Thermochimica Acta, 185 (1991) 205–210
Elsevier Science Publishers B.V., Amsterdam

Use of databases in thermal analysis. Part 2

Leo Reich

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030 (USA)

(Received 20 November 1990)

Abstract

A powerful relational database manager (DB), Paradox 3.0, was previously applied satisfactorily by the author to ascertain values of reaction order (n) and rate constant (k) from isothermal TG (ITG) data. This DB possessed an extensive Paradox Application Language (PAL) which could be utilized to write scripts pertaining to the determination of kinetic parameters from TG data.

The aim of this paper is to extend the application of DBs such as Paradox 3.0 to thermal analysis. Thus, PAL was employed to write a script (just as macros in spreadsheets were previously written and used in thermal analysis by the author) to determine values of n and activation energy (E) from non-isothermal TG (NITG) data. In this regard, a PAL script was written and applied to theoretical NITG data as well as to NITG data for calcium oxalate monohydrate, calcium carbonate, teflon and benzenediazonium chloride.

INTRODUCTION

Many spreadsheets (SHTS) have recently become commercially available for microcomputers (see ref. 1 for a listing). There are various built-in functions in SHTS which could be employed in the determination of kinetic parameters from TG data such as rate constant (k), reaction order (n) and activation energy (E). Some such functions (in the case of Lotus 2) are summation, standard deviation, single and multiple regression analysis, etc.

Because of the availability of such functions, the present author has, in the recent past, employed SHTS to estimate n and E from TG (and DTA) data [2–6]. Macros were used which allowed for the automatic utilization of TG data in worksheets for the determination of these kinetic parameters, whose values were found to be in satisfactory agreement with previously reported results.

In addition, various commercial programs for microcomputers (primarily for business purposes) which can be utilized to manage databases (DBs) have also recently become available (see ref. 7 for a listing). Such relational DB managers can provide, similar to the case of SHTS, various functions,

0040-6031/91/$03.50 © 1991 – Elsevier Science Publishers B.V.

such as those that are mathematical, statistical, financial, etc. However, it should be noted here that in contrast to SHTS, data placed in DBs are restricted primarily to tables (and forms) whereas in SHTS they may be placed in any of thousands of cells (restricted by the size of the computer memory). In view of this, the author recently employed a DB script (similar to the macros employed in SHTS) to estimate the kinetic parameters n and k from isothermal TG (ITG) data [7]. The powerful Paradox 3.0 DB was used because it possessed an extensive paradox application language (PAL) which could be utilized to write scripts pertaining to the determination of kinetic parameters from TG data.

The aim of this paper is to extend the previous utilization of the Paradox DB in the estimation of kinetic parameters from ITG data. Thus, a PAL script was written and applied to non-isothermal TG (NITG) data to estimate n and E for theoretical NITG data and for data pertaining to calcium oxalate monohydrate, benzenediazonium chloride, calcium carbonate and teflon.

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 [8]

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

where α is the degree of conversion at the temperature T (K). From eqn. (1), values of E/R can be evaluated for various sets of $\alpha - T$ values at arbitrarily selected values of n. However, if uniqueness is assumed, only one pair of E/R and n values will be the most probable.

Various values of E/R can be obtained at various n values by employing various α–T values. However, the E/R values obtained should not deviate (or should deviate minimally) from each other at only one unique value of n. This value may be established by employing the concept of the standard deviation (STD). Thus, the E/R values at a particular value of n, which affords the smallest STD value, will be considered to also afford the most probable values of E(avg) and n.

RESULTS AND DISCUSSION

As previously indicated, the DB employed in this paper was Paradox 3.0, which can provide many advanced script commands via PAL. Such commands were applied to theoretical NITG data and to data for calcium oxalate monohydrate (COX), calcium carbonate (CAC), benzenediazonium chloride (in aqueous solution) (BDC) and teflon (TF).

TABLE 1

End-of-run database analysis of theoretical TG data ($n = 0.5$)

α	T	Order	LHS1	Y	X	E/R
0.13190	405	0.510	0.00000041			
0.20195	410		0.00000062	−0.42192	−0.00003011	14012
0.30261	415		0.00000094	−0.41207	−0.00002939	14023
0.44105	420		0.00000141	−0.40262	−0.00002869	14035
0.61869	425		0.00000208	−0.39383	−0.00002801	14060
0.81878	430		0.00000307	−0.38596	−0.00002736	14107
0.97883	435		0.00000449	−0.38040	−0.00002673	14231

The Paradox script employed to estimate values of kinetic parameters from NITG data is depicted with annotation in the Appendix. In this script, the initial value of n was arbitrarily assigned a value of 0.2. Also, the initial increment used for n was 0.10001 (b) since eqn. (1) is not valid for $n = 1$. Values of LHS1 (defined in the script) were calculated for all the records (for example, see Table 1). Then values of Y (the left hand side of eqn. (1)), X (the moiety on the right-hand-side of eqn. (1) that involves T (K)) and E/R (Y/X), were calculated. From the resulting tabular values, the average values of E and STD values of E/R were calculated and displayed for various particular values of n. An iteration procedure was carried out until a minimum value of STD (STDMIN) was attained. In order to obtain more refined values of E(avg) and n (to 2 significant figures), the value of n at the initial STDMIN was then decreased by 0.15 and subsequent values of n were incremented by 0.01 until another STDMIN was attained. In order to ascertain this minimum value of STD, it was necessary to increase the most probable value of n by 0.01 (this applies to Tables 1–5). Final values of n and E(avg) were obtained by utilizing previously stored values of STD, n and E(avg) (see the 3rd line from bottom of the script).

Table 1 represents a database analysis of theoretical NITG data. Final values were $n = 0.50$ and $E(\text{avg}) = 28.0$ kcal mol^{-1} (ref. 9 gives values of

TABLE 2

End-of-run database analysis of COX TG data

α	T	Order	LHS1	Y	X	E/R
0.020	423.2	1.05	−0.00000001			
0.075	443.2		−0.00000002	−1.2594937	−0.0001066	11812
0.205	463.2		−0.00000005	−0.9948313	−0.0000974	10211
0.305	473.2		−0.00000008	−0.4218558	−0.0000456	9246
0.442	483.2		−0.00000013	−0.4358385	−0.0000437	9965
0.607	493.2		−0.00000020	−0.4384184	−0.0000420	10448
0.773	503.2		−0.00000030	−0.4360117	−0.0000403	10821

TABLE 3

End-of-run database analysis of TG data for BDC

α	T	Order	LHS1	Y	X	E/R
0.038	306.3	1.03	−0.00000001			
0.074	310.6		−0.00000002	−0.658058	−0.00004520	14559
0.123	314.9		−0.00000004	−0.508151	−0.00004396	11558
0.225	319.2		−0.00000008	−0.638487	−0.00004278	14925
0.386	323.5		−0.00000014	−0.625731	−0.00004164	15026
0.576	327.8		−0.00000024	−0.543986	−0.00004055	13415
0.769	332.1		−0.00000041	−0.518337	−0.00003950	13123
0.922	336.4		−0.00000071	−0.545187	−0.00003849	14165

1/2 and 28 respectively). For the given α–T values in Table 1, near-final values of n (as previously indicated, 0.01 above the most probable value of n), LHS1, Y, X and E/R are listed.

In Table 2, a database analysis of NITG data is depicted for the dehydration of COX. Final values were found to be $n = 1.04$ and $E(\text{avg}) = 20.8$ kcal mol^{-1} (in ref. 8, 1.05 and 20.8 respectively). A database analysis of DTA data for the decomposition of BDC in aqueous solution is shown in Table 3. From the $\alpha - T$ values, the final parameter values obtained were $n = 1.02$ and $E(\text{avg}) = 27.6$ kcal mol^{-1} (in ref. 8, 1.05 and 27.8 respectively). Table 4 depicts a database analysis of NITG data for the decomposition of CAC. Final values were determined as $n = 0.61$ and $E(\text{avg}) = 41.6$ kcal mol^{-1} (in ref. 8, 0.60 and 41.5 respectively). Finally, a database analysis was carried out for TF as indicated in Table 5. Final values obtained were $n = 0.98$ and $E(\text{avg}) = 65.8$ kcal mol^{-1} (in ref. 9, 1.0 and 67 respectively).

From the preceding results, it can be observed that database analysis, like spreadsheet analysis, of TG data for the estimation of kinetic parameters, as presented here, gives final values in good agreement with the corresponding theoretical and reported values. This indicates that database, as well as

TABLE 4

End-of-run database analysis of CAC TG data

α	T	Order	LHS1	Y	X	E/R
0.050	981.2	0.62	0.00000002			
0.075	1008.2		0.00000003	−0.35931899	−0.00002729	13165
0.160	1035.7		0.00000006	−0.73288087	−0.00002634	27828
0.315	1064.7		0.00000012	−0.68139488	−0.00002630	25910
0.485	1095.2		0.00000019	−0.45298610	−0.00002616	17318
0.740	1127.7		0.00000032	−0.52794031	−0.00002631	20063

TABLE 5

End-of-run database analysis of teflon TG data

α	T	Order	LHS1	Y	X	E/R
0.016	773.2	0.990	0.00000000			
0.087	803.2		0.00000000	−1.6539270	−0.00004831	34238
0.216	823.2		0.00000000	−0.9334673	−0.00003025	30860
0.333	833.2		0.00000001	−0.4843664	−0.00001458	33222
0.489	843.2		0.00000001	−0.4803627	−0.00001423	33748
0.663	853.2		0.00000001	−0.4568121	−0.00001390	32864
0.826	863.2		0.00000002	−0.4482601	−0.00001358	33014

spreadsheet, analysis procedures can be instituted satisfactorily in the field of thermal analysis, either as primary or corroborative methods.

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 and S.S. Stivala, Thermochim. Acta, 25 (1978) 367.
9 L. Reich and S.S. Stivala, Thermochim. Acta, 24 (1978) 9.

APPENDIX: PAL SCRIPT TO ESTIMATE KINETIC PARAMETERS *n* AND *E*(avg) FROM NITG DATA.

```
                                        Script: D:\pdx3\sample\nitgpal1

; database pgm. to calc n (2 dec. places) and E(avg)/non-isothermal TG

Clear ?"Which database table do you want analyzed (no extension needed): "
Accept "A8" To tbl
Clear aa=1E+9 b=0.10001 mrkr=0        ; initial variable vals.
View tbl                              ; database to be analyzed
Home Editkey [Order]=0.2 Do_It!       ; set initial n=0.2
For counter From 1                    ; infinite loop
Home Editkey
o=[Order]
nr=nrecords(tbl)
For cnt From 1 To nr                  ; calc LHS1 vals. for all records
a=[Alpha] t=[T]
[LHS1]=(1-pow((1-a),(1-o)))/(t*t)
down
endfor
Home
nrs=nrecords(tbl)-1
For i From 1 To nrs-1                 ; accounts for previous 'down'
z=[LHS1]  q=[T]                       ; calc vals. of Y, X, ER for records-1
down
z1=[LHS1] q1=[T]
[Y]=Ln(z/z1) [X]=((1/q1)-(1/q))
[ER]=[Y]/[X]
endfor
Do_It!

;------------------ display intermediate vals. of STD, n and E(avg)
EE=caverage(tbl,"ER")  l=cstd(tbl,"ER")
Clear @10,20 ?" STD= ",l," for n= ",o," and E= ",int(EE*2)  sleep 1000

;------------------ display final vals. of n and E(avg)
if l>=aa and mrkr=1 then Clear @10,20
?"Final vals.: n=",oo," and E=",int(E*2)," cals/mol"
sleep 9000 clearall quit
endif

if l<aa and mrkr=1 then aa=l
endif
if l>=aa and mrkr=0 then mrkr=1 aa=1E+9
Home Editkey
[Order]=[Order]-0.15       ; decrement Order by 0.15
b=0.01                     ; Order increment of 0.01 via b-variable
endif
if l<aa and mrkr=0 then aa=l
endif
Home Editkey
ll=l oo=[Order]  E=EE      ; save previous vals. STD, Order and ER
[Order]=[Order]+b Do_It!
endfor
```