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Use of databases in thermal analysis. Part 6

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Abstract

In our previous publication (Thermochim. Acta 222 (1993) 85), a computer algorithm was devised which allowed the concurrent determination of two rate constants, k_1 and k_2, for two consecutive irreversible first-order reactions. The Paradox 3.5 database was employed, and database analyses were carried out using both theoretical and experimental data. The k values obtained were in satisfactory agreement with assumed and observed values. In all the runs made, the values of k_1 were much larger than those corresponding to k_2. The preceding algorithm, however, did not hold for cases where k_2 was greater than k_1.

The aim of the present paper is to modify the preceding script so that the resulting script will be applicable to both cases, $k_1 > k_2$ and $k_2 > k_1$. Limitations of the method will be described where applicable.

Keywords: Algorithm; Database; TA

1. Introduction

A mathematical expression was recently developed for the concurrent evaluation of two rate constants for two consecutive irreversible first-order reactions [1]. A computer algorithm was devised to implement this expression wherein a database analysis was utilized. Thus, the database employed was Paradox 3.5 which possesses

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a powerful script language (PAL) and which was used in the analysis. This PAL script is listed in the Appendix and is denoted as *x2ks*.

In the previous paper [1], the algorithm developed was only applied to cases where one rate constant (k_1) was greater than the other (k_2). This algorithm afforded values for k_1 and k_2 which were in satisfactory agreement with corresponding theoretical and experimental values.

The aim of the present paper is to devise a more general computer algorithm which will also include cases where $k_2 > k_1$ and which will distinguish between the two types of cases. Limitations of the method will be described where applicable.

2. Theoretical aspects

Two consecutive irreversible first-order reactions can be represented as

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} + \mathrm{gas} \tag{1a}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C} + \mathrm{gas} \tag{1b}$$

In the preceding expressions, A, B and C denote the starting material, intermediate production, and final product, respectively, while k_1 and k_2 denote the rate constants for the two steps, as shown. The utilization of isothermal TG should allow the estimation of the extent of the reactions depicted in Eqs. (1a) and (1b), based on the amount of gas liberated.

In order to estimate values of k_1 and k_2 concurrently, the following mathematical expressions were derived [2]

$$\rho - k_2(1-\alpha) = (k_1 - 2k_2)\exp(-k_1 t)/2 \tag{2a}$$

$$\rho - k_1(1-\alpha) = -k_1 \exp(-k_2 t)/2 \tag{2b}$$

where ρ (or rate) $= \mathrm{d}\alpha/\mathrm{d}t$, α is the degree of conversion, and t the reaction time. From Eqs. (2a) and (2b), the following expressions may now be derived

$$\ln\{[\rho - k_2(1-\alpha)]_0/[\rho - k_2(1-\alpha)]\} = k_1(t - t_0) \tag{3a}$$

$$\ln\{[\rho - k_1(1-\alpha)]_0/[\rho - k_1(1-\alpha)]\} = k_2(t - t_0) \tag{3b}$$

where the subscript 0 refers to an initial set of data values. From Eqs. (3a) and (3b), it can be seen that, if we make the left-hand side of each of these equations equal to Y, then

$$Y = A_2 X + A_1 \tag{4}$$

where $A_2 = k_1$ (or k_2), $X = t - t_0$, and $A_1 = 0$.

By utilizing Eq. (4) along with a least-squares treatment and PAL, a database analysis should afford the determination of the two rate constants. Values of k_1 and k_2 will be estimated via an iteration procedure where by a minimum value of A_1 will be attained for the condition employed. At the start of the analysis, the value of k_2 will be taken as zero and subsequently incremented. Because the value of k_1 is exceedingly sensitive to very small changes in k_2, a final incremental value was used so that the final value of k_2 was obtained up to nine decimal places (for the corresponding minimum value of the intercept). In all the theoretical and experimental data examined previously, [1], k_1 was always greater than k_2. In order to include cases wherein $k_2 > k_1$, the previous computer algorithm [1] was modified and is listed in the Appendix.

3. Results and discussion

In order to include the case wherein $k_2 > k_1$, the script in the Appendix has been modified from the one previously reported [1]. Thus, in lines 7–8, a delimiter is requested ('Num' or 'tmp'). When 'tmp' (lines 43–45) is chosen, a database analysis is carried out as previously (until $ztmp < ztmp2$) (lines 15, 16, 69) and when 'Num' (lines 47–49) is selected, the delimiter becomes $z > 0.1$ (lines 15 and 69). In the latter case, it is assumed that the value of k_2 will not exceed a value of 0.1. Depending on the selection of 'tmp' or 'Num', either the statement in lines 43–45 or in lines 47–49 may apply.

The tables to be described subsequently possess the same column headings as previously indicated [1]. Again, owing to spatial limitations of the Paradox Report function (nine columns per printed page), it was decided to maintain one printed page per table by omitting a 'tmp' column which was located between the Y and k_{1b} columns. This 'tmp' column is mentioned in the PAL script in the appendix and must be included during the creation of the tables via Paradox. Further, a rating higher than a 486-25 computer is recommended because the use of the "25" and the delimiter, $z > 0.1$, may require over 15 min. In the following, tables containing data where $k_1 > k_2$ will be considered initially.

In Table 1A, the 'tmp' delimiter was chosen initially. In the database analysis, $ztmp$ was set equal to 1E-04. This table (and 1B) was created using values of $k_2 = 0.00275$ and $k_1 = 0.0222$ (initial values of $t = 70$, $\alpha = 0.4385$, and $\rho = 3.3094\text{E}-03$ were used, see lines 20–28 of script in the appendix). The following values of k_2 and k_1 were obtained respectively, 0.00277 and 0.0219, which were in very good agreement with the corresponding theoretical values. Then the 'Num' delimiter was selected (see Table 1B). The following values of k_2 and k_1 were obtained respectively, 0.0222 and 0.00275. These values represent a reversal of the theoretical values. Thus, the k_2 value is now equal to the k_1 theoretical value, and the k_1 value is now equal to the k_2 theoretical value. This phenomenon is explained below and applies to all the tables presented in this paper where $k_1 > k_2$.

When the value of k_2 exceeds the theoretical k_2 value, e.g. it ranges from 0.004 to 0.010, the k_1 value remained constant at 0.00497, and all the Y values (line 51) and $\rho - k_2(1-\alpha)$ (RMINUS) values were negative. As k_2 increased to 0.011, the k_1 value remained at 0.00497, and the RMINUS values were still all negative; however, some of the Y values were now positive. When a k_2 value of 0.012 was reached, the k_1 value was now -0.00358, and there were more positive Y values. When k_2 attained values ranging from 0.013 to 0.022, the values of k_1 ranged from

Table 1A
Database analysis of theoretical TG data using $k_2 < k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.5199	0.002227	100	30	0.002769	0.00089767	0.670110	0.0223	−0.00609
0.5769	0.001630	130	60		0.00045782	1.343441		
0.6201	0.001284	160	90		0.00023195	2.023389		
0.6552	0.001071	190	120		0.00011625	2.714154		
0.6851	0.00929	220	150		0.00005708	3.425403		
0.7562	0.000679	310	240		0.00000374	6.151091		
0.7757	0.000621	340	270		−0.00000000	20.353256		

Table 1B
Database analysis of theoretical TG data using $k_2 < k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.5199	0.002227	100	30	0.10000	−0.04578280	0.143371	0.0027	0.00000
0.5769	0.001630	130	60		−0.04068050	0.261531		
0.6201	0.001284	160	90		−0.03670600	0.364340		
0.6552	0.001071	190	120		−0.03340890	0.458458		
0.6851	0.00929	220	150		−0.03056087	0.547559		
0.7562	0.000679	310	240		−0.02370111	0.801758		

0.00241 to 0.00275, and, except for the k_2 value of 0.013, all the other Y values were now positive (the RMINUS values remained negative throughout). When the k_2 values ranged from 0.023 to 0.1, the k_1 value remained constant at 0.00275, and the intercept remained constant at −0.00116. (In order to obtain the preceding in a reasonable time, the initial *ztmp* value employed was 1E − 03.) The final values were, as previously indicated, $k_2 = 0.0222$ and $k_1 = 0.00275$.

The preceding reversal of k values may be explained as follows. From Eq. (3a), when $k_2 = 0.00275$, a value of $k_1 = 0.0219$ is attained. Similarly, from Eq. (3b), when $k_1 = 0.00275$, the corresponding value of $k_2 = 0.022$ should result as these values follow from a least-squares treatment wherein the intercept with the lowest value of A_1 is reached (see Eq. (4)).

In Table 2, values of $k_1 = 0.0138$ and $k_2 = 0.00456$ were utilized to create the α, rate, time, and X data (the initial values employed were $t = 70$, $\alpha = 0.3609$, and rate = 3.8048E − 03). When the 'tmp' delimiter was selected, the following k values were obtained (*ztmp*) = 1E − 04, $k_1 = 0.0147$ and $k_2 = 0.0046$, which were in good agreement with the theoretical values. However, when the 'Num' delimiter was chosen, a reversal in k values was obtained. Thus, $k_1 = 0.000468$ and $k_2 = 0.0155$. Finally, Table 3 data were obtained based on assumed value of $k_2 = 0.00265$ and $k_1 = 0.0167$. Contrary to the procedure used for Tables 1 and 2, a plot of α vs. t was constructed in order to determine the values of the slope ρ at various times and values of α. The initial values at $t = 60$ were employed. When the 'tmp' delimiter was used, the following values were obtained, $k_2 = 0.00265$ and $k_1 = 0.0181$. How-

Table 2
Database analysis of theoretical TG data using $k_2 < k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.4630	0.003089	100	30	0.1000000	−0.05066250	0.170910	0.0047	−0.00354
0.5451	0.002464	130	60		−0.04302650	0.334280		
0.6122	0002026	160	90		−0.03675420	0.491844		
0.6676	0.001686	190	120		−0.03155430	0.644386		
0.7140	0001417	220	150		−0.02718350	0.793486		
0.8148	0.000877	310	240		−0.01764316	1.225748		
0.8392	0.000755	340	270		−0.01532550	1.366578		

Table 3
Database analysis of theoretical TG data using $k_2 < k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.4420	0.002700	90	30	0.002654	0.00121927	0.421900	0.0181	−0.05547
0.5680	0.001550	150	90		0.00040363	1.527409		
0.6120	0.001240	180	120		0.00021039	2.178943		
0.6790	0.001000	240	180		0.00148118	2.529454		
0.7300	0.000720	300	240		0.00000352	6.269555		
0.7890	0.000580	390	330		0.00002008	4.527995		
0.8210	0.000475	450	390		0.00000000	17.411596		
0.8470	0.000408	510	450		0.00000199	6.837539		

ever, when the 'Num' delimiter was utilized, $k_2 = 0.0147$ and $k_1 = 0.00264$, which is a reversal of values, as anticipated.

In the following, the case of $k_2 > k_1$ will be presented. In Table 4A, the values of $k_2 = 0.0123$ and $k_1 = 0.0066$ were used in the creation of the table. When the 'tmp' delimiter was used, the following final k values were obtained, $k_2 = 0.0021$ and $k_1 = 0.00337$. These values were in very poor agreement with the assumed k values. As k_2 increased from 1E − 03 to 2.13 − 03, the Y values and the RMINUS values kept decreasing. After $k_2 = 2.2/2\text{E} - 03$, the k_1 and the intercept values remained constant (these were k_1 values at the minimum intercept encountered). When k_2 attained a value of 4.4E − 03, all the Y values became negative. Upon reaching a value of 4.7E − 03, $z_1/zdiff < 0$ and lines 43–45 of the script became applicable (see also lines 35, 39). Then values of *ztmp* quickly attained the limiting value of $ztmp_2$ and final values were as previously indicated.

The values in Table 4 were then subjected to the 'Num' limitation (see lines 47–49 and 69 of the script). When the value of k_2 attained a value of 4.5E − 03, the RMINUS values were positive but decreasing, whereas all the Y values were negative and decreasing. This trend continued until k_2 reached a value of 5.2E − 03. At this k_2 value, Y values began to become positive, and RMINUS values started to become negative. Then, between k_2 values of (5.3–5.8)E − 03, this trend continued, but now $z_1/zdiff < 0$ and k_2 values quickly attained a value of 6.4E − 03,

Table 4A
Database analysis of theoretical TG data using $k_2 > k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.3531	0.003305	100	30	0.004740	0.00023831	−16.07020	0.0034	0.07779
0.4475	0.002980	130	60		0.00036058	−16.48434		
0.5317	0.002630	160	90		0.00041000	−16.61278		
0.6054	0.002286	190	120		0.00041524	−16.62550		
0.6690	0.001964	220	150		0.00039492	−16.57531		
0.8087	0.001190	310	240		0.00282911	−16.24177		
0.8414	0.000996	340	270		0.00024447	−16.09575		

Table 4B
Database analysis of theoretical TG data using $k_2 > k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.3531	0.003305	100	30	0.100000	−0.06138530	0.151756	0.0066	−0.00003
0.4475	0.002980	130	60		−0.05227050	0.312494		
0.5317	0.002630	160	90		−0.04420020	0.480197		
0.6054	0.002286	190	120		−0.03717430	0.653309		
0.6690	0.001964	220	150		−0.03113610	0.830559		
0.8087	0.001190	310	240		−0.01794030	1.381877		
0.8414	0.000996	340	270		−0.01486374	1.570002		

at which point all the Y values became positive, and all the RMINUS values negative. As the k_2 values kept increasing, the positive Y values kept decreasing, and the k_1 values and the intercept values kept decreasing until k_2 attained a value of 1.23E − 02, at which point the k_1 and intercept values remained constant at $k_1 = 0.0060$ and intercept = −3E − 05. These values (at the minimum intercept value) were maintained until $z > 0.1$ (see Table 4B). The final values were now $k_2 = 1.23\text{E}-02$, $k_1 = 0.0060$, and intercept = −3E − 05, in good agreement with assumed values for k_2 and k_1. In the following, other cases of $k_2 > k_1$ will be examined.

In Table 5, values were obtained using $k_2 = 0.0444$ and $k_1 = 0.00667$. When the 'tmp' delimiter was employed, the following k values were obtained, $k_2 = 0.0019$ and $k_1 = 0.00631$. These values agreed poorly with the assumed values. However, when the 'Num' delimiter was used, the final k values obtained were $k_2 = 0.0447$ and $k_1 = 0.00667$, in good agreement with the assumed k values (see Table 5). Finally, Table 6 was constructed using $k_2 = 0.0555$ and $k_1 = 0.00222$. Use of the 'tmp' delimiter afforded k values of $k_2 = 0.0007$ and $k_1 = 0.00209$, in poor agreement with assumed values. However, when the 'Num' delimiter was utilized, final k values were $k_2 = 0.0620$ and $k_1 = 0.00222$, in good agreement with assumed values (see Table 6).

From the preceding, the utilization of the 'tmp' and 'Num' delimiters in the script presented allow the user to obtain good k_1 and k_2 values and will indicate to the user whether $k_1 > k_2$ or vice-versa. Thus, if the 'tmp' delimiter is used and the

Table 5
Database analysis of theoretical TG data using $k_2 > k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.4424	0.00360	100	30	0.100000	−0.05208030	0.197688	0.0067	0.00000
0.5430	0.003038	130	60		−0.04266200	0.397166		
0.6257	0.002494	160	90		−0.03493610	0.596954		
0.6935	0.002043	190	120		−0.02860660	0.796837		
0.7491	0.001673	220	150		−0.02341670	0.997025		
0.8623	0.000918	310	240		−0.01285184	1.596987		
0.8873	0.000752	340	270		−0.01051835	1.797353		

Table 6
Database analysis of theoretical TG data using $k_2 > k_1$

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_{1b}	Intcpt1
0.183	0.001811	100	30	0.100000	−0.07993940	0.066472	0.0022	−0.00000
0.235	0.001697	130	60		−0.07479270	0.133020		
0.284	0.001589	160	90		−0.06997140	0.199654		
0.331	0.001486	190	120		−0.06546370	0.266245		
0.374	0.001391	220	150		−0.6124940	0.332787		
0.487	0.001139	310	240		−0.05015130	0.532696		
0.520	0.001065	340	270		−0.04692460	0.599199		

resulting k values are reversed when the 'Num' delimiter is used, then the value of k_1 is probably greater than k_2. However, when both delimiters are utilized and both sets of k values differ greatly, then the values obtained using the 'Num' delimiter are probably the more acceptable and $k_2 > k_1$.

There are limitations to the method presented. Thus, from Eq. (2A), it can be seen that the sign of RMINUS can change depending upon the ratio of k_1/k_2, and may thereby affect the final values of k_1 and k_2. In this regard, runs ('tmp' delimiter) were carried out using the following ratios of k_1 to k_2: $k_1 = 1.5k_2$, $k_1 = 2k_2$, and $k_1 = 2.7k_2$. In the first case, values of $k_1 = 0.0222$ and $k_2 = 0.0145$ were assumed (because this ratio is less than 2, it may affect the final k values obtained from a run). A run afforded values of $k_1 = 0.0128$ and $k_2 = 0.0049$, which were in poor agreement with the assumed values. In the second case, the assumed values were $k_1 = 0.0222$ and $k_2 = 0.111$. Again, a run yielded k values, $k_1 = 0.0111$ and $k_2 = 0.0022$, which were in poor agreement with the assumed values. In the last case, the k values assumed were $k_1 = 0.0222$ and $k_2 = 0.0080$. A run yielded k values, $k_1 = 0.0223$ and $k_2 = 0.0080$, in good agreement with the assumed values. The preceding indicates that certain ratios of k_1 to k_2 can exert an influence on the final k values. It may be further mentioned here that the runs carried out as depicted in Tables 1–3 all involved k_1/k_2 ratios much greater than 2. The ultimate testing for the veracity of the k_1 and k_2 values is to calculate corresponding values of α for various values of t (see Ref. [2]) and to compare them with theoretical or experimental α values.

Appendix

The PAL script (*x2ks*) used for the database analysis.

```
; This database (Paradox 3) program allows the estimation of 2 rate
; constants (k1, k2), cf. TA, 124 (1988) 139 and TA, 173 (1990) 253.     ;2

Clear  @5,5 ?? "Enter table to be analyzed (x2ks, x2ksx2, or x2ksx3): "  ;4
Accept "A8" Required To tbl  ; a non-blank value is required
                                                                         ;6
@7,5 ?? "Enter delimeter 'Num' (z >.1) or 'tmp' (ztmp < ztmp2): "
Accept "A4" Required To input                                            ;8

Edit tbl                                                                 ;10
Echo Normal ; see changes in derived values on workspace during analysis
                                                                         ;12
Intcpt1=100  [Intcpt1]=Intcpt1
sx=0 sy=0 sxx=0 sxy=0      ; initialize least squares params.            ;14
z=0 ztmp= 1E-04 [Tmp]=ztmp ; initialize value of z(K2) and its increment(ztmp)
ztmp2=1E-10 ; delimiting value of the increment                          ;16

;--------------------select 1 of 3 tables to be analyzed----------------  ;18
;--------------------and provide initial values-------------------------
If tbl="x2ks" Then                                                       ;20
zalpha=.5065 zrate=1.544E-03 ztime=70    ;lines 20-28 apply to tables used
Endif                                    ;in Part 5 [TA, 222 (1993) 85]  ;22
If tbl="x2ksx2" Then                     ;but the table names and data
zalpha=.344 zrate=3.60E-03 ztime=60      ;were adjusted to conform with  ;24
Endif                                    ;Part 6 [this paper]; these
If tbl="x2ksx3" Then                     ;lines were merely included to  ;26
zalpha=.1265 zrate=1.9163E-03 ztime=70   ;illustrate that this procedure in
Endif                                    ;Part 5 was also used in Part 6 ;28
NR=Nrecords(tbl)
                                                                         ;30
While True
[K2]=z                                                                   ;32

For n From 1 To NR                                                       ;34
zdiff=zrate-z*(1-zalpha)
Moveto [X]                                                               ;36
Right Right
[]=[Rate]-z*(1-[Alpha])                                                  ;38
z1=[]
                                                                         ;40
;---------prevent logarithm of negative values---------
                                                                         ;42
If ((z1/zdiff)<0 And input="tmp") Then Moveto [K2] Home z=z-ztmp
[K2]=z sx=0 sy=0 sxx=0 sxy=0 n=1 ztmp=ztmp/10 [Tmp]=ztmp Loop            ;44
Endif
                                                                         ;46
If ((z1/zdiff)<0 And input="num") Then Moveto [K2] Home z=z+ztmp
[K2]=z sx=0 sy=0 sxx=0 sxy=0 n=1 [Tmp]=ztmp Loop                         ;48
Endif
                                                                         ;50
Right [Y]=Ln(zdiff/z1)     ; LHS of eqn.
sx=sx+[X] sy=sy+[Y] sxy=sxy+[X]*[Y] sxx=sxx+[X]*[X]                      ;52
Moveto [X]
Down                                                                     ;54
If Isblank([]) Then Del
Endif                                                                    ;56

Endfor
```

```
;----------calc least squares values of slope and intercept-----------
K1=(NR*sxy-sx*sy)/(NR*sxx-sx*sx)
Intcpt=(sy/NR)-K1*(sx/NR)

;-----------save values with the smallest intercept------------
If (Abs(Intcpt) < Abs(Intcpt1)) Then Intcpt1=Intcpt
k1b=k1 k2b=z  sx=0  sy=0  sxx=0  sxy=0
Endif
Moveto [K1b] Home [K1b]=k1b Right [Intcpt1]=Intcpt1

If ztmp < ztmp2 OR z > .1 Then Do_It! clear clearall
@10,5  ?? "k2= "+strval(k2b)+",  "+"k1= "+strval(k1b)
@12,5  ?? "intercept= "+ strval(Intcpt1)
@16,5  ?? "Press a key to clear screen."
n=getchar() quitloop
Endif

z=z+ztmp   ; increment z(K2) values
Endwhile
```

References

[1] L. Reich and S.H. Patel, Thermochim. Acta, 222 (1993) 85.
[2] L. Reich and S.S. Stivala, Thermochim. Acta, 124 (1988) 139.