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USE OF SPREADSHEETS IN THERMAL ANALYSIS. PART 4

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ABSTRACT

Recently, spreadsheet procedures were successfully utilized by the present author to ascertain the activation energy E and reaction order n, or E and the mechanism, from TG or DTA data.

In this paper, such procedures are applied, using another algorithm, to theoretical TG data, to TG data for magnesium hydroxide (MH) and finally to DTA data for benzenediazonium chloride in aqueous solution (BDC).

The aim of this paper is to popularize and extend the implementation of spreadsheets in thermal analysis.

INTRODUCTION

Recently [1–3], spreadsheet analysis was successfully applied to a range of materials in order to determine various kinetic parameters such as activation energy and reaction order, using various algorithms.

There are many advantages to the utilization of spreadsheets: they provide neat formats of data and results, and possess many desirable built-in functions. Some such functions, e.g. in the case of Lotus 2, are: summations, standard deviations, maximum and minimum values, single and multiple linear regression analysis, etc. An important development that spreadsheets subsequently provided (e.g. Lotus 2) was the use of macros. These allowed the automatic utilization of worksheets so that values such as kinetic parameters could be conveniently determined.

This paper is one of a series whose purpose is to popularize and extend the implementation of spreadsheets for the estimation of kinetic parameters from TG, DTA or DSC data.

THEORETICAL ASPECTS

In a previous publication [4], it was demonstrated how values of reaction order n could be obtained from TG (or DTA) data by means of a cubic

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expression (values of the activation energy E were not estimated). In that report

$$LH = \left[(1-\alpha_1)^n - (1-\alpha_1)\right] / \left[(1-\alpha_2)^n - (1-\alpha_2)\right] \tag{1}$$

where $LH = [(RT)_1/(RT)_2](T_1/T_2)^2$, $RT = d\alpha/dT$ and α is the degree of conversion. From eqn. (1), for various fixed values of α_1 and α_2, values of LH could be determined for various values of n. In this manner, the following 9 arbitrary ratios of α_1/α_2 were employed: 0.2/0.8, 0.2/0.9, 0.25/0.75, 0.3/0.6, 0.3/0.7, 0.3/0.8, 0.4/0.8, and 0.5/0.8, while the values of n were allowed to range from 0.1 to 2. Then the calculated values of LH and n were correlated via a cubic equation such as

$$n = A0 + A1(LH) + A2(LH)^2 + A3(LH)^3 \tag{2}$$

In the present paper, E will now also be estimated concurrently with n. Thus, after the average value of n has been determined from various α ratios, a value of E can be calculated from the following expression using a least-squares treatment

$$LHS \equiv LN(LHS1) = (-E/R)(1/T_1 - 1/T_2) \tag{3}$$

where $LHS1 = (T_2/T_1)^2[(1-(1-\alpha_1)^{1-n})/(1-(1-\alpha_2)^{1-n})]$.

RESULTS AND DISCUSSION

A spreadsheet analysis (using Lotus 1-2-3, Release 2) of BDC data [5] is depicted in Table 1. In this table, values of RT were obtained from the reported values of ΔT(in). For clarity, a 'range names table' has been included (columns L1 and M1). In this worksheet, RA denotes the α_1/α_2 ratio (to 2 decimal places, as a string), LH and LHS are as previously defined and ΔT(K) denotes the value of the last term in parenthesis in eqn. (3). For the various α_1/α_2 values (row 15), corresponding calculated n-values are summarized in cells H5–H10 under NVALS (NTABLE) and values for LHS and ΔT(K) are in cells I5–I10 and J5–J10, respectively. The n values were obtained from eqn. (2) using the expressions shown in rows G33–G40 (one of the two 0.50 ratios was not included). Then an average n value (0.98 ± 0.02) was obtained (using @AVG(NTABLE)). From this average n value, a value of E was next estimated using a linear regression analysis (the X-, Y- and output ranges were previously specified in row 26), see rows 30–37. In this manner, an X-coefficient (row 36) of -14276 was obtained which led to a final value of $E = 28.6$ kcal mol^{-1} (cf. literature values, of $n = 1$–1.1 and $E = 28$–30 [5–8]).

The spreadsheet analysis was extended to theoretical data [9] and to magnesium hydroxide, trace 1 (MH) [10]. In order to save space and to avoid duplication, the Macro and the equations in Table 1 were not included

TABLE 1

Spreadsheet analysis of BDC DTA data [5]

```
     A      B      C     D     E      F      G       H       I       J          K       L         M
1             CALCN. OF 'N' AND 'E' USING A CUBIC EQUATION                          RANGE NAMES TABLE
2 ========================================================================              0.22      G34
3                                                                                        0.25      G33
4 Alpha1 Alpha2  T1(K) T2(K)  RT1    RT2     LH     NVALS   LHS  Delta T(K)             0.33      G35
5   0.20   0.80  316.7 331.0  3.26   5.38 0.55472 1.0039 -1.874 0.000136                0.38      G38
6   0.30   0.70  319.8 328.8  4.41   6.20 0.67288 0.9375 -1.153 0.000085                0.43      G37
7   0.30   0.80  319.8 331.0  4.41   5.38 0.76516 0.9803 -1.426 0.000105                0.50      G36
8   0.40   0.70  322.2 328.8  5.41   6.20 0.83790 0.9639 -0.810 0.000062                0.57      G39
9   0.40   0.80  322.2 331.0  5.41   5.38 0.95281 1.0025 -1.083 0.000082                0.63      G40
10  0.50   0.80  324.5 331.0  6.02   5.38 1.07544 0.9978 -0.794 0.000060                   B      B20
11                                                                                          ER      C36
12                                                                                    FRESULTS      F28
13                                                                                           N      H29
14                                                                                      REGRES      A29
15 RA     0.25   0.43   0.38  0.57  0.50   0.63                                          TEMP      B40
16                                                                                          \A      B19
17                                                                                          \C      B26
18
19     \a {goto}a15~/rnlr~{goto}g4~/rnld.{r}~{d}{r}/rncntable~.{d 9}~{paneloff}
20      b {goto}{ra}~{if @cellpointer("type")="b"}/rndlh~/rndra~/rndnvals~/rndntable~{branch \c}
21        /c~temp~{goto}temp~{edit}{home}{del}+~
22        {goto}nvals~/rvtemp~~
23        {goto}ra~{r}/rndra~/rncra~~
24        {goto}nvals~{d}/rndnvals~/rncnvals~~{goto}lh~{d}/rndlh~/rnclh~~
25        {branch b}
26     \c {goto}i5~/drry.{end}{d}~{l}~{r}.{end}{d}~{r 2}~regres~g~
27        {home}{goto}fresults~{beep 4}{quit}
28 ==================================================================================
29        Regression Output:                   Avg n=  0.981     +/-    0.024
30 Constant              0.078                     E= 28553  cal/mol
31 Std Err of Y Est      0.011                 ==============================
32 R Squared             0.999
33 No. of Observations       6         0.25   -1.2147+5.8805*(lh)-4.2998*(lh)^2+1.6385*(lh)^3
34 Degrees of Freedom        4         0.22   -.55484+2.9658*($lh)-1.5047*($lh)^2+.36425*($lh)^3
35                                     0.33   -1.6883+6.28063*($lh)-4.06885*($lh)^2+1.47885*($lh)^3
36  X Coefficient(-14276               0.50   -1.5997+3.967*($lh)-1.7376*($lh)^2+0.4623*($lh)^3
37 Std Err of Coe173.03                0.43   -2.3594+7.0252*($lh)-4.1749*($lh)^2+1.51003*($lh)^3
38 =========================           0.38   -1.3615+4.4313*($lh)-2.3062*($lh)^2+0.67288*($lh)^3
39                                     0.57   -2.9409+6.8085*(lh)-3.634*(lh)^2+1.2772*(lh)^3
40 temp   0.9978                       0.63   -2.01+4.1452*($lh)-1.7912*($lh)^2+0.49977*($lh)^3
```

in Table 2 (theoretical data) or in Table 3 (MH). In Table 2, the values of *RT* were obtained by multiplying by 1000. From this table, the following values of n and E were obtained, respectively, 1.00 ± 0.005 and 30.2 kcal mol^{-1} (literature values [9], $n = 1$ and $E = 30$). Finally, in Table 3, the values of *RT* were obtained using a multiplication factor of 100. The following values of n and E were obtained for trace 1, 1.83 ± 0.05 and 62.6 kcal mol^{-1} (literature values [10], $n = 1.5$–1.7 and $E = 53$–57). From the preceding, the values of n and E obtained from spreadsheet analysis, using

TABLE 2

Spreadsheet analysis of theoretical NITG data [9]

CALCN. OF 'N' AND 'E' USING A CUBIC EQUATION

Alpha1	Alpha2	T1(K)	T2(K)	RT1	RT2	LH	NVALS	LHS	Delta T(K)
0.20	0.80	750.6	824.0	4.784	7.130	0.55675	1.0092	-1 792	0.000118
0.25	0.75	759.0	818.0	5.618	7.793	0.62066	0.9960	-1.425	0.000095
0.30	0.70	766.8	812.4	6.400	8.240	0.69195	1.0030	-1.102	0.000073
0.30	0.80	766.8	824.0	6.400	7.130	0.77732	1.0056	-1.365	0.000090
0.40	0.70	779.8	812.4	7.612	8.240	0.85113	1.0089	-0.776	0.000051
0.50	0.80	790.8	824.0	8.342	7.130	1.07760	1.0022	-0.762	0.000050

RA 0.25 0.33 0.43 0.38 0.57 0.63

Regression Output:

Constant	0.005	Avg n= 1.004 +/- 0.005
Std Err of Y Est	0.004	E= 30242 cal/mol
R Squared	0.999	
No. of Observations	6	
Degrees of Freedom	4	

X Coefficient(-15121

Std Err of Coe76.337

TABLE 3

Spreadsheet analysis of MH NITG data [10]

CALCN. OF 'N' AND 'E' USING A CUBIC EQUATION

Alpha1	Alpha2	T1(K)	T2(K)	RT1	RT2	LH	NVALS	LHS	Delta T(K)
0.25	0.75	651.0	679.6	1.407	1.337	0.96564	1.9140	-1.993	0.000064
0.30	0.60	654.5	670.6	1.590	1.836	0.82492	1.7421	-1.146	0.000036
0.30	0.70	654.5	676.4	1.590	1.567	0.95003	1.8414	-1.538	0.000049
0.40	0.70	659.5	676.4	1.795	1.567	1.08897	1.8132	-1.127	0.000037

RA 0.33 0.50 0.43 0.57

Regression Output:

Constant	0.025	Avg n= 1.83 +/- 0.06
Std Err of Y Est	0.031	E= 62633 cal/mol
R Squared	0.996	
No. of Observations	4	
Degrees of Freedom	2	

X Coefficient(-31316

Std Err of Coe1386.8

the previously mentioned algorithm, were in reasonably good agreement with reported values.

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