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USE OF SPREADSHEETS IN THERMAL ANALYSIS. PART 3.

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ABSTRACT

Spreadsheets have rarely been used to analyze TG and DTA (or DSC) data to obtain activation energy E and reaction order n (or mechanism).

In the recent past and in this paper spreadsheet procedures have been successfully used to ascertain E and n or E and mechanism. In this paper, these procedures are applied to theoretical TG data, to TG data for calcium oxalate, calcium carbonate, teflon and sodium bicarbonate and to DTA data for benzenediazonium chloride. In addition, some of the many advantages of using such procedures are mentioned. The aim of this paper is to extend the implementation of spreadsheets in thermal analysis.

INTRODUCTION

Spreadsheet analysis of TG, DTA or DSC data to obtain activation energy E and reaction order n or mechanism has been used only rarely in the past. Thus, previous determinations of E and n generally employed graphical and/or computer methods [1]. However, recently [2–4], spreadsheet procedures have been successfully used for the determination of E and n [2,3] or of E and mechanism [4]. There are many advantages to the use of spreadsheets [5,6]. Thus, they can provide neat formats of data and results and possess many built-in functions. Some of these functions (in the case of Lotus 2) are as follows: summations (@SUM), standard deviations (@STD), maximum and minimum values (@MAX and @MIN), single and multiple linear regression analysis, graphics, sorting, etc. Furthermore, Macros allow the automatic utilization of worksheets for the estimation of the kinetic parameters E and n (and mechanism).

This paper is one of a planned series whose aim is to extend the implementation of spreadsheets for the analysis of TG, DTA or DSC data to obtain values of E and n (or mechanism).

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THEORETICAL ASPECTS

For two pairs of given values of α and T(K), i.e. α_1, T_1 and α_2, T_2, it can be shown that [7]

$$\ln \frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}} \left(\frac{T_2}{T_1}\right)^2 = \frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad (1)$$

where α = conversion at temperature T(K). From eqn. (1), values of E/R can be calculated for various sets of α–T values at arbitrarily selected values of reaction order n. However, if uniqueness is assumed, only one pair of E/R and n values will be relevant.

Various values of E/R can be obtained at various n values by employing various pairs of α–T values. However, the E/R values should not deviate (or deviate minimally) at only one unique value of n. This value can be established by utilizing the concept of the standard deviation (STD). Thus, the E/R values at a particular value of n, which afford the smallest STD value, also yield final values E(avg) and n.

RESULTS AND DISCUSSION

The spreadsheet employed in this paper was Lotus 1-2-3, release 2, which can provide many advanced Macro commands. Such commands were applied in this paper to theoretical non-isothermal TG (NITG) data, to NITG data for calcium oxalate (COX), calcium carbonate (CAC), teflon (TF) and sodium bicarbonate (SB) and to DTA data for benzenediazonium chloride (BDC).

Table 1 represents a spreadsheet analysis of theoretical TG data. Final values (cf. row 29) were $n = 0.50$ and $E = 28.0$ kcal mol^{-1} (ref. 8, 1/2 and 28). The cell contents for the worksheet in Table 1 are depicted in Table 2. From the latter table it can be seen that cells E4–E9 denote values of the left-hand-side logarithm term for various α–T(K) values. Thus, for example, the value in cell E4 is equal to the LN(value in cell D3/value in cell D4), etc. down the Y column. The X values in cells F4–F9 represent the term in parentheses on the right-hand side of eqn. (1) (see Table 2). Finally, the E/R values in cells G4–G9 are equal to the corresponding values of the ratios of Y/X, and the average E/R value is depicted in cell G11.

The starting n value was taken as 0.10001 and was incremented initially in increments of 0.1; an initial arbitrary value of 1E + 11 was placed in cell E15 (SD2) (cf. rows 17 and 18). When E/R values yielded standard deviations in cell D15 (SD1) which were less than the values in SD2, the corresponding n values were automatically placed in cell F15 and the SD1 and E/R(avg) values were automatically placed in cells E15 (SD2) and G15,

TABLE 1.

Spreadsheet analysis of theoretical TG data ($n = 1/2$) [8]

```
      A         B      C        D           E           F          G
1  Alpha      T(K)    N       LHS1          Y           X         E/R
2  ===============================================================
3  0.13190     405  0.600  3.35E-07
4  0.20195     410         5.13E-07  -0.42559  -3.01E-05  1.41E+04
5  0.30261     415         7.80E-07  -0.41787  -2.94E-05  1.42E+04
6  0.44105     420         1.18E-06  -0.41188  -2.87E-05  1.44E+04
7  0.61869     425         1.77E-06  -0.40907  -2.80E-05  1.46E+04
8  0.81978     430         2.68E-06  -0.41289  -2.74E-05  1.51E+04
9  0.97883     435         4.15E-06  -0.43934  -2.67E-05  1.64E+04
10 ===============================================================
11                                          E/R(AVG)=>1.48E+04
12 ===============================================================
13   Mrkr     Inc             SD1       SD2      rctnordr  E/R(2)
14 ===============================================================
15       1     0.01          7.93E+02 8.49E-01  5.00E-01 1.40E+04
16
17 \a-->    {let mrkr,0}{let inc,.1}{let sd2,1E+11}{let n,.10001}~{paneloff}
18 \d-->    {goto}n~{let n,+n+inc}~
19          {if mrkr=1#and#+n-f15>.1}{goto}a27~{quit}
20          {if +sd1<sd2}{let sd2,sd1}{let rctnordr,+n}{let g15,g11}
21          {if +c3>2}{branch \b}
22          {branch \d}
23
24 \b-->    {goto}n~{let n,+f15-inc}~
25          {goto}inc~{let inc,+inc/10}~
26          {let mrkr,1}{branch \d}
27
28 =======================         ===========================
29 rctnordr=        0.500    and          E=     27999 cal/mol
30 =======================         ===========================
```

respectively (see row 20). This continued until n values up to 2 had been scanned. When $n > 2$, the value of n was automatically decreased by the increment value (Inc) and the Inc was decreased by a factor of 10 (cf. rows 24 and 25). The value of n was then automatically incremented over a range of $(n - 0.1)$ to $(n + 0.1)$ using Inc = 0.01, after which the final value of n (from cell F15) and the final value of E (from cell G15) were automatically recorded in row 29.

TABLE 2.

Cell contents of worksheet for theoretical TG data ($n=1/2$)

```
A1: [W8] ^Alpha
B1: [W8] "T(K)
C1: [W6] ^N
D1: [W10] ^LHS1
E1: ^Y
F1: [W10] ^X
G1: [W9] ^E/R
A2: [W8] \=
B2: [W8] \=
C2: [W6] \=
D2: [W10] \=
E2: \=
F2: [W10] \=
G2: [W9] \=
A3: (F5) [W8] 0.1319
B3: [W8] 405
C3: [W6] 0.50001
D3: (S2) [W10] ((1-(1-A3)^(1-$N))/B3^2)
A4: (F5) [W8] 0.20195
B4: [W8] 410
D4: (S2) [W10] ((1-(1-A4)^(1-$N))/B4^2)
E4: @LN(+D3/D4)
F4: (S2) [W10] 1/B4-1/B3
G4: (S2) [W9] +E4/F4
A5: (F5) [W8] 0.30261
B5: [W8] 415
D5: (S2) [W10] ((1-(1-A5)^(1-$N))/B5^2)
E5: @LN(+D4/D5)
F5: (S2) [W10] 1/B5-1/B4
G5: (S2) [W9] +E5/F5
A6: (F5) [W8] 0.44105
B6: [W8] 420
D6: (S2) [W10] ((1-(1-A6)^(1-$N))/B6^2)
E6: @LN(+D5/D6)
F6: (S2) [W10] 1/B6-1/B5
G6: (S2) [W9] +E6/F6
A7: (F5) [W8] 0.61869
B7: [W8] 425
D7: (S2) [W10] ((1-(1-A7)^(1-$N))/B7^2)
E7: @LN(+D6/D7)
F7: (S2) [W10] 1/B7-1/B6
G7: (S2) [W9] +E7/F7
A8: (F5) [W8] 0.81878
B8: [W8] 430
D8: (S2) [W10] ((1-(1-A8)^(1-$N))/B8^2)
E8: @LN(+D7/D8)
F8: (S2) [W10] 1/B8-1/B7
G8: (S2) [W9] +E8/F8
A9: (F5) [W8] 0.97883
B9: [W8] 435
D9: (S2) [W10] ((1-(1-A9)^(1-$N))/B9^2)
E9: @LN(+D8/D9)
F9: (S2) [W10] 1/B9-1/B8
G9: (S2) [W9] +E9/F9
A10: [W8] \=
B10: [W8] \=
C10: [W6] \=
D10: [W10] \=
E10: \=
F10: (S2) [W10] \=
G10: (S2) [W9] \=
F11: (S2) [W10] "E/R(AVG)=>
G11: (S2) [W9] @AVG(E/R)
A12: [W8] \=
B12: [W8] \=
C12: [W6] \=
D12: [W10] \=
E12: \=
F12: [W10] \=
G12: [W9] \=
A13: [W8] ^Mrkr
B13: [W8] ^Inc
D13: [W10] ^SD1
E13: (S2) ^SD2
F13: (S2) [W10] ^rctnordr
G13: [W9] ^E/R(2)
A14: [W8] \=
B14: [W8] \=
C14: [W6] \=
D14: [W10] \=
E14: (S2) \=
F14: (S2) [W10] \=
G14: [W9] \=
A15: [W8] 1
B15: [W8] 0.01
D15: (S2) [W10] @STD(E/R)
E15: (S2) 0.8494362672
F15: (S2) [W10] 0.50001
G15: (S2) [W9] 13999.934997
A17: [W8] '\a--}
B17: [W8] '{let mrkr,0}{let inc,.1}{let sd2,1E+11}{let n,.10001}^{paneloff}
A18: [W8] '\d--}
B18: [W8] '{goto}n^{let n,+n+inc}^
B19: [W8] '{if mrkr=1#and#+n-f15).1}{goto}a27^{quit}
B20: [W8] '{if +sd1<sd2}{let sd2,sd1}{let rctnordr,+n}{let g15,g11}
B21: [W8] '{if +c3>2}{branch \b}
B22: [W8] '{branch \d}
A24: [W8] '\b--}
B24: [W8] '{goto}n^{let n,+f15-inc}^
B25: [W8] '{goto}inc^{let inc,+inc/10}^
B26: [W8] '{let mrkr,1}{branch \d}
A28: [W8] \=
B28: [W8] \=
C28: [W6] \=
E28: \=
F28: [W10] \=
G28: [W9] \=
A29: [W8] "rctnordr=
C29: (F3) [W6] +RCTNORDR
D29: [W10] ^and
E29: "E=
F29: [W10] @INT(+ER2#2)
G29: [W9] 'cal/mol
A30: [W8] \=
B30: [W8] \=
C30: [W6] \=
E30: \=
F30: [W10] \=
G30: [W9] \=
```

TABLE 3.

Spreadsheet analysis of theoretical TG data (n=1) [9]

Alpha	T(K)	N	LHS1	Y	X	E/R
0.1001	726	1.100	-2.01E-08			
0.2669	762		-5.43E-08	-0.99314	-6.51E-05	1.53E+04
0.4019	780		-8.67E-08	-0.46767	-3.03E-05	1.54E+04
0.5087	792		-1.17E-07	-0.30343	-1.94E-05	1.56E+04
0.7333	816		-2.12E-07	-0.59173	-3.71E-05	1.59E+04
0.8313	828		-2.84E-07	-0.29183	-1.78E-05	1.64E+04
					E/R(AVG)=>1.57E+04	

Mrkr	Inc	SD1	SD2	rctnordr	E/R(2)
1	0.01	4.12E+02	4.24E+00	1.00E+00	1.51E+04

rctnordr=	1.000	and	E=	30209 cal/mol

In order to conserve space, Macro commands (which are similar to those in Tables 1 and 2) are not included in Tables 3–6. Table 3 portrays the final results for the spreadsheet analysis of another set of theoretical TG values (α–T(K)). Final results were determined to be $n = 1.00$ and $E = 30.2$ kcal mol^{-1} (ref. 9, 1 and 30).

TABLE 4.

Spreadsheet analysis of TG data for COX [7]

Alpha	T(K)	N	LHS1	Y	X	E/R
0.0200	423.2	1.140	-1.58E-08			
0.0750	443.2		-5.59E-08	-1.26209	-1.07E-04	1.18E+04
0.2050	463.2		-1.52E-07	-1.00167	-9.74E-05	1.03E+04
0.3050	473.2		-2.33E-07	-0.42795	-4.56E-05	9.38E+03
0.4420	483.2		-3.65E-07	-0.44585	-4.37E-05	1.02E+04
0.6070	493.2		-5.74E-07	-0.45455	-4.20E-05	1.08E+04
0.7730	503.2		-9.11E-07	-0.46163	-4.03E-05	1.15E+04
					E/R(AVG)=>1.07E+04	

Mrkr	Inc	SD1	SD2	rctnordr	E/R(2)
1	0.01	8.21E+02	7.88E+02	1.04E+00	1.04E+04

rctnordr=	1.040	and	E=	20780 cal/mol

TABLE 5.

Spreadsheet analysis of TG data for BDC [7]

Alpha	T(K)	N	LHS1	Y	X	E/R
0.038	306.3	1.120	-4.97E-08			
0.074	310.6		-9.61E-08	-0.65977	-4.52E-05	1.46E+04
0.123	314.9		-1.60E-07	-0.51060	-4.40E-05	1.16E+04
0.225	319.2		-3.05E-07	-0.64407	-4.28E-05	1.51E+04
0.386	323.5		-5.76E-07	-0.63629	-4.16E-05	1.53E+04
0.576	327.8		-1.01E-06	-0.56091	-4.05E-05	1.38E+04
0.769	332.1		-1.74E-06	-0.54643	-3.95E-05	1.38E+04
0.922	336.4		-3.17E-06	-0.59645	-3.85E-05	1.55E+04
					E/R(AVG)=>	1.42E+04

Mrkr	Inc	SD1	SD2	rctnordr	E/R(2)
1	0.01	1.24E+03	1.14E+03	1.02E+00	1.38E+04

rctnordr= 1.020 and E= 27557 cal/mol

A spreadsheet analysis of TG data for the dehydration of the monohydrate of COX is depicted in Table 4. Final values were determined to be $n = 1.04$ and $E = 20.8$ kcal mol^{-1} (ref. 7, 1.05 and 20.8). A spreadsheet analysis of DTA data for the decomposition of BDC in aqueous solution is shown in Table 5. From these α–T(K) values, the final values obtained were

TABLE 6.

Spreadsheet analysis of TG data for CAC [7]

Alpha	T(K)	N	LHS1	Y	X	E/R
0.0500	981.2	0.710	1.53E-08			
0.0750	1008.2		2.20E-08	-0.36050	-2.73E-05	1.32E+04
0.1600	1035.7		4.60E-08	-0.73715	-2.63E-05	2.80E+04
0.3150	1064.7		9.17E-08	-0.69028	-2.63E-05	2.62E+04
0.4850	1095.2		1.46E-07	-0.46507	-2.62E-05	1.78E+04
0.7400	1127.7		2.54E-07	-0.55524	-2.63E-05	2.11E+04
					E/R(AVG)=>	2.13E+04

Mrkr	Inc	SD1	SD2	rctnordr	E/R(2)
1	0.01	5.42E+03	5.41E+03	6.10E-01	2.08E+04

rctnordr= 0.610 and E= 41623 cal/mol

$n = 1.02$ and $E = 27.6$ kcal mol^{-1} (ref. 7, 1.05 and 27.8). Finally, an analysis of TG data for the decomposition of CAC is depicted in Table 6. Final values were determined to be $n = 0.61$ and $E = 41.6$ kcal mol^{-1} (ref. 7, 0.60 and 41.5).

TG data were also analyzed for TF and SB using spreadsheet analysis as previously indicated. Final values of n and E (kcal mol^{-1}) obtained for TF and SB were 0.98 and 65.6 and 0.82 and 24.2, respectively (ref. 8, 1.0 and 67 and 0.7 and 22).

From the preceding results it can be concluded that spreadsheet analysis of TG data for the estimation of kinetic parameters, as presented here, gives final values in good agreement with corresponding theoretical and reported values. This further supports previous recommendations [3,4] that spreadsheet analysis procedures be instituted to a greater extent in the field of thermal analysis whenever possible either as primary or corroborative methods.

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