Thermochimica Acta, 138 (1989) 177–185
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

USE OF SPREADSHEETS IN THERMAL ANALYSIS. PART 2

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(Received 25 February 1988)

ABSTRACT

Many highly capable spreadsheets are now commercially available. They have found much use in various business applications such as business reports and as graphic generators. However, spreadsheets have been little employed in the field of thermal analysis.

The aim of this paper is to extend the utilization of spreadsheets to dynamic thermogravimetric analysis (TG) (as well as to similar techniques as differential scanning calorimetry) for the estimation of kinetic parameters and mechanism during the decomposition of various materials. To this end, various worksheets containing Macro commands were employed in this paper for the spreadsheet analysis of TG data. In this manner, analyses were carried out for the determination of the activation energy E and the mechanism, employing TG theoretical data and TG data for materials such as sodium bicarbonate. Final results are presented and compared with reported and theoretical results.

INTRODUCTION

There are many spreadsheets which have become commercially available in the past few years. Several such spreadsheets designed for the IBM and compatible computers are listed in the following: Lotus 1-2-3 (Lotus Development Corp., Cambridge, MA), Multiplan 3 (Microsoft Corp., Redmond, WA), PFS: Professional Plan 1 (Software Publishing Corp., Mountain View, CA), Planning Assistant 2 (IBM Corp.), PlanPerfect 3 (WordPerfect Corp., Orem, UT) and SuperCalc4 1 (Computer Associates International, Inc., San Jose, CA). The list prices of the preceding spreadsheets vary from $195 to 495. Some less expensive and less extensive spreadsheets are: The Twin Classic (Mosaic Software Inc., Cambridge, MA), VP-Planner 1.34 (Paperback Software Inc., Berkeley, CA) and Words & Figures 1 (Lifetree Software Inc., Monterey, CA) whose list prices are generally ca. $100. Recent reviews of the capabilities of the above spreadsheets have been presented [1,2].

Spreadsheets have been employed in the preparation of business reports, modeling, forecasting, as small database managers, as graphics generators and in electronic circuit simulation. However, they have been little utilized

0040-6031/89/$03.50

TABLE 1

Spreadsheet analysis of theoretical data (R2) [5]

```
     A         B      C         D          E        F        G       H
 1  Alpha     T(K)    Y         X                   Regression Output:
 2  0.4411     420                       Constant                   -3.3940
 3  0.1319     405 -6.0830 0.000088 Std Err of Y Est               0.08489
 4  0.2020     410 -5.2018 0.000058 R Squared                      0.99868
 5  0.3026     415 -4.3332 0.000028 No. of Observations                  6
 6  0.6187     425 -2.6066 -0.00002 Degrees of Freedom                   4
 7  0.8188     430 -1.7158 -0.00005
 8  0.9788     435 -0.7182 -0.00008 X Coefficient(s) -31189.4
 9 ================================Std Err of Coef. 565.3897
10                                  ================================
11
12                                                i====>     10
13
14      \a {paneloff}{home}/remech~{let c,0}~
15         {goto}d3~(1/b3)-(1/$b$2)~/c~{d}.{end}{d}{u}~
16         {for i,0,9,1,getequ}
17         {branch proc}
18
19  getequ {let $xt5,+$B$2}~{let c3,+@index(list,0,i)}{goto}c3~
20        ~{edit}{home}{r}{bs}~/c~{d}.{end}{d}{u}~
21         /drg
22         {let diff,@abs((@index(values,0,i)-$h$2)/$h$2)}~
23         {put results,0,i,+diff}~{put results,1,i,-$g$8/500}~
24         {put results,2,i,+$h$4}~
25
26    proc {goto}a41~{goto}results~
27      \b {if @cellpointer("contents")/@min(delta)<1.03}{branch sub}
28      \c {d}{if @cellpointer("type")<>"b"}{branch \b}
29
30     sub {r 3}{let z,@cellpointer("contents")}~{put mech,0,c,+z}~
31         {l 2}{let z1,@cellpointer("contents")}~{put mech,1,c,+z1}~
32         {let c,c+1}~{l 1}{branch \c}
33
34    List @ln(($xt5/b3)^2*(-@ln(1-a3))^.25)
35         @ln(($xt5/b3)^2*(-@ln(1-a3))^.33)
36         @ln(($xt5/b3)^2*(-@ln(1-a3))^.5)
37         @ln(($xt5/b3)^2*(1-(1-a3)^.5))
38         @ln(($xt5/b3)^2*(1-(1-a3)^(1/3)))
39         @ln(($xt5/b3)^2*(-@ln(1-a3)))
40         @ln(($xt5/b3)^2*(a3)^2)
41         @ln(($B$2/B3)^2*(A3+(1-A3)*@ln(1-A3)))
42         @ln(($B$2/B3)^2*(1-(2*A3/3)-(1-A3)^(2/3)))
43         @ln(($B$2/B3)^2*(1-(1-A3)^(1/3))^2)
```

TABLE 1 (continued)

44						
45	values -0.13545		Diff	E(K/M)	r^2	Mechnsm
46	-0.18060		==========	==========	==========	==========
47	-0.27090	results	0.32381533	7.71	0.982745	A4
48	-1.37685		0.33928550	10.72	0.984305	A3
49	-1.73580		0.32910695	17.10	0.985733	A2
50	-0.54180		0.00000264	27.99	0.999999	R2
51	-1.63719		0.02266640	30.35	0.998630	R3
52	-2.15492		0.33026321	35.88	0.986934	F1
53	-3.59661		0.09223238	46.36	0.991240	D1
54	-3.47160		0.03517788	52.86	0.998158	D2
55			0.00810027	55.91	0.999748	D4
56			0.02286565	62.37	0.998687	D3
57						
58	###Prob. mech. & E======>		R2	28.0	Kcal/Mol	
59						

in the field of thermal analysis. Recently, Multiplan and Lotus 1-2-3 were employed for the estimation of the kinetic parameters, activation energy E and reaction order n, during the decomposition of various materials by means of dynamic thermogravimetric analysis (TG). This procedure was successfully applied to theoretical data, benzenediazonium chloride, Teflon, magnesium hydroxide, calcium oxalate monohydrate and sodium bicarbonate [3,4]. It was easier to apply Lotus rather than Multiplan since the former possessed many Macro commands whereas the latter did not possess any.

The aim of the present paper is to extend the use of spreadsheets in the analysis of TG (or differential scanning calorimetry) data for the estimation of E and mechanism.

THEORETICAL ASPECTS

It was previously shown [5] that

$$\ln\left[g(\alpha)(T*/T)^2\right] = \ln\left[g(\alpha*)\right] - (E/R)\left[(1/T) - (1/T*)\right] \quad (1)$$

where $g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$, α is conversion and $T*$ is an arbitrarily selected reference temperature(K) at conversion $\alpha*$. For each of the ten different possible decomposition mechanisms employed, the corresponding slope and intercept of eqn. (1) can be obtained from TG data using a least-squares treatment. Then the mechanism whose intercept value affords the smallest

deviation from the corresponding theoretical value of $\ln[g(\alpha*)]$ was considered to be the most probable mechanism. The corresponding E value could also then be obtained from the value of the slope.

RESULTS AND DISCUSSION

The spreadsheet employed in this paper was Lotus 1-2-3, release 2, which is capable of employing many advanced Macro commands (ca. 40). This spreadsheet appears to be the standard by which others are measured, and is considered to be the world's most popular applications program (it sold more than 3 million copies in the second quarter of 1987 alone [2]). It can be used to handle complex mathematical models via its powerful built-in Macro language, and was applied in this paper to theoretical TG data as well as to TG data for sodium bicarbonate (SB) and TG data reported by Szako [6].

Table 1 depicts a spreadsheet analysis of theoretical TG data [5,7] wherein a final value of $E = 28.0$ kcal mol^{-1} and an R2 mechanism were obtained (theoretically 28 and R2), cf. row 58. In this table, values of α and T are given in the first 2 columns (A and B). In column C, Y represents the left-hand-side of eqn. (1) while in column D X denotes the last term in eqn. (1) $(1/T - 1/T*)$. The linear regression output (columns E–H) represent values for $i = 10$ (the last mechanism in "List" (B43)). The ten mechanisms tested are given in cells B34–B43. Theoretical values of $\ln[g(\alpha*)]$ at $T* = 420$ K and $\alpha* = 0.4411$ (A2 and B2) are depicted for the various mechanisms in cells B45–B54. Results are summarized in rows 47–56 wherein values of E, the square of the correlation coefficient, and "Diff" are presented for the various mechanisms tested. "Diff" is a function of the absolute difference between theoretical and calculated (the "Constant" in cell H2) values of intercept. Thus, for example, for the D3-mechanism Diff is equal to $(3.4716-3.3940)/3.3940 = 0.02286$ (cf. cells B22 and E56). After the results were automatically compiled, the subroutine "proc" (row 26) processed these results to obtain the most probable mechanism (MPM) and the corresponding value of E. The MPM was restricted to those values of [Diff/(minimum value of Diff obtained)] which were less than 1.03 (cf. cell B27). The linear regression output was obtained via the Macro command in B21 (the X, Y and output ranges had been previously designated). The E values were obtained from the values shown in cell G8. It may also be noted here that the r^2 value for the R2 mechanism was closest to unity.

In order to conserve space, Macro commands (which are similar to those in Table 1) have not been included in Tables 2–4. Table 2 portrays final results for the spreadsheet analysis of another set of theoretical TG values [α – T(K)] [5]. Final results were determined to be: $E = 29.9$ kcal mol^{-1} and mechanism D3 (theoretically 30 and D3). Again the r^2 value of the MPM

TABLE 2

Spreadsheet analysis of theoretical data (D3) [5]

Alpha	T(K)	Y	X	Regression Output:	
0.3910	720			Constant	-3.7636
0.0720	620	-7.1118	0.000224	Std Err of Y Est	0.00057
0.1070	640	-6.3580	0.000173	R Squared	1.00000
0.1544	660	-5.6500	0.000126	No. of Observations	10
0.2166	680	-4.9839	0.000081	Degrees of Freedom	8
0.2953	700	-4.3559	0.000039		
0.5019	740	-3.2021	-0.00003	X Coefficient(s)	-14942.6
0.6231	760	-2.6709	-0.00007	Std Err of Coef.	1.3823
0.7459	780	-2.1671	-0.00010		
0.8575	800	-1.6886	-0.00013		
0.9428	820	-1.2334	-0.00016	i====>	10.0000

values			Diff	E(K/M)	r^2	Mechnsm
	-0.17533					
	-0.23378					
	-0.35067	results	0.059269	1.71	0.99199	A4
	-1.51591		0.083395	3.17	0.99469	A3
	-1.88147		0.087054	6.27	0.99597	A2
	-0.70134		0.022038	12.68	0.99879	R2
	-1.87815		0.002412	13.52	0.99998	R3
	-2.41946		0.101501	15.39	0.99664	F1
	-3.87005		0.096766	23.87	0.98891	D1
	-3.76293		0.047363	26.48	0.99640	D2
			0.020862	27.59	0.99845	D4
			0.000169	29.89	1.00000	D3

***Prob. mech.& E=======> D3 29.9 Kcal/Mol

TABLE 3

Spreadsheet analysis of $NaHCO_3$ TG data [5]

Alpha	T(K)	Y	X	Regression Output:	
0.528	423.2			Constant	-3.0457
0.208	408.2	-5.1140	0.000086	Std Err of Y Est	0.04578
0.300	413.2	-4.3289	0.000057	R Squared	0.99928
0.403	418.2	-3.6668	0.000028	No. of Observations	6
0.667	428.2	-2.3861	-0.00002	Degrees of Freedom	4
0.806	433.2	-1.7764	-0.00005		
0.917	438.2	-1.2157	-0.00008	X Coefficient(s)	-23117.3
				Std Err of Coef.	309.5622

i====> 10

values			Diff	E(K/M)	r^2	Mechnsm
	-0.07166					
	-0.09554					
	-0.14332	results	0.12109697	5.28	0.998705	A4
	-1.16162		0.13522531	7.51	0.998852	A3
	-1.50778		0.12683775	12.25	0.998979	A2
	-0.28664		0.02957771	20.52	0.997308	R2
	-1.27731		0.01012770	22.27	0.999210	R3
	-1.75080		0.12973025	26.18	0.999080	F1
	-3.17526		0.11095399	33.81	0.985285	D1
	-3.01556		0.06018413	39.12	0.993766	D2
			0.02632198	41.44	0.996415	D4
			0.00991602	46.23	0.999283	D3

***Prob. mech. & E======> R3 22.27 Kcal/Mol
D3 46.23

TABLE 4

Spreadsheet analysis of Szako data [5]

Alpha	T(K)	Y	X		
0.1910	453.2			Regression Output:	
0.0112	413.2	-10.982	0.000213	Constant	-5.4942
0.0224	423.2	-9.6361	0.000156	Std Err of Y Est	0.27829
0.0393	433.2	-8.5520	0.000101	R Squared	0.99558
0.0786	443.2	-7.1839	0.000049	No. of Observations	8
0.3427	463.2	-4.1159	-0.00004	Degrees of Freedom	6
0.5842	473.2	-2.8298	-0.00009	X Coefficient(s)	-26946.0
0.8764	483.2	-1.5070	-0.00013	Std Err of Coef.	732.9044
0.9719	493.2	-0.8939	-0.00017		

i====> 10

values			Diff	E(K/M)	r^2	Mechnsm
	-0.38784					
	-0.51712					
	-0.77568	results	0.02457499	5.73	0.990664	A4
	-2.29704		0.03734731	8.14	0.991686	A3
	-2.68510		0.02953495	13.26	0.992572	A2
	-1.55137		0.04645394	25.04	0.994494	R2
	-3.31096		0.02322670	26.04	0.995308	R3
	-3.93594		0.03203299	28.32	0.993282	F1
	-5.41675		0.12038323	46.91	0.988656	D1
	-5.37021		0.07502585	49.85	0.992795	D2
			0.04517823	51.16	0.994230	D4
			0.02257827	53.89	0.995580	D3

***Prob. mech.& E=======> R3 26.0 Kcal/Mol

D3 53.9

was closest to unity. The arbitrarily chosen reference values for $T*$ and $\alpha*$ were 720 and 0.3910, respectively.

A worksheet analysis of TG data for the decomposition of SB is depicted in Table 3. Contrary to the theoretical TG data in Tables 1 and 2, the TG data for SB afforded 2 sets of results for E and mechanism. Although values of Diff for D3 and R3 were different, this difference was considered too small to be significant. Thus, the following results were obtained: $E = 22.3$ kcal mol^{-1} for an R3 mechanism and $E = 46.2$ kcal mol^{-1} for a D3 mechanism. These results are in excellent agreement with those previously obtained [5].

Finally, a worksheet analysis of TG data obtained by Szako [6] is shown in Table 4. As in the case for Table 3 data, 2 sets of results for E and mechanism were obtained. Again, although values of Diff for D3 and R3 were different, this difference was considered too small to be significant. The following results were obtained: $E = 26.0$ kcal mol^{-1} for an R3 mechanism and $E = 53.9$ kcal mol^{-1} for a D3 mechanism, which are in excellent agreement with those previously reported [5].

FINAL REMARKS

Although Macros allow the automatic utilization of spreadsheets, final results of analyses may also be readily obtained using manual and automatic procedures in tandem. Further, while spreadsheet analysis may be slower when compared with a similar analysis via computer programming, it possesses certain salient advantages. Thus, it can provide neat formats of data and results and provide many automatic functions, such as for summations, standard deviations, sorting, data regression, graphics, etc. One of its best features is that it allows the user to observe various derived intermediate and final results in tabular form at a glance during analysis. Also, from the preceding, the spreadsheet worksheets presented for the estimation of kinetic parameters (and mechanism) can yield final values from TG data in satisfactory agreement with corresponding theoretical and reported values. Thus, it is highly recommended that spreadsheet procedures be utilized to a greater extent in the field of thermal analysis whenever possible either as primary or secondary methods.

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