqrt{1 - \alpha}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D ₄	$(1 - \frac{2}{3}\alpha) - 3\sqrt{(1 - \alpha)^2} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein equation
F ₁	$-\ln (1 - \alpha) = kt$	Random nucleation, one nucleus on each particle
A ₂	$\sqrt{-\ln (1 - \alpha)} = kt$	Random nucleation; Avrami equation
A ₃	$\sqrt[3]{-\ln (1 - \alpha)} = kt$	Random nucleation; Avrami equation
R ₂	$1 - \sqrt{1 - \alpha} = kt$	Phase boundary reaction, cylindrical symmetry
R ₃	$1 - \sqrt[3]{1 - \alpha} = kt$	Phase boundary reaction, spherical symmetry

Notable methods of calculating kinetic parameters from thermal analysis curves have been developed by Freeman and Carroll [12], Coates and Redfern [13], Ozawa [14] and Sharp and Wentworth [15]. These have been compared by Ozawa [16].

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APPENDIX A

PROGRAM TGA2

```

IMPLICIT REAL*8(A-H,O-Z)
DIMENSION B(15,50)
DIMENSION DTDH(50)
DIMENSION EAKT(50)
DIMENSION G(15,50)
DIMENSION H(50)
DIMENSION ORDER(15)
DIMENSION PX(50)
DIMENSION T(50)
DIMENSION TC(50)

C
PLANCK=6.624E-27
BOLTZ=1.380E-16
R=1.98700
READ(5,10) NDATA
10 FORMAT(I2)
READ(5,15) HDIF
15 FORMAT(F6.3)
READ(5,16) (ORDER(J),J=1,15)
16 FORMAT(15A4)
READ(5,20) (H(I),I=1,NDATA)
20 FORMAT(F7.4)
100 READ(5,8) IRUN,STEP,RANGE,QM
8 FORMAT(I8,2A8,F8.3)
Q=QM/60.
IF(IRUN) 101,101,102
101 STOP
102 READ(5,21) (TC(I),I=1,NDATA)
21 FORMAT(F7.1)
DO 22 I=1,NDATA
T(I)=TC(I)+273.200
22 CONTINUE
CALL SLOPE(T,NDATA,HDIF,DTDH)
DHDT=1./DTDH(1)
WRITE(6,9) IRUN,STEP,RANGE,NDATA,QM
9 FORMAT('1', 'RUN', I8, 2A8, 4X, 'NDATA=', I2, 4X, 'HEATING RATE =', F8.3, '°
1 DEG.C.PER MIN.'//)
L=(NDATA+1)/2
WRITE(6,17) TC(L)
17 FORMAT(' TEMPERATURE FOR HALF WEIGHT LOSS IN THIS STEP =', F7.1, 2X
1, 'DEG.C.//)
EAPROX=(-R*(T(4)**2)*DHDT)/(-DLOG(H(4)))
WRITE(6,18) H(4),DHDT
18 FORMAT(' THE SLOPE DH/DT(AT H=', F7.4, ') =', F12.2//)
WRITE(6,19) EAPROX
19 FORMAT(' A ROUGH ESTIMATE OF ACT.ENERGY =', -3PF10.2, ' KCAL/MOLE '
1//)
WRITE(6,11)
11 FORMAT(' THE BEST FIT IS INDICATED BY THE MINIMUM SIGMA IN// TH
1E FOLOWING TABLE SO USE THE VALUES IN THAT LINE.// NOTE, THEY AR
1E EMPIRICAL AND DEPEND ON THE EXPTL.METHOD.//)
WRITE(6,50)
50 FORMAT(49X, 'Z// REACTION', 15X, 'ACT.ENERGY', 12X, 'PRE EXP.', 4X, 'ACT
1.ENTROPY'
1 Z', 4X, 'FACTOR', 3X, '(CAL/DEG.MOLE)//)

```

```

DO 55 J=1,6
  ITEST=2
  5 CALL V001AD(ITEST,EAPROX,F,100,25.000,0.000100,500.000)
    GO TO (1,2,3,4),ITEST
  1 DO 44 I=1,NDATA
110 G(1,I)=1.-H(I)
111 G(2,I)=3./2.*(1.-(H(I)**(2./3.)))
112 G(3,I)=2.*(1.-DSQRT(H(I)))
113 G(4,I)=3.*(1.-(H(I)**(2./3.)))
114 G(5,I)=-DLOG(H(I))
115 G(6,I)=(1.-H(I))/H(I)
116 EART(I)=EAPROX/(R*T(I))
    IF(EART(I)-2.100)109,109,117
109 F=1000.000
    GO TO 5
117 PX(I)=DEXP(-EART(I))*((1./(EART(I)**2))-2./(EART(I)**3)))
118 B(J,I)=(DLOG(G(J,I))-DLOG(PX(I)))/2.30300
  44 CONTINUE
    F=0.000
    FS=0.000
    DO 45 I=1,NDATA
119 F=F+B(J,I)**2
120 FS=FS+B(J,I)
  45 CONTINUE
    F=DSQRT((F-(FS**2)/FLOAT(NDATA))/FLOAT(NDATA-1))
    GO TO 5
  2 IF(EART(NDATA)-4.000)252,251,251
251 BBAR=FS/FLOAT(NDATA)
    ZLOG=BBAR+DLOG(R*Q)/2.30300-DLOG(EAPROX)/2.30300
    Z=10.**ZLOG
    S=R*DLOG((Z*PLANCK)/(BOLTZ*T(L)))
    WRITE(6,60) ORDER(J),F,EAPROX,ZLOG,Z,S
  60 FORMAT(3X,A4,3X,E12.3,-3PF10.2,0PF10.2,E12.3,F13.2)
    GO TO 55
252 WRITE(6,253) ORDER(J),F,EAPROX
253 FORMAT(3X,A4,3X,E12.3,-3PF10.2,' CALCULATION INACCURATE AT THIS LO
1W VALUE.')
    GO TO 55
  3 WRITE(6,65)
  65 FORMAT(20X,'ROUNDING ERRORS')
    GO TO 55
  4 WRITE(6,70)
  70 FORMAT(20X,'MAXFUN VALUE TOO SMALL'//)
  55 CONTINUE
    GO TO 100
  END

```

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```
SUBROUTINE SLOPE(Y,N,XDIF,DYDX)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION DYDX(50)
DIMENSION Y(50)
```

C

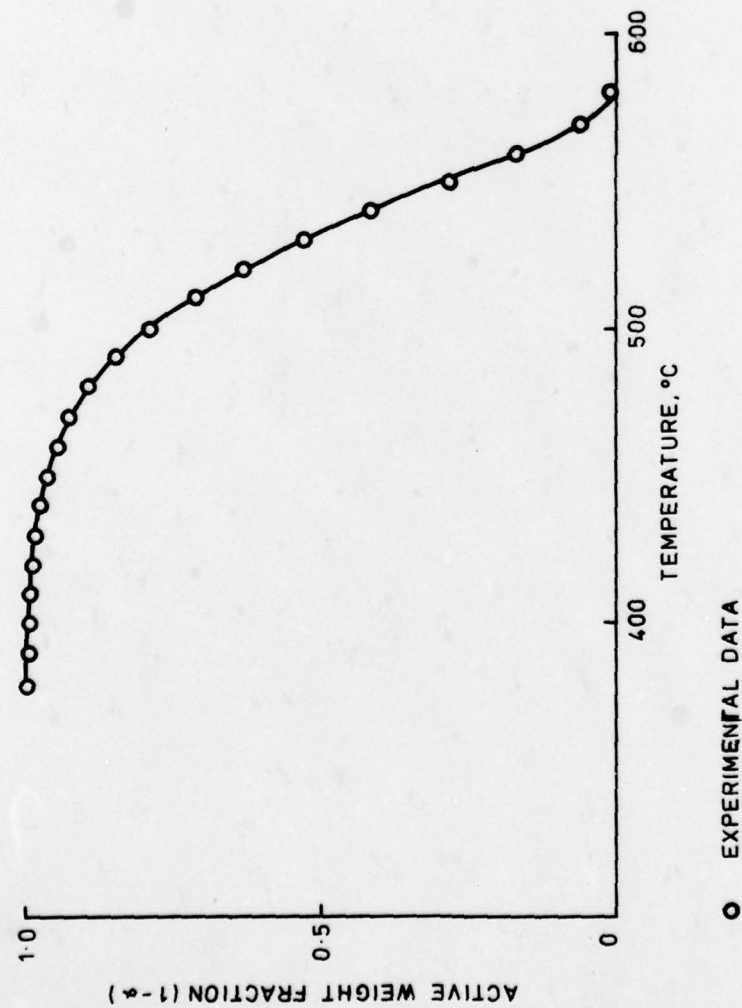
```
DIMENSION DYF1(50)
DIMENSION DYF2(50)
DIMENSION DYF3(50)
DIMENSION DYF4(50)
DIMENSION DYF5(50)
DIMENSION YMU1(50)
DIMENSION YMU3(50)
DIMENSION YMU5(50)
```

C

C

```
      NM1=N-1
      DO 5 I=1,NM1
        DYF1(I)=Y(I+1)-Y(I)
5     CONTINUE
      NM2=N-2
      DO 10 I=1,NM2
        YMU1(I)=(DYF1(I)+DYF1(I+1))/2.
        DYF2(I)=DYF1(I+1)-DYF1(I)
10    CONTINUE
      NM3=N-3
      DO 15 I=1,NM3
        DYF3(I)=DYF2(I+1)-DYF2(I)
15    CONTINUE
      NM4=N-4
      DO 20 I=1,NM4
        YMU3(I)=(DYF3(I)+DYF3(I+1))/2.
        DYF4(I)=DYF3(I+1)-DYF3(I)
20    CONTINUE
      NM5=N-5
      DO 30 I=1,NM5
        DYF5(I)=DYF4(I+1)-DYF4(I)
30    CONTINUE
      NM6=N-6
      DO 35 I=1,NM6
        YMU5(I)=(DYF5(I)+DYF5(I+1))/2.
35    CONTINUE
      DO 40 I=1,NM6
        DYDX(I)=(YMU1(I+2)-(YMU3(I+1)/6.)+(YMU5(I)/30.))/XDIF
40    CONTINUE
      RETURN
      END
```

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VALUES OF ACTIVE WEIGHT FRACTION AND TEMPERATURE FROM THE SMOOTHED CURVE	
(1- α)	T °C
0.95	458.0
0.90	478.0
0.85	489.5
0.80	499.0
0.75	506.5
0.70	512.5
0.65	518.0
0.60	523.5
0.55	528.5
0.50	533.0
0.45	537.0
0.40	541.0
0.35	545.0
0.30	548.5
0.25	552.0
0.20	556.0
0.15	560.5
0.10	565.0
0.05	571.0

FIGURE 1 Smoothed (1- α) versus Temperature Plot for Run 73 Step 2

RUN 73 STEP2 380/580 NDATA=19 HEATING RATE = 0.685DEG.C.PER MIN.

TEMPERATURE FOR HALF WEIGHT LOSS IN THIS STEP = 533.0 DEG.C.

THE SLOPE dh/dt (AT $H = 0.8000$) = $-0.580-02$

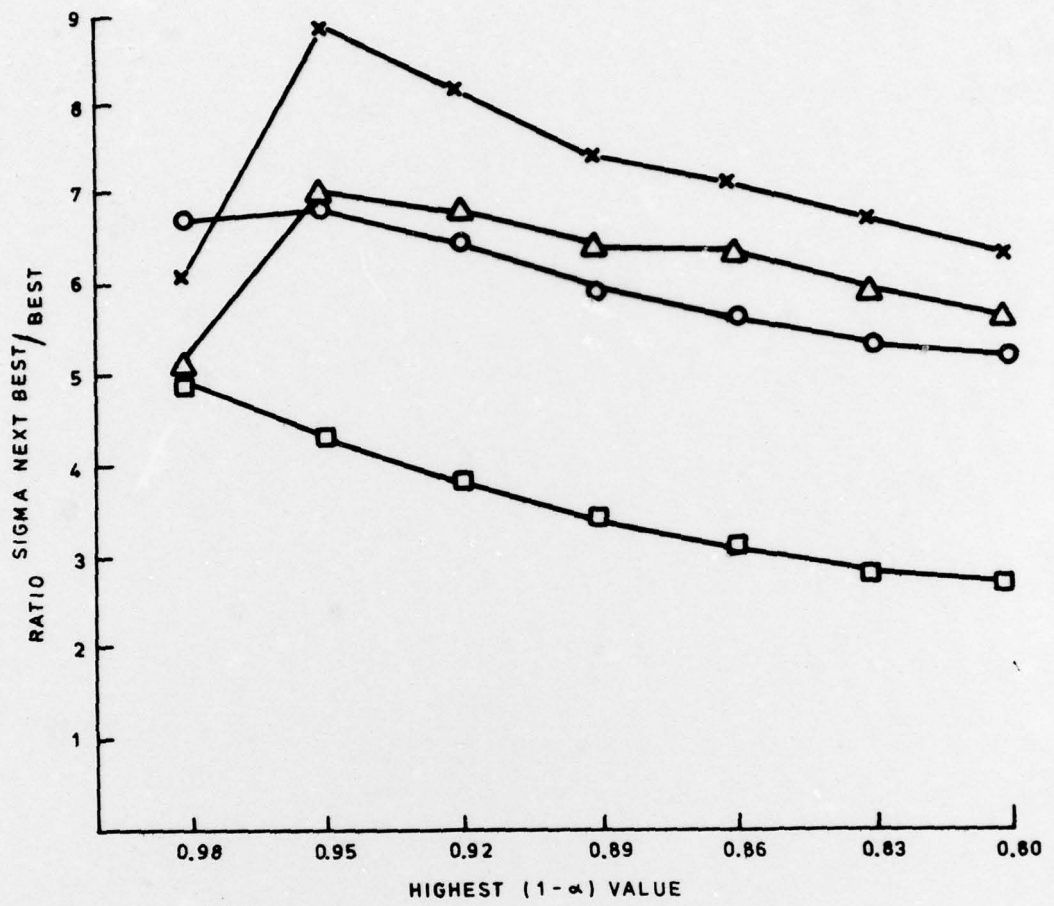
A ROUGH ESTIMATE OF ACT.ENERGY = 30.96 KCAL/MOLE

THE BEST FIT IS INDICATED BY THE MINIMUM SIGMA IN THE FOLLOWING TABLE SO USE THE VALUES IN THAT LINE.

NOTE, THEY ARE EMPIRICAL AND DEPEND ON THE EXPTL.METHOD.

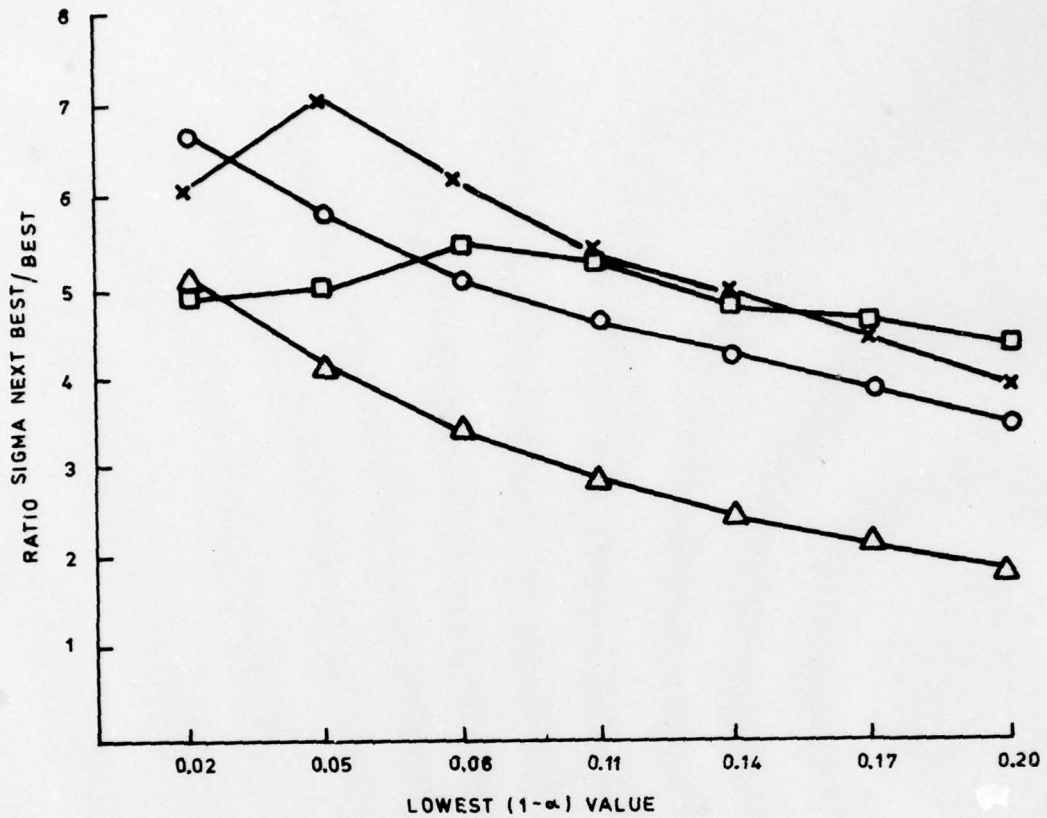
REACTION ORDER	SIGMA	ACT.ENERGY (KCAL/MOLE)	LOG 2	PRE EXP. FACTOR	ACT.ENTROPY (CAL/DEG.MOLE)
ZERO	0.3830-01	29.26	4.07	0.1170 05	-41.90
1/3	0.2220-01	32.46	5.03	0.1080 06	-37.49
1/2	0.1240-01	34.24	5.57	0.3710 06	-35.03
2/3	0.4450-02	36.17	6.15	0.1400 07	-32.38
1	0.2830-01	40.44	7.42	0.2650 08	-26.55
2	0.1500 00	56.56	12.19	0.1550 13	-4.73

FIGURE 2 OUTPUT FROM PROGRAM TGA 2



E / LOG Z
 x 10 / 2.4
 o 30 / 10.0
 Δ 50 / 15.0
 □ 66 / 19.0

FIGURE 3 Effect on Sigma Values of Progressive Removal of Top of Standard Curve



E / LOG Z
 x 10 / 2.4
 o 30 / 10.0
 Δ 50 / 15.0
 \square 66 / 19.0

FIGURE 4 Effect on Sigma Values of Progressive Removal of Bottom of Standard Curves

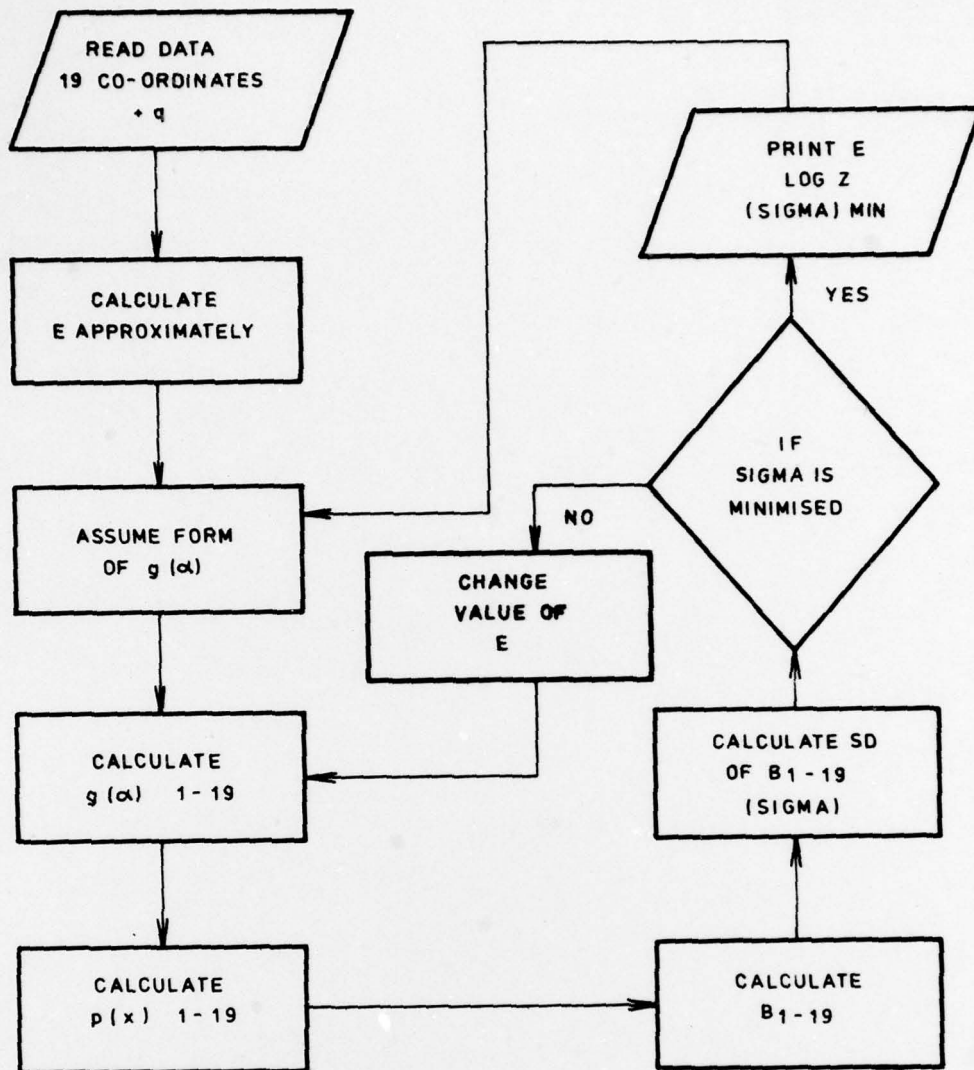


FIGURE 5 Simplified Flow Chart TGA2

DOCUMENT CONTROL SHEET

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5. Originator's Code (if known) -	6. Originator (Corporate Author) Name and Location Atomic Weapons Research Establishment, Aldermaston, Berkshire		
5a. Sponsoring Agency's Code (if known) -	6a. Sponsoring Agency (Contract Authority) Name and Location -		
7. Title Kinetic Analysis of Thermogravimetric Data. Computer Program TGA2			
7a. Title in Foreign Language (in the case of Translation) -			
7b. Presented at (for Conference Papers). Title, Place and Date of Conference -			
8. Author 1. Surname, Initials Briscall H	9a. Author 2 -	9b. Authors 3, 4 -	10. Date pp ref March 1979 26 16
11. Contract Number -	12. Period -	13. Project -	14. Other References -
15. Distribution Statement No restrictions			
16. Descriptors (or Keywords) (TEST) Kinetics Curve fitting Thermogravimetry Computer program TGA2			
<p><i>alpha</i></p> <p>Abstract Zsako has modified a curve fitting method reported by Doyle and in this report the method is further simplified to allow the use of a digital computer. The best description of the thermogram step was found to be given by 19 equally spaced co-ordinates between the $(1 - \alpha)$ limits of 0.05 to 0.95. These co-ordinates, together with the heating rate, are used to calculate E and log Z, by an iterative process which minimises the standard deviation of the $\log g(\alpha) - \log p(x)$ values. The standard deviation allows a comparative assessment of the validity of the kinetic equations chosen to represent the mechanism of the reaction. A further simplification involved the use of an approximate equation for $-\log p(x)$ in place of tabulated values. The TGA2 method of calculation was shown to be valid by re-calculating E and log Z for standard curves which were generated from tables of $-\log p(x)$. Published data by Doyle and Zsako were re-calculated and the answers were in good agreement with the original results.</p>			

Some Metric and SI Unit Conversion Factors

(Based on DEF STAN 00-11/2 "Metric Units for Use by the Ministry of Defence",
DS Met 5501 "AWRE Metric Guide" and other British Standards)

Quantity	Unit	Symbol	Conversion
<u>Basic Units</u>			
Length	metre	m	1 m = 3.2808 ft 1 ft = 0.3048 m
Mass	kilogram	kg	1 kg = 2.2046 lb 1 lb = 0.45359237 kg 1 ton = 1016.05 kg
<u>Derived Units</u>			
Force	newton	N = kg m/s ²	1 N = 0.2248 lbf 1 lbf = 4.44822 N
Work, Energy, Quantity of Heat	joule	J = N m	1 J = 0.737562 ft lbf 1 J = 9.47817 × 10 ⁻⁴ Btu 1 J = 2.38846 × 10 ⁻⁴ kcal 1 ft lbf = 1.35582 J 1 Btu = 1055.06 J 1 kcal = 4186.8 J
Power	watt	W = J/s	1 W = 0.238846 cal/s 1 cal/s = 4.1868 W
Electric Charge	coulomb	C = A s	-
Electric Potential	volt	V = W/A = J/C	-
Electrical Capacitance	farad	F = A s/V = C/V	-
Electric Resistance	ohm	Ω = V/A	-
Conductance	siemen	S = 1 Ω ⁻¹	-
Magnetic Flux	weber	Wb = V s	-
Magnetic Flux Density	tesla	T = Wb/m ²	-
Inductance	henry	H = V s/A = Wb/A	-
<u>Complex Derived Units</u>			
Angular Velocity	radian per second	rad/s	1 rad/s = 0.159155 rev/s 1 rev/s = 6.28319 rad/s
Acceleration	metre per square second	m/s ²	1 m/s ² = 3.28084 ft/s ² 1 ft/s ² = 0.3048 m/s ²
Angular Acceleration	radian per square second	rad/s ²	-
Pressure	newton per square metre	N/m ² = Pa	1 N/m ² = 145.038 × 10 ⁻⁶ lbf/in ² 1 lbf/in ² = 6.89476 × 10 ³ N/m ²
	bar	bar = 10 ⁵ N/m ²	-
Torque	newton metre	N m	1 in. Hg = 3386.39 N/m ² 1 N m = 0.737562 lbf ft 1 lbf ft = 1.35582 N m
Surface Tension	newton per metre	N/m	1 N/m = 0.0685 lbf/ft 1 lbf/ft = 14.5939 N/m
Dynamic Viscosity	newton second per square metre	N s/m ²	1 N s/m ² = 0.0208854 lbf s/ft ² 1 lbf s/ft ² = 47.8803 N s/m ²
Kinematic Viscosity	square metre per second	m ² /s	1 m ² /s = 10.7639 ft ² /s 1 ft ² /s = 0.0929 m ² /s
Thermal Conductivity	watt per metre kelvin	W/m K	-
<u>Odd Units*</u>			
Radioactivity	becquerel	Bq	1 Bq = 2.7027 × 10 ⁻¹¹ Ci 1 Ci = 3.700 × 10 ¹⁰ Bq
Absorbed Dose	gray	Gy	1 Gy = 100 rad 1 rad = 0.01 Gy
Dose Equivalent	sievert	Sv	1 Sv = 100 rem 1 rem = 0.01 Sv
Exposure	coulomb per kilogram	C/kg	1 C/kg = 3876 R 1 R = 2.58 × 10 ⁻⁴ C/kg
Rate of Leak (Vacuum Systems)	millibar litre per second	mb l/s	1 mb = 0.750062 torr 1 torr = 1.33322 mb

*These terms are recognised terms within the metric system.