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Use of databases in thermal analysis. Part 3

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Abstract

Spreadsheet analysis (SHTS) of TG (and DTA) data has been employed by the present author to satisfactorily determine kinetic parameters such as activation energy (E) and reaction order (n), as well as mechanism.

Many of the functions used in the macros for SHTS were found to have counterparts in relational database managers. Thus, the PARADOX 3 manager was utilized to determine a "most probable mechanism" (MPM) from among 10 possible decomposition mechanisms using TG data, as well as the corresponding value of E. Database analysis was carried out on theoretical and experimental data employing a previously described algorithm.

INTRODUCTION

The present author has employed spreadsheet analysis (SHTS) extensively, using LOTUS 1-2-3 version 2.2, to satisfactorily determine kinetic parameters (activation energy (E) and reaction order (n)) and mechanism from TG and DTA data [1–6].

Many of the functions utilized in the macros for SHTS were found to have counterparts in relational database managers (DBs). Thus, PARADOX 3 (Borland International) was employed to ascertain E and n from TG data [7,8]. However, in contrast to SHTS, data used in DBs are restricted primarily to tables and forms, whereas in SHTS they may be placed in any of thousands of cells (restricted only by the size of the computer memory).

In view of the preceding, a DB script was recently used by the present author (vis-à-vis macros employed in SHTS) to determine values of kinetic parameters from isothermal TG data [7] and non-isothermal TG data (NITG) [8]. The versatile PARADOX 3 DB was utilized because it possesses the Paradox Application Language (PAL) which can be employed to write scripts relevant to the determination of kinetic parameters from TG data.

The aim of this paper is to continue the utilization of the PARADOX 3 DB and to determine a "most probable mechanism" (MPM) using TG data. To this end, DB analysis of NITG data for sodium bicarbonate and of NITG

data reported by Szako was carried out, together with a similar analysis for theoretical NITG data.

THEORETICAL ASPECTS

It was previously shown [2,9] that

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

where $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$, α = degree of conversion and $T*$ is an arbitrarily selected reference temperature (K) at conversion $\alpha*$. For each of the 10 different possible decomposition mechanisms employed (see the "zmechx" script, Appendix 2), the corresponding slope and intercept values of eqn. (1) obtained from NITG data were analysed using a least-squares (LSQ) treatment. Then the mechanism(s) whose intercept value affords the smallest deviation from the corresponding calculated value of $\ln(g(\alpha*))$, based on the reference values of $T*$ and $\alpha*$, was considered to be the MPM. The corresponding E value could then also be obtained from the value of the slope.

RESULTS AND DISCUSSION

For the sake of convenience, the database analysis of NITG data was carried out employing 2 tables (A and B) for each set of data used, to ascertain the MPM out of 10 possible mechanisms. Thus, for example, in the analysis of the theoretical NITG data (R2 mechanism), Tables 1A and 1B were utilized. Given values of α and temperature (K) were entered into Table 1A and arbitrary reference values were entered into Table 1B (also as α and T(K)).

Equation (1) may be written symbolically as

$$Y = A1 + A2X \quad (2)$$

TABLE 1A

Database analysis of theoretical data (R2)

α	T (K)	Y	X
0.1319	405	−6.0831	0.00008818
0.2020	410	−5.2013	0.00005807
0.3026	415	−4.3333	0.00002869
0.6187	425	−2.6067	−0.00002801
0.8188	430	−1.7159	−0.00005537
0.9788	435	−0.7182	−0.00008210

TABLE 1B

Database analysis of theoretical data (R2)

α	T (K)	Theor$A$1	Diff	E	Mechnsm
0.4411	420	−0.13541	0.323565	7.7	A4
0.4411	420	−0.18055	0.325707	10.8	A3
0.4411	420	−0.27083	0.327856	17.1	A2
0.4411	420	−1.37672	0.000072	28.0	R2 [a]
0.4411	420	−1.73566	0.022607	30.3	R3
0.4411	420	−0.54165	0.330012	35.9	F1
0.4411	420	−1.63697	0.092323	46.4	D1
0.4411	420	−2.15468	0.035259	52.9	D2
0.4411	420	−3.59635	0.008152	55.9	D4
0.4411	420	−3.47133	0.022806	62.4	D3

[a] The MPM is R2 with $E = 28.0$ kcal mol^{-1}.

TABLE 2A

Database analysis of sodium bicarbonate data

α	T (K)	Y	X
0.2080	408	−5.1140	0.00008683
0.3000	413	−4.3290	0.00005719
0.4030	418	−3.6669	0.00002825
0.6670	428	−2.3862	−0.00002759
0.8060	433	−1.7765	−0.00005455
0.9170	438	−1.2158	−0.00008089

TABLE 2B

Database analysis of sodium bicarbonate data

α	T (K)	Theor$A$1	Diff	E	Mechnsm
0.5280	423.2	−0.07166	0.121097	5.3	A4
0.5280	423.2	−0.09555	0.123960	7.6	A3
0.5280	423.2	−0.14332	0.126838	12.2	A2
0.5280	423.2	−1.16162	0.029578	20.5	R2
0.5280	423.2	−1.50778	0.010128	22.3	R3 [a]
0.5280	423.2	−0.28665	0.129730	26.2	F1
0.5280	423.2	−1.27732	0.110954	33.8	D1
0.5280	423.2	−1.75081	0.060184	39.1	D2
0.5280	423.2	−3.17526	0.026322	41.4	D4
0.5280	423.2	−3.01556	0.009916	46.2	D3 [b]

[a] The MPM is R3 with $E = 22.3$ kcal mol^{-1}.
[b] The MPM is D3 with $E = 46.2$ kcal mol^{-1}.

TABLE 3A

Database analysis of theoretical data (D3)

α	T (K)	Y	X
0.0720	620	−7.1109	0.00022401
0.1070	640	−6.3570	0.00017361
0.1544	660	−5.6499	0.00012626
0.2166	680	−4.9840	0.00008170
0.2953	700	−4.3562	0.00003968
0.5019	740	−3.2019	−0.00003754
0.6231	760	−2.6709	−0.00007310
0.7459	780	−2.1670	−0.00010684
0.8575	800	−1.6884	−0.00013889
0.9428	820	−1.2333	−0.00016938

TABLE 3B

Database analysis of theoretical data (D3)

α	T (K)	Theor $A1$	Diff	E	Mechnsm
0.3910	720.0	−0.17533	0.059411	1.7	A4
0.3910	720.0	−0.23377	0.073128	3.2	A3
0.3910	720.0	−0.35065	0.087205	6.3	A2
0.3910	720.0	−1.51588	0.021992	12.7	R2
0.3910	720.0	−1.88144	0.002371	13.5	R3
0.3910	720.0	−0.70131	0.101657	15.4	F1
0.3910	720.0	−1.87810	0.096712	23.9	D1
0.3910	720.0	−2.41941	0.047811	26.5	D2
0.3910	720.0	−3.86999	0.020827	27.6	D4
0.3910	720.0	−3.76287	0.000128	29.9	D3 [a]

[a] The MPM is D3 with $E = 29.9$ kcal mol^{-1}.

TABLE 4A

Database analysis of Szako data [11]

α	T (K)	Y	X
0.0112	413	−10.9886	0.00021360
0.0224	423	−9.6426	0.00015642
0.0393	433	−8.5534	0.00010187
0.0786	443	−7.1853	0.00004979
0.3427	463	−4.1160	−0.00004764
0.5842	473	−2.8302	−0.00009326
0.8764	483	−1.5070	−0.00013699
0.9719	493	−0.8940	−0.00017896

TABLE 4B

Database analysis of Szako data [11]

α	T (K)	Theor$A1$	Diff	E	Mechnsm
0.1910	453.2	−0.38784	0.023933	5.7	A4
0.1910	453.2	−0.51712	0.026404	8.2	A3
0.1910	453.2	−0.77569	0.028887	13.3	A2
0.1910	453.2	−2.29704	0.046822	25.1	R2
0.1910	453.2	−2.68511	0.023559	26.1	R3 [a]
0.1910	453.2	−1.55137	0.031382	28.3	F1
0.1910	453.2	−3.31096	0.120811	46.9	D1
0.1910	453.2	−3.93594	0.075427	49.9	D2
0.1910	453.2	−5.41675	0.045490	51.2	D4
0.1910	453.2	−5.37021	0.022911	53.9	D3 [b]

[a] The MPM is R3 with $E = 26.1$ kcal mol^{-1}.
[b] The MPM is D3 with $E = 53.9$ kcal mol^{-1}.

TABLE 5A

Database analysis of theoretical data (A3)

α	T (K)	Y	X
0.0528	810	−7.9860	0.00003553
0.1091	820	−6.5193	0.00002047
0.1884	828	−5.3854	0.00000869
0.3918	840	−3.7723	−0.00000856
0.5327	846	−3.0210	−0.00001701
0.6857	852	−2.3212	−0.00002533
0.8264	858	−1.6891	−0.00003354
0.9282	864	−1.1450	−0.00004163
0.9806	870	−0.7105	−0.00004962

TABLE 5B

Database analysis of theoretical data (A3)

α	T (K)	Theor$A1$	Diff	E	Mechnsm
0.2761	834.0	−0.28244	0.000437	21.8	A4
0.2761	834.0	−0.37658	0.000004	30.2	A3 [a]
0.2761	834.0	−0.56487	0.000445	47.0	A2
0.2761	834.0	−1.90258	0.045245	80.0	R2
0.2761	834.0	−2.28173	0.026811	85.2	R3
0.2761	834.0	−1.12974	0.000886	97.3	F1
0.2761	834.0	−2.57391	0.107842	138.1	D1
0.2761	834.0	−3.16511	0.069480	152.8	D2
0.2761	834.0	−4.63395	0.041469	159.6	D4
0.2761	834.0	−4.56345	0.026708	173.8	D3

[a] The MPM is A3 with $E = 30.2$ kcal mol^{-1}.

TABLE 6A

Database analysis of theoretical data (D2)

α	T (K)	Y	X
0.0577	614	−7.6064	0.00019600
0.1194	650	−6.2217	0.00010580
0.1664	668	−5.5778	0.00006434
0.3336	710	−4.1684	−0.00002421
0.4728	734	−3.3996	−0.00007027
0.5988	752	−2.8245	−0.00010288
0.7399	770	−2.2306	−0.00013396
0.8861	788	−1.5689	−0.00016363
0.9735	800	−0.9804	−0.00018266

where Y is the left-hand-side of eqn. (1), $X = (1/T) - (1/T*)$ and $A1 = \ln(g(\alpha*))$. Calculated values of Y and X for each pair of $\alpha - T$(K) values were automatically entered into the A tables employing the scripts in Appendices 1 and 2, "zmech" and "zmechx", respectively (see lines 25–29 in Appendix 1). In the determination of Y values, an array, arr, of size 10 was utilized to represent each of the 10 possible mechanisms (see Appendix 2). In Appendix 1, it was necessary to insert the reference values which were also depicted as αi and ti (see line 11 of Appendix 1; the particular reference values given applied to Tables 4A and 4B). Further, in the listings, $z = (ti) * (ti)$ and the value of p denotes the number of data pairs used (excluding the reference values) (see lines 9–11 in Appendix 1). In the B tables, the values of $A1$ based on the values selected for $\alpha* - T*$ were calculated and entered under field "Theor$A1$" (see lines 15–19 of Appendix 1).

TABLE 6B

Database analysis of theoretical data (D2)

α	T (K)	Theor$A1$	Diff	E	Mechnsm
0.2765	698.0	−0.28203	0.107311	2.4	A4
0.2765	698.0	−0.37604	0.116025	4.1	A3
0.2765	698.0	−0.56406	0.124877	7.5	A2
0.2765	698.0	−1.90109	0.015259	14.7	R2
0.2765	698.0	−2.28019	0.027035	15.7	R3
0.2765	698.0	−1.12812	0.133871	17.9	F1
0.2765	698.0	−2.57116	0.032900	27.3	D1
0.2765	698.0	−3.16220	0.000026	30.2	D2 [a]
0.2765	698.0	−4.63099	0.009021	31.5	D4
0.2765	698.0	−4.56038	0.028878	34.1	D3

[a] The MPM is D2 with $E = 30.2$ kcal mol^{-1}.

LSQ was applied to the values obtained for Y and X to yield values for A1 and E (kcal mol^{-1}) from the value of $A2$ (see lines 31 and 32 in Appendix 1). Also, the value of "Diff" could then be estimated as the absolute value of $(A1\text{–Theor}A1)/A1$ (see lines 35 and 36 in Appendix 1 and the B tables). The smallest value of Diff from among the 10 mechanisms afforded the MPM. Thus, from Table 1B, the MPM was found to be R2 with $E = 28.0$ kcal mol^{-1} (R2 and 28, theoretically). As will be seen subsequently, by means of this algorithm, more than 1 mechanism can be the MPM. The MPM was restricted to those values of (Diff/(minimum value of Diff obtained)) which were in the range 1.00–1.03 (see line 41 of Appendix 1). From the theoretical data utilized in Tables 1, 3, 5 and 6 it was observed that the results obtained are in excellent agreement with theoretical values of E and mechanism. Thus, the theoretical data in Tables 5 and 6 [10] afforded the following values of E and mechanism, respectively: 30.2 and A3; 30.2 and D2, in very good agreement with anticipated values. Similar remarks apply to the theoretical data [9] in Table 3. However, when experimental values were employed, as in Tables 2 and 4, for sodium bicarbonate [9] and for data provided by Szako [11], respectively, more than 1 mechanism was found to be possible. Thus, for example, in the case of sodium bicarbonate, mechanisms R3 with $E = 22.3$ kcal mol^{-1} and D3 with $E = 46.2$ kcal mol^{-1} were found to be MPMs. Similarly, for the data in Table 4, mechanisms R3 with $E = 26.1$ kcal mol^{-1} and D3 with $E = 53.9$ kcal mol^{-1} were found to be MPMs. These results are in excellent agreement with results observed using SHTS [9], and may have been obtained due to the greater accuracy required than was possible for the experimental data. Nevertheless, from the preceding, the database analysis reported herein can be employed as a corroborative or possibly a primary method [12].

REFERENCES

1 L.S. Reich and S.H. Patel, Am. Lab., 19(9) (1987) 23.
2 L. Reich, Thermochim. Acta, 138 (1989) 177.
3 L. Reich, Thermochim. Acta, 141 (1989) 311.
4 L. Reich, Thermochim. Acta, 164 (1990) 1.
5 L. Reich, Thermochim. Acta, 164 (1990) 7.
6 L. Reich, Thermochim. Acta, 173 (1990) 253.
7 L. Reich, Thermochim. Acta, 180 (1991) 303.
8 L. Reich, Thermochim. Acta, 185 (1991) 205.
9 L. Reich and S.S. Stivala, Thermochim. Acta, 75 (1984) 405.
10 K. Böhme, S. Boy, K. Heide and W. Höland, Thermochim. Acta, 23 (1978) 17.
11 J. Szako, J. Phys. Chem., 72 (1968) 2405.
12 L. Reich, S.H. Patel and S.S. Stivala, Thermochim. Acta, 138 (1989) 147.

APPENDIX 1

Database analysis of NITG data to ascertain the MPM from among 10 mechanisms listed in Appendix 2.

```
                                        Script: D:\pdx3\sample\zmech

; Database analysis of data to ascertain the most probable
; mechanism (MPM) from among 10 possible mechanisms

clear
View "zmech1"   ; table containing initial values
View "zmech2"   ; table containing final values
Editkey
array arr[10]
n=0  p=8
; p=number of data pairs used (excluding ref. values)
ti=453.2 ai=.191 z=ti*ti ; these particular ref. values, ti and ai, are for
                         ; certain data (Table A), and such values are to be
                         ; placed here and also in the final values table (B)

Scan
Play "zmechx"
n=n+1
[TheorA1]=arr[n]         ; calc theoretical intercepts
Endscan

For n From 1 To 10    ; 10 possible mechanisms used
sx=0 sy=0 sxx=0 sxy=0
Upimage
@5,2 ?? "The current mechnsm. being used = ",n," out of 10"
Scan
Play "zmechx"     ; subroutine containing 10 mechnsms.
[Y]=arr[n]  [X]=(1/[TK])-(1/ti) ; calc initial table values
sx=sx+[x] sy=sy+[y] sxx=sxx+[x]*[x] sxy=sxy+[x]*[y]
Endscan

A2=(p*sxy-sx*sy)/(p*sxx-(sx)*(sx))
A1=(sy/p)-A2*(sx/p)
Downimage
Moveto record n
[E]= -A2*2/1000        ; calc final table values
[Diff]=Abs((A1-[TheorA1])/A1)
Endfor
; --------- determine final values --------------
Clear
minval=Cmin("zmech2","Diff")
Scan For (([Diff]/minval)>=1 And ([Diff]/minval)<1.03)
? "The MPM is ",[Mechnsm]," with E= ",Format("W5.1",[E])," kcal/mol"
Endscan
Sleep 10000
Do_It!
```

APPENDIX 2

Subroutine listing 10 possible mechanisms to be used with Appendix 1.

Script: D:\pdx3\sample\zmechx

```
; subroutine lists 10 possible mechanisms,
; and is to be used with 'zmech'

arr[1]=Ln((z/([TK]*[TK]))*(pow(-Ln(1-[Alpha]),.25)))                    ; A4

arr[2]=Ln((z/([TK]*[TK]))*(pow(-Ln(1-[Alpha]),(1/3))))                  ; A3

arr[3]=Ln((z/([TK]*[TK]))*(pow(-Ln(1-[Alpha]),.5)))                     ; A2

arr[4]=Ln(z)+Ln((1-pow((1-[Alpha]),.5))/([TK]*[TK]))                    ; R2

arr[5]=Ln(z)+Ln((1-pow((1-[Alpha]),(1/3)))/([TK]*[TK]))                 ; R3

arr[6]=Ln((z/([TK]*[TK]))*(pow(-Ln(1-[Alpha]),1)))                      ; F1

arr[7]=Ln((z/([TK]*[TK]))*(pow([Alpha],2)))                             ; D1

arr[8]=Ln((z/([TK]*[TK]))*([Alpha]+(1-[Alpha])*Ln(1-[Alpha])))          ; D2

arr[9]=Ln((z/([TK]*[TK]))*(1-(2*[Alpha]/3)-pow((1-[Alpha]),(2/3))))     ; D4

arr[10]=Ln(z/([TK]*[TK]))+2*LN((1-pow((1-[Alpha]),(1/3))))              ; D3

return
```