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USE OF SPREADSHEETS IN THERMAL ANALYSIS. PART 6

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ABSTRACT

In a recent report [1], a mathematical expression was developed for the concurrent evaluation of two rate constants in two consecutive first-order reactions. When this expression was implemented using a computer program, the values of the rate constants obtained agreed favorably with theoretically assumed and reported experimental values.

In the present paper, the preceding expression will be implemented utilizing spreadsheet analysis. To this end, the computer program used to implement the above expression has been modified and adapted for spreadsheet use. The resulting macro has then been utilized to analyze both theoretical and experimental data. The calculated values of rate constants obtained have been compared with theoretically assumed and reported experimental values.

INTRODUCTION

Recently, an expression was developed for the concurrent estimation of two rate constants for two consecutive first-order reactions [1]. Subsequently, a computer algorithm was developed to implement this expression; BASICA (IBM) was employed for the testing of the experimental data involved. Values of the rate constants obtained agreed favorably with theoretically assumed and reported experimental values.

In the present paper, the preceding reaction type will be used and the preceding algorithm will now be modified and adapted for the spreadsheet analysis of theoretical and experimental data in order to evaluate concurrently the two rate constants. Their calculated values will be compared with theoretically assumed and reported experimental values. It may also be mentioned here that the spreadsheet utilized was Lotus 1-2-3, Release 2.2.

SOME THEORETICAL ASPECTS

A symbolic representation of two consecutive irreversible first-order reactions follows:

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

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

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In the preceding expressions, A, B and C denote 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:

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

where $\rho = \mathrm{d}\alpha/\mathrm{d}t$, 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

$$Y = A_2 X + A_1 \qquad (3)$$

where

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

By using eqn. (3), we can now employ the concept of a spreadsheet macro based on a computer algorithm previously devised and modified [1–3]. Values of k_1 and k_2 will be determined by means of an iteration procedure wherein a minimum value of A_1 will be obtained for the conditions employed.

APPLICATIONS OF THE METHOD

The procedure was initially tested using two sets of theoretical data. In the first case, values of $k_1 = 0.0444$ and $k_2 = 0.00123$ were assumed in deriving data. In Table 1, values of α, reaction rate (arbitrary units) and reaction time (arbitrary units) are displayed in the range A5–C11. The initial set of data values used (subscript 0) is shown in columns A1–C1. At the bottom of Table 1 there is a listing of the various range names employed. Furthermore, in Table 2 the cell contents of the worksheet in Table 1 are listed, so that although the macro in Table 1 is not visible in its entirety the complete macro may be gleaned from a perusal of Table 2. It may be noted here that the run time for this and subsequent worksheets mentioned varies between about 15 s and 20 s (with windowsoff and utilizing a 386-20 computer). Initial values of tmp and k_2 were 1×10^{-5} and 0, respectively, for all the runs made. The final results obtained can be viewed in row A29 in Table 1. These calculated values are virtually identical with the assumed values for k_1 and k_2.

It should also be mentioned here that the algorithm employed, eqns. (2) and (3), did not act as a well-behaved function. Thus, as the values of k_2 were incremented and began to exceed the most likely final value of k_2, the

TABLE 1

Worksheet to determine k_1 and k_2 from theoretical data [1]

```
     A      B        C      D        E      F          G         H       I
 1 0.5065 1.544E-03   70                   0.0009369
 2 ===================================================================================
 3  Alpha    Rate    Time     k2       X                  Y        X*X      Y*Y
 4 ===================================================================================
 5 0.5395 8.137E-04  100 0.0012301   30  2.47E-04  1.33230     900 1.775014
 6 0.5602 6.062E-04  130              60  6.52E-05  2.66526    3600 7.103606
 7 0.5772 5.372E-04  160              90  1.71E-05  4.00323    8100 16.02583
 8 0.5928 5.054E-04  190             120  4.50E-06  5.33962   14400 28.51152
 9 0.6076 4.838E-04  220             150  1.10E-06  6.74648   22500 45.51493
10 0.6488 4.320E-04  310             240  3.19E-08 10.28914   57600 105.8664
11 0.6615 4.164E-04  340             270  4.38E-09 12.27332   72900 150.6344
12 ===================================================================================
13 Totals----->                      960           42.64934 180000 355.4318
14 ===================================================================================
15   X*Y      Tmp     k1   Macro                             Intcpt Intcpt1
16 ===================================================================================
17 39.968    1E-10 0.04 {let intcpt1,100}          <==\a  0.0018 0.001872
18 159.91               {goto}xk2~{let xk2,+xk2+  <==\d    k1b     k2b
19 360.29               {if +intcpt>0}{branch \d}          ================
20 640.75          loop {home}{goto}xk2~{let xk2,+xk2-tmp0.0444 0.001230
21 1011.9               {if @iserr(+intcpt)=1}{branch loop}
22 2469.3               {if @abs(+intcpt)<@abs(+intcpt1)}{let intcpt1,int
23 3313.7               {if +intcpt<0}{branch loop}
24 =======              {goto}tmp~{let tmp,+tmp/10}
25 7996.0               {if +tmp<1E-9}{branch done1}
26                      {branch \d}
27                 done1{goto}final~{beep 3}RUN IS OVER! {wait @now+@time
28
29 Final values k1 & k2;    0.0444      0.00123
```

Range Name Table

DONE1	D27	SYY	I13
FINAL	A29	TMP	B17
INTCPT	H17	X	E5..E11
INTCPT1	I17	XK1	C17
K1	C17	XK2	D5
K1B	H20	XX	H5..H11
K2B	I20	XY	A17..A23
LOOP	D20	Y	G5..G11
LOOP2	D24	YY	I5..I11
SX	E13	\A	D17
SXX	H13	\D	D18
SXY	A25		
SY	G13		

cells for the intercept and k_1 displayed an "ERR" message. The macro statements D20 and D21 were therefore used. Upon encountering the error message, there occurs a branching to "loop" whereby the value of k_2 is decreased until the "ERR" message disappears (at this point the now positive value of k_2 should be very close to the most probable value). Furthermore, there may now occur an exchange of values between intcpt

TABLE 2

Cell contents of worksheet in Table 1

```
A1: [W7] 0.5065
B1: (S3) [W10] 0.001544
C1: [W5] 70
F1: [W10] +B1-$XK2*(1-A1)
A2: [W7] \=
B2: (F7) [W10] \=
C2: [W5] \=
D2: [W10] \=
E2: [W4] \=
F2: [W10] \=
G2: [W9] \=
H2: [W7] \=
I2: \=
A3: [W7] ^Alpha
B3: [W10] ^Rate
C3: [W5] "Time
D3: [W10] ^k2
E3: [W4] ^X
G3: [W9] ^Y
H3: [W7] ^X*X
I3: ^Y*Y
A4: [W7] \=
B4: [W10] \=
C4: [W5] \=
D4: [W10] \=
E4: [W4] \=
F4: [W10] \=
G4: [W9] \=
H4: [W7] \=
I4: \=
A5: [W7] 0.5395
B5: (S3) [W10] 0.0008137
C5: [W5] 100
D5: [W10] 0.00123012
E5: [W4] +C5-$C$1
F5: (S2) [W10] +B5-$XK2*(1-A5)
G5: (F5) [W9] @LN($F$1/F5)
H5: [W7] +E5*E5
I5: +G5*G5
A6: [W7] 0.5602
B6: (S3) [W10] 0.0006062
C6: [W5] 130
E6: [W4] +C6-$C$1
F6: (S2) [W10] +B6-$XK2*(1-A6)
G6: (F5) [W9] @LN($F$1/F6)
H6: [W7] +E6*E6
I6: +G6*G6
A7: [W7] 0.5772
B7: (S3) [W10] 0.0005372
C7: [W5] 160
E7: [W4] +C7-$C$1
F7: (S2) [W10] +B7-$XK2*(1-A7)
G7: (F5) [W9] @LN($F$1/F7)
H7: [W7] +E7*E7
I7: +G7*G7
A8: [W7] 0.5928
B8: (S3) [W10] 0.0005054
C8: [W5] 190
E8: [W4] +C8-$C$1
F8: (S2) [W10] +B8-$XK2*(1-A8)
G8: (F5) [W9] @LN($F$1/F8)
H8: [W7] +E8*E8
I8: +G8*G8
A9: [W7] 0.6076
B9: (S3) [W10] 0.0004838
C9: [W5] 220
E9: [W4] +C9-$C$1
F9: (S2) [W10] +B9-$XK2*(1-A9)
G9: (F5) [W9] @LN($F$1/F9)
H9: [W7] +E9*E9
I9: +G9*G9
A10: [W7] 0.6488
B10: (S3) [W10] 0.00043205
C10: [W5] 310
E10: [W4] +C10-$C$1
F10: (S2) [W10] +B10-$XK2*(1-A10)
G10: (F5) [W9] @LN($F$1/F10)
H10: [W7] +E10*E10
I10: +G10*G10
A11: [W7] 0.6615
B11: (S3) [W10] 0.0004164
C11: [W5] 340
E11: [W4] +C11-$C$1
F11: (S2) [W10] +B11-$XK2*(1-A11)
G11: (F5) [W9] @LN($F$1/F11)
H11: [W7] +E11*E11
I11: +G11*G11
A12: [W7] \=
B12: [W10] \=
C12: [W5] \=
D12: [W10] \=
E12: [W4] \=
F12: [W10] \=
G12: [W9] \=
H12: [W7] \=
I12: \=
A13: [W7] 'Totals----->
E13: [W4] @SUM(X)
G13: [W9] @SUM(Y)
H13: [W7] @SUM(XX)
I13: @SUM(YY)
A14: [W7] \=
B14: [W10] \=
C14: [W5] \=
D14: [W10] \=
E14: [W4] \=
F14: [W10] \=
G14: [W9] \=
H14: [W7] \=
I14: \=
A15: [W7] ^X*Y
B15: [W10] ^Tmp
```

TABLE 2 (continued)

Cell contents of worksheet in Table 1

```
C15: [W5] ^k1
D15: [W10] ^Macro
H15: [W7] 'Intcpt
I15: 'Intcpt1
A16: [W7] \=
B16: [W10] \=
C16: [W5] \=
D16: [W10] \=
E16: [W4] \=
F16: [W10] \=
G16: [W9] \=
H16: [W7] \=
I16: \=
A17: [W7] +E5*G5
B17: (S0) [W10] 1.0000000E-10
C17: [W5] (@ROWS(X)*SXY-SX*SY)/(@ROWS(X)*SXX-(SX)^2)
D17: [W10] '{let intcpt1,100}
G17: [W9] ^<==\a
H17: [W7] (SY/@ROWS(X))-$K1*(SX/@ROWS(X))
I17: 0.0018725353
A18: [W7] +E6*G6
D18: [W10] '{goto}xk2~{let xk2,+xk2+tmp}~
G18: [W9] ^<==\d
H18: [W7] ^k1b
I18: ^k2b
A19: [W7] +E7*G7
D19: [W10] '{if +intcpt>0}{branch \d}
H19: [W7] \=
I19: \=
A20: [W7] +E8*G8
C20: [W5] 'loop
D20: [W10] '{home}{goto}xk2~{let xk2,+xk2-tmp}~
H20: [W7] 0.044412747
I20: 0.00123012
A21: [W7] +E9*G9
D21: [W10] '{if @iserr(+intcpt)=1}{branch loop}
A22: [W7] +E10*G10
D22: [W10] '{if @abs(+intcpt)<@abs(+intcpt1)}{let intcpt1,intcpt}{let k2b,+xk2}{let k1b,+xk1}
A23: [W7] +E11*G11
D23: [W10] '{if +intcpt<0}{branch loop}
A24: [W7] \=
D24: [W10] '{goto}tmp~{let tmp,+tmp/10}
A25: [W7] @SUM(XY)
D25: [W10] '{if +tmp<1E-9}{branch done1}
D26: [W10] '{branch \d}
C27: [W5] 'done1
D27: [W10] '{goto}final~{beep 3}RUN IS OVER! {wait @now+@time(0,0,5)}{escape}
A29: [W7] 'Final values k1 & k2;
D29: (F4) [W10] +K1B
F29: (F5) [W10] +K2B
```

and intcpt1, k_{2b} and xk_2 and k_{1b} and xk_1 (cf. Table 2, D22). Tmp is then decreased in value by a factor of 10 and the iteration is either restarted or final values are displayed, depending on the value of tmp (the run is concluded when the value of tmp is less than 1×10^{-9}).

TABLE 3

Abbreviated worksheet to determine k_1 and k_2 from theoretical data [1]

0.344	3.600E-03	60			0.0018596			
Alpha	Rate	Time	k2	X		Y	X*X	Y*Y
0.442	2.70E-03	90	0.0026529	30	1.22E-03	0.42183	900	0.177938
0.568	1.55E-03	150		90	4.04E-04	1.52691	8100	2.331447
0.612	1.24E-03	180		120	2.11E-04	2.17790	14400	4.743253
0.679	1.00E-03	240		180	1.48E-04	2.52819	32400	6.391729
0.730	7.20E-04	300		240	3.71E-06	6.21757	57600	38.65815
0.789	5.80E-04	390		330	2.02E-05	4.52092	108900	20.43875
0.821	4.75E-04	450		390	1.25E-07	9.60622	152100	92.27954
0.847	4.08E-04	510		450	2.10E-06	6.78555	202500	46.04371

X*Y			
12.654			
137.42			
261.34			
455.07	Final values k1 & k2=======>	0.0185	0.00265
1492.2			
1491.9			
3746.4			
3053.4			
=======			
10650.			

In the second case, where theoretical values were again used to test the spreadsheet macro, values of $k_1 = 0.0167$ and $k_2 = 0.00265$ were assumed. Contrary to the first case a plot of α vs. t was now constructed using the

TABLE 4

Abbreviated worksheet to determine k_1 and k_2 from experimental data [4]

0.432	3.390E-03	90			0.0019719			
Alpha	Rate	Time	k2	X		Y	X*X	Y*Y
0.518	2.25E-03	120	0.0024966	30	1.05E-03	0.63344	900	0.401242
0.621	1.32E-03	180		90	3.74E-04	1.66311	8100	2.765937
0.692	9.00E-04	240		150	1.31E-04	2.71130	22500	7.351168
0.738	6.88E-04	300		210	3.39E-05	4.06396	44100	16.51577

X*Y			
19.003			
149.67			
406.69	Final values k1 & k2=======>	1.134	0.150
853.43			
=======			
1428.8			

theoretically derived values, in order to determine values of the slope (ρ) at various times (rather than use theoretical values). The values obtained are displayed in the worksheet in Table 3 (abbreviated to avoid repetition of the macro already described) under and above the heading "Rate". The nine data triads used afforded values of $k_1 = 0.0185$ and $k_2 = 0.00265$ (a computer program used with this data [1] gave values for k_1 and k_2 of 0.0174 and 0.00265, respectively). It may also be noted here that many values of α and t are necessary in order to obtain the required accurate slopes. The experimental data to be utilized next had relatively few such values.

The spreadsheet macro was finally tested using experimental data previously reported [4]. The data obtained in this report were for the hydrolysis of 2,7-dicyanonaphthalene. From a smooth plot of these experimental data, values were obtained as depicted in the worksheet in Table 4 (abbreviated to avoid repetition of the macro already described). Units are in terms of minutes. Final values, in terms of hours, were $k_1 = 1.13$ and $k_2 = 0.150$. When the same data were analyzed using a computer program [1], these k-values were 1.12 and 0.150, respectively.

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