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Use of databases in thermal analysis. Part 4

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Abstract

A relational database manager (DB) was previously employed to estimate values of kinetic parameters from isothermal TG (ITG) and from non-isothermal TG (NITG) data. The Paradox 3 DB, which possesses a powerful application language (PAL), was utilized to estimate values of reaction order n and activation energy E, and to ascertain the most probable decomposition mechanism from among 10 possibilities. When these results were compared with reported values, they were found to be in satisfactory agreement.

The aim of this paper is to extend the utilization of PAL in the determination of values of E and n from NITG data. A cubic expression was employed which involves the use of slopes from TG curves at particular values of α. Analyses were carried out using theoretical TG data, benzenediazonium chloride, and magnesium hydroxide.

INTRODUCTION

The present author has previously utilized a relational database manager (DB) to ascertain values of kinetic parameters from isothermal TG data (ITG) [1] and from non-isothermal TG data (NITG) [2,3]. Thus, the versatile Paradox 3 DB (Borland International) was employed to determine reaction order n, activation energy E, and a 'most probable mechanism' from among 10 possibilities, using ITG and NITG. Paradox 3 was employed because it possesses the powerful Paradox Application Language (PAL) which can be used to create scripts relevant to the estimation of kinetic parameters from TG data.

The purpose of this paper is to continue the application of PAL and to determine values of E and n from NITG employing a cubic equation [4,5]. To this end, DB analyses of NITG were carried out using PAL for theoreti-

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cal data, benzenediazonium chloride (BDC), and magnesium hydroxide (MH).

THEORETICAL ASPECTS

It can be readily shown [6] that

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

where $\mathrm{LH} = [(RT)_1/(RT)_2](T_1/T_2)^2$, $RT = \mathrm{d}\alpha/\mathrm{d}T$ and α is the degree of conversion. From eqn. (1), for various fixed values of α_1 and α_2, values of LH can be calculated for various values of n. Thus, the following nine arbitrary values of α_1/α_2 were used: 0.2/0.8, 0.2/0.9, 0.25/0.75, 0.3/0.6, 0.3/0.7, 0.3/0.8, 0.4/0.7, 0.4/0.8, and 0.5/0.8. The values of n used ranged from 0.1 to 2. Then the calculated values of LH and n were correlated by means of a cubic expression such as

$$n = A_0 + A_1(\mathrm{LH}) + A_2(\mathrm{LH})^2 + A_3(\mathrm{LH})^3 \quad (2)$$

Correlation coefficients varied from 0.9998 to 0.9999 and standard error of estimate values ranged from 0.00016 to 0.013.

After an average value of n was obtained from the various α ratios, a value of E could be calculated from the following expression using a least-squares treatment [5]

$$\mathrm{LHS} \equiv \mathrm{LN}(\mathrm{LHS}_1) = (-E/R)(1/T_1 - 1/T_2) \quad (3)$$

where $\mathrm{LHS}_1 = (T_2/T_1)^2/[(1-(1-\alpha_1)^{1-n})/(1-(1-\alpha_2)^{1-n})]$.

RESULTS AND DISCUSSION

Values of α_1 and α_2, T_1 and T_2 (K), and RT_1 and RT_2 are listed in Tables 1–3, employing values in ref. 5. These values were analyzed by means of the script, cubicpal (CP), listed in the Appendix. In script CP, eight 'If–Endif' statements were used in the analysis of the TG data in the three tables, even though there are only six sets of data in Table 1 for BDC and six in Table 2 for theoretical TG data, and only four sets of TG data in Table 3 for MH. This was done in order to make the script more general and also to use the data for the various α_1/α_2 ratios given in the three tables.

From the CP script, it can be observed that for the various values of α_1 and α_2, corresponding values of the coefficients in eqn. (2) are listed. During the scan, when the appropriate α_1/α_2 value is encountered, values of the coefficients in the corresponding row in CP are utilized to estimate n (values of LH are also employed). After an average value of n has been obtained from the various sets of α values, a value of E can then be determined by means of eqn. (3) (see the expressions in CP following the

TABLE 1

Database analysis of BDC DTA data using a cubic equation

α_1	α_2	T_1	T_2	RT_1	RT_2	LH	n	LHS	Delta
0.20	0.80	316.7	331.0	3.26	5.38	0.55472	1.0039	−1.8902	0.0001364
0.30	0.70	319.8	328.8	4.41	6.20	0.67288	0.9375	−1.1348	0.0000856
0.30	0.80	319.8	331.0	4.41	5.38	0.76517	0.9804	−1.4257	0.0001058
0.40	0.70	322.2	328.8	5.41	6.20	0.83790	0.9639	−0.8044	0.0000623
0.40	0.80	322.2	331.0	5.41	5.38	0.95282	1.0025	−1.0951	0.0000825
0.50	0.80	324.5	331.0	6.02	5.38	1.07544	0.9979	−0.8018	0.0000605

TABLE 2

Database analysis of theoretical TG data using a cubic equation

α_1	α_2	T_1	T_2	RT_1	RT_2	LH	n	LHS	Delta
0.20	0.80	750.6	824.0	4.784	7.130	0.55676	1.0092	−1.7956	0.0001187
0.25	0.75	759.0	818.0	5.618	7.793	0.62066	0.9960	−1.4206	0.0000950
0.30	0.70	766.8	812.4	6.400	8.240	0.69195	1.0031	−1.1023	0.0000732
0.30	0.80	766.8	824.0	6.400	7.130	0.77732	1.0056	−1.3664	0.0000905
0.40	0.70	779.8	812.4	7.612	8.240	0.85113	1.0090	−0.7786	0.0000515
0.50	0.80	790.8	824.0	8.342	7.130	1.07760	1.0023	−0.7612	0.0000510

TABLE 3

Database analysis of MH TG data using a cubic equation

α_1	α_2	T_1	T_2	RT_1	RT_2	LH	n	LHS	Delta
0.25	0.75	651.0	679.6	1.407	1.337	0.96565	1.9141	−2.0518	0.0000646
0.30	0.60	654.5	670.6	1.590	1.836	0.82493	1.7422	−1.1189	0.0000367
0.30	0.70	654.5	676.4	1.590	1.567	0.95004	1.8415	−1.5459	0.0000495
0.40	0.70	659.5	676.4	1.795	1.567	1.08897	1.8133	−1.1211	0.0000379

TABLE 4

Database analysis of BDC using a cubic equation

α_1	α_2	T_1	T_2	RT_1	RT_2	LH	AA_0	AA_1	AA_2	AA_3	n	LHS	Delta
0.20	0.80	316.7	331.0	3.26	5.38	0.55472	−1.2147	5.8805	−4.2998	1.6385	1.0039	−1.89021	0.0001364
0.30	0.80	319.8	331.0	4.41	5.38	0.76517	−1.3615	4.4313	−2.3062	0.6729	0.9804	−1.42573	0.0001058
0.30	0.70	319.8	328.8	4.41	6.20	0.67288	−2.3594	7.0252	−4.1749	1.5100	0.9375	−1.13479	0.0000856
0.40	0.80	322.2	331.0	5.41	5.38	0.95282	−1.5997	3.9670	−1.7376	0.4623	1.0025	−1.09511	0.0000825
0.40	0.70	322.2	328.8	5.41	6.20	0.83790	−2.9409	6.8085	−3.6340	1.2772	0.9639	−0.80437	0.0000623
0.50	0.80	324.5	331.0	6.02	5.38	1.07544	−2.0100	4.1452	−1.7912	0.4998	0.9979	−0.80177	0.0000605

'Endif' statement). From this, the following values for E (cal mol^{-1}), n, and standard deviation were obtained for BDC, the theoretical data and MH (see Tables 1–3), respectively: 28878, 0.981, 0.0240 (ref. 5 gives corresponding values of 28553, 0.981, 0.024); 30275, 1.004, 0.0045 (ref. 5 gives corresponding values of 30242, 1.004, 0.005); 68122, 1.828, 0.0616 (ref. 5 gives corresponding values of 62633, 1.83, 0.06). These values are in satisfactory agreement with values reported from the utilization of the Lotus spreadsheet (Release 2.2) analysis.

In order to simplify the CP script, Table 4 was created and BDC was arbitrarily selected. In this table, known values of the coefficients in eqn. (2) were also entered for the various values of α_1 and α_2. A new script, cubicsht (CS), was devised to obtain values of kinetic parameters from Table 4 (see the Appendix). This CS script no longer includes the various 'If-Endif' statements contained in the CP script, thus allowing for a smaller script. The kinetic results obtained for BDC using the CS script are almost identical with those reported previously using the CP script.

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APPENDIX

```
                                        Script: D:\pdx3\sample\cubicpal

; Calculate values of n and E using a cubic equation
; Cf. Thermochim. Acta, 164 (1990) 1

Clear sx=0 sy=0 sxx=0 sxy=0     ; initialize for LSQ's
? " Which table to analyze (extension not reqd.): "
Accept "A8" To tbl
View tbl
Editkey Home
; ----------------Insert calcd. vals. of LH, N, LHS, Delta into tbl

Scan
a1=[Alpha1] a2=[Alpha2] T1=[T1] T2=[T2] RT1=[RT1] RT2=[RT2]
LH=(RT1/RT2)*(T1/T2)*(T1/T2) [LH]=LH
[Delta]=(1/T1)-(1/T2)
If a1=0.2 and a2=0.8 then AA0=-1.2147 AA1=5.8805 AA2=-4.2998 AA3=1.6385
Endif
If a1=0.25 and a2=0.75 then AA0=-1.6883 AA1=6.28063 AA2=-4.06885 AA3=1.47885
Endif
If a1=0.4 and a2=0.8 then AA0=-1.5997 AA1=3.967 AA2=-1.7376 AA3=0.4623
Endif
If a1=0.3 and a2=0.6 then AA0=-3.89949 AA1=10.41649 AA2=-6.60883 AA3=2.75432
Endif
If a1=0.3 and a2=0.7 then AA0=-2.3594 AA1=7.0252 AA2=-4.1749 AA3=1.51003
Endif
```

```
If a1=0.3 and a2=0.8 then AA0=-1.3615 AA1=4.4313 AA2=-2.3062 AA3=0.67288
Endif
If a1=0.4 and a2=0.7 then AA0=-2.9409 AA1=6.8085 AA2=-3.634 AA3=1.2772
Endif
If a1=0.5 and a2=0.8 then AA0=-2.01 AA1=4.1452 AA2=-1.7912 AA3=0.49977
Endif
n=AA0+AA1*(1h)+AA2*(1h)*(1h)+AA3*(1h)*(1h)*(1h) [N]=n
LHS1=(T2/T1)*(T2/T1)*((1-pow((1-a1),(1-n)))/(1-pow((1-a2),(1-n))))
[LHS]=LN(LHS1)
sy=sy+[LHS] sx=sx+[Delta]     ; calc summations for LSQ's
sxx=sxx+[Delta]*[Delta] sxy=sxy+[LHS]*[Delta]
Endscan
; ----------------Calc final values of n(avg), STD and E(LSQ's)

Do_It! Home
navg=caverage(tbl,"N") nstd=cstd(tbl,"N")
nrs=Nrecords(tbl)
AAA2=(nrs*sxy-sx*sy)/(nrs*sxx-(sx*sx))
Clear @10,10
? " Average value of n =",Format("W6.3",navg),
" with a STD of",Format("W6.4",nstd)
@12,10
? " LSQ's value of E =",abs(int(AAA2*2))," cal/mol"
sleep 9000
```

Script: D:\pdx3\sample\cubicsht

```
: Calculate values of n and E using a cubic equation.
: This script was applied to Table4→(BDC data).
: Table4→differs from Table 1 (BDC data), in that it
: contains parameters for the cubic equation.

Clear sx=0 sy=0 sxx=0 sxy=0  : initialize for LSQ's
?"Which table to analyze (extension not req'd.): "
Accept "A8" To tbl
Edit tbl

:Insert calcd. vals. of LH, N, LHS, Delta into Table 1A (also 'cubicsht')

Scan
a1=[Alpha1] a2=[Alpha2] T1=[T1] T2=[T2] RT1=[RT1] RT2=[RT2]
LH=(RT1/RT2)*(T1/T2)*(T1/T2) [LH]=LH
[Delta]=(1/T1)-(1/T2)

n=[AA0]+[AA1]*(1h)+[AA2]*(1h)*(1h)+[AA3]*(1h)*(1h)*(1h) [N]=n
LHS1=(T2/T1)*(T2/T1)*((1-pow((1-a1),(1-n)))/(1-pow((1-a2),(1-n))))
[LHS]=LN(LHS1)

: ----------------------calc summations for LSQ's

sy=sy+[LHS] sx=sx+[Delta]
sxx=sxx+[Delta]*[Delta] sxy=sxy+[LHS]*[Delta]
Endscan

: -----------------Calc final values of n(avg), STD and E(LSQ's)

Do It' Home
navg=caverage(tbl,"N") nstd=cstd(tbl,"N")
nrs=Nrecords(tbl)
AAA2=(nrs*sxy-sx*sy)/(nrs*sxx-(sx*sx))
Clear @10,10
?" Average value of n =",Format("W6.3",navg),
" with an STD of",Format("W6.4",nstd)
@12,10
?" LSQ's value of E =",abs(int(AAA2*2))," cal/mol"
Sleep 9000
```