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Use of databases in thermal analysis. Part 5

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Abstract

A mathematical expression was previously derived for the concurrent determination of two rate constants, k_1 and k_2, for two consecutive irreversible first-order reactions. This expression required the measurement of slopes in order to ascertain the required reaction rates.

In this paper, a relational database manager (DB) was employed to estimate values of the two rate constants using this expression. For this purpose, a computer algorithm was developed using the Paradox 3 DB which possesses a powerful script language (PAL).

Database analyses were carried out using both theoretical and experimental data. The PAL script employed is described and the resulting k_1 and k_2 values are compared with the assumed and reported values.

INTRODUCTION

A mathematical expression was recently developed for the concurrent evaluation of two rate constants for two consecutive irreversible first-order reactions [1]. Subsequently, a computer algorithm was devised to implement this expression. BASICA (IBM) [1] and spreadsheets (LOTUS 1-2-3 Release 2.2) [2] were utilized for the testing of both theoretical and experimental data. The resulting rate constants obtained were in satisfactory agreement with both types of data.

In the present paper, the same reaction type is used and the algorithm is modified in order to accommodate a database analysis. By this means, two rate constants will be obtained concurrently for theoretical and experimental data. Their calculated values will be compared with theoretically assumed and reported experimental values. The database employed was Paradox 3 which possesses a powerful script language (PAL) and which was

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utilized in the analysis. This PAL script which is listed in the Appendix is denoted as x2ks.

THEORETICAL ASPECTS

Two consecutive irreversible first-order reactions can be represented as

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

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

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

In order to estimate k_1 and k_2 concurrently, the following mathematical expression was derived

$$\ln\{[\rho - k_2(1-\alpha)]_0/[\rho - k_2(1-\alpha)]\} = k_1(t - t_0) \tag{2}$$

where $\rho = d\alpha/dt$, α is the degree of conversion and the subscript 0 refers to an initial set of data values. It can readily be seen from eqn. (2) that if we make the left-hand side of eqn. (2) equal to Y then

$$Y = A_2X + A_1 \tag{3}$$

where $A_2 = k_1$, $X = t - t_0$ and $A_1 = 0$.

By utilizing eqn. (3) 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 whereby 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).

RESULTS AND DISCUSSION

Tables 1–3 list the values of α (also as ‘A’), rate (ρ, also as ‘R’) and reaction time obtained as indicated previously [1, 2]. These tables are arbitrarily named x2ks, x2ksx2 and x2ksx3, respectively. Also, due to spatial limitations of the Paradox Report function (9 columns per printed page for the tables used), it was decided to maintain one printed page per table by omitting a ‘Tmp’ column which was located between the Y and k_1b

TABLE 1

Database analysis of theoretical TG data for k_1 and k_2

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)$	Y	k_1b	Intercept 1
0.5395	0.000814	100	30	0.001230	0.00024725	1.332228	0.0442	0.01942
0.5602	0.000606	130	60		0.00006522	2.664938		
0.5772	0.000537	160	90		0.00001713	4.001979		
0.5928	0.000505	190	120		0.00000452	5.334974		
0.6076	0.000484	220	150		0.00000112	6.728243		
0.6488	0.000432	310	240		0.00000000	18.090131		
0.6615	0.000416	340	270		0.00000002	10.664804		

columns. This 'Tmp' column is mentioned in the PAL script in the Appendix (see lines 12 and 42) and must be included during the creation of the tables via Paradox.

The following comments are made with regard to the PAL script. In line 5, one of the 3 preceding table names must be entered; just pressing the 'Enter' key will not allow the script program to continue. Any other entry will lead to an error statement. Because a run may require around 2 or more minutes, depending upon the type of computer used, the amount of data employed in the tables and the initial value of ztmp, it was decided that

TABLE 2

Database analysis of theoretical TG data for k_1 and k_2

α	Rate ρ	Time	X	k_2	$\rho - k_2(1-\alpha)Y$		k_1b	Intercept 1
0.4420	0.002700	90	30	0.002645	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		0.00014818	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		

TABLE 3

Database analysis of experimental data for k_1 and k_2

α	Rate ρ	Time	x	k_2	$\rho - k_2(1-\alpha)$	Y	k_1b	Intercept 1
0.518	0.002250	120	30	0.002626	0.00098429	0.656877	0.0200	0.01437
0.621	0.001320	180	90		0.00032476	1.765700		
0.692	0.000900	240	150		0.00009121	3.035675		
0.738	0.000688	300	210		−0.00000000	17.413064		

it would be more interesting to observe the changes occurring in the derived values on the workspace during the analysis; therefore line 8 was included (although it can increase the run time).

As indicated previously, values of k_1 are very sensitive to small changes in the values of k_2; therefore, values of k_2 were carried up to 9 decimal places in order to obtain the final values. Thus, the delimiting value of the increment (ztmp2) was set to a value of 1E − 10 (line 13). The initial values of the increment (ztmp) of 1E − 03 and 1E − 04 each afforded the same values of k_1 and k_2 for each of the 3 tables. However, in this respect, it may be noted that for all the tables, an initial ztmp greater than 1E − 03, e.g. 1E − 02, led to negative values which were not compatible with the computer algorithm employed. In order to indicate that such values were incompatible, lines 38–43 were inserted into the script. Thus, a warning is issued (line 40) that the initial ztmp value (line 11) will be lowered; after several automatic adjustments of values, the run is successfully completed.

A run proceeds smoothly when the logarithmic argument in eqn. (2) possesses a positive value. However, as the value of k_2 is increased and approaches its 'true' value, a negative argument results. When this condition is encountered (see lines 40–43) then the k_2 value is decreased, the least-squares parameters set to zero, n is reset to unity, the increment is decreased to one-tenth of its previous value and the loop involved is repeated. Otherwise, those values of k_2 and the corresponding k_1 values (k_1b) are saved, which involve the smallest intercept encountered during the run (lines 62–64), and the run continues (line 74). These values obtained are based on a least-squares analysis (lines 57–59). Finally, when the limiting value of ztmp2 is reached, final values of k_2, k_1 and intercept are displayed on the screen (lines 67–72).

The following results were obtained from the various tables using the x2ks script. The theoretical x2ks table (Table 1) was constructed based on theoretical values of $k_2 = 0.00123$ and $k_1 = 0.0444$. Three runs were carried out using initial ztmp values of 1E − 02, 1E − 03 and 1E − 04. The value of 1E − 02 resulted in a warning that the ztmp value will be lowered. The other two values of ztmp each afforded the same values for k_2 and k_1, i.e. 0.00123 and 0.0442, respectively. The run with ztmp = 1E − 03 required approx. 1.8 min; when the 'Echo Normal' statement (line 8) was omitted, the run time was reduced to approx. 1.3 min. The preceding results, as well as those below, were obtained using a 386SX 20 computer. The initial values were based on $t = 70$.

The x2ksx2 (Table 2) data was based on assumed values of $k_2 = 0.00265$ and $k_1 = 0.0167$. Contrary to the procedure used for Table 1, a plot of α versus t was now constructed using the theoretical values in order to determine values of the slope (ρ) at various times and values of α. This is also the procedure applied to experimental values of α and t discussed below. In Table 2, an initial $t = 60$ was employed. As in the case of Table 1, an initial value of ztmp (1E − 02) resulted in a warning that the value will be decreased. However, values of 1E − 03 and 1E − 04 each afforded values of $k_2 = 0.00265$ and $k_1 = 0.0181$.

For the x2ksx3 table (Table 3), experimenal values were utilized. As for the previous tables, the use of initial values of ztmp was important. For initial ztmp values of 1E − 03 or 1E − 04, values of $k_2 = 0.00262\ \text{min}^{-1}$ and $k_1 = 0.0200\ \text{min}^{-1}$ were obtained (or $k_2 = 0.157\ \text{h}^{-1}$ and $k_1 = 1.20\ \text{h}^{-1}$). By utilizing a manual method, Kaufler [3] reported values of $k_2 = 0.161\ \text{h}^{-1}$ and $k_1 = 1.01\ \text{h}^{-1}$, whereas using tables and graphs, Swain [4] reported values of $k_2 = 0.180\ \text{h}^{-1}$ and $k_1 = 0.937\ \text{h}^{-1}$. Differences between the results obtained in this paper and the results reported by Kaufler and Swain may lie in the poor accuracy of values obtained by means of slopes (Kaufler and Swain did not employ slopes in their procedures). Furthermore, the database analysis involved a relatively small amount of experimental data (see Table 3). When slopes are employed, in particular, a large amount of data should yield more accurate results (a smoother plot can be constructed). Nevertheless, the database procedure is promising in view of its success with theoretical data, and we look forward to its employment in the future.

REFERENCES

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APPENDIX

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

```
                                   Script: C:\paradox\sample\x2ks

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

Clear  @5,5 ?? "Enter table to be analyzed (x2ks, x2ksx2, or x2ksx3): "
Accept "A8" Required To tbl  ; a non-blank value is required

Edit tbl
Echo Normal ; see changes in derived values on workspace during analysis

Intcpt1=100  [Intcpt1]=Intcpt1
sx=0 sy=0 sxx=0 sxy=0     ; initialize least squares params.
z=0 ztmp= 1E-03 [Tmp]=ztmp ; initialize value of z(K2) and its increment(ztmp)
ztmp2=1E-10 ; delimiting value of the increment

;-------------------select 1 of 3 tables to be analyzed----------------
;-------------------and provide initial values-------------------------
If tbl="x2ks" Then
zalpha=.5065  zrate=1.544E-03  ztime=70
Endif
If tbl="x2ksx2" Then
zalpha=.344 zrate=3.60E-03 ztime=60
Endif
If tbl="x2ksx3" Then
```

```
zalpha=.432 zrate=3.39E-03 ztime=90
Endif
NR=Nrecords(tbl)

While True
[K2]=z

For n From 1 To NR
zdiff=zrate-z*(1-zalpha)
Moveto [X]
Right Right
[]=[Rate]-z*(1-[Alpha])
z1=[]

;---------set a trap for very high values of ztmp (line 12)---------

If zdiff<0 Then @10,4 ??" Lowering the initial high ztmp value!" sleep 5000
Echo Normal Moveto [K2] Home [K2]=[K2]/10 z=[K2] sx=0 sy=0 sxx=0 sxy=0
n=1 ztmp=ztmp/10 [Tmp]=ztmp Loop
Endif

If z1 < 0 and zdiff > 0  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
Endif

Right [Y]=Ln(zdiff/z1)      ; LHS of eqn.
sx=sx+[X] sy=sy+[Y] sxy=sxy+[X]*[Y] sxx=sxx+[X]*[X]
Moveto [X]
Down
If Isblank([]) Then Del
Endif
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 Then Do_It! Clear Clearall
@10,5  ?? "k2= "+strval(k2b)+",  "+"k1= "+strval(k1b)
@12,5  ?? "intercept= "+ strval(Intcpt1)
@14,5  ?? "Press a key to clear screen."
n=getchar() quitloop
Endif

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