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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XV

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In previous publications, values of reaction order (n) were estimated for "n-type" unimolecular or pseudo-unimolecular decompositions without the need for any initial determination of activation energy (E) [1–5]. The procedures described involved the estimation of slopes of TG curves (RT) at various degrees of conversion (α) and corresponding temperatures (T, K) [data from DTA (and DSC) traces can also be readily utilized]. Then values of n could be determined directly by graphical procedures [2–4] or indirectly by iterative methods [5]. The aim of this paper is to extend previously reported procedures so that the value of n can now be determined directly by means of cubic equations which use data from TG or DTA (or DSC) traces.

THEORY

It can be readily shown (cf. ref. 1) that

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

where $\mathrm{LH} = [(RT)_1/(RT)_2](T_1/T_2)^2$, and $RT = \mathrm{d}\alpha/\mathrm{d}T$. From eqn. (1), for various fixed values of α_1 and α_2, values of LH can be calculated for various values of n. In this manner, the following 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 while 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

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

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

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TESTING THE METHOD

In the Appendix a computer program (CP) is presented whereby values of n can be rapidly calculated from values of T_1, $(RT)_1$ [or $(\Delta T)_1$ in the case of DTA], T_2, and $(RT)_2$, once values of α_1/α_2 have been specified. In the CP, line numbers (LN) 110–190 depict values of A_0, $A1$, $A2$, and $A3$ which correspond to the ratios of α_1/α_2 in LN 10. The CP was tested in the following cases: (1) theoretical TG data for $n = 0.5$; (2) theoretical TG data for $n = 1$ [6]; (3) experimental DTA data for benzenediazonium chloride (BDC) in aqueous solution [7]; (4) experimental TG data for magnesium hydroxide (MH) [8]; (5) experimental DTA data for bulk polypropylene (PP) [9]. Values corresponding to the ratios in LN 10 of the CP were obtained by interpolation where necessary.

In cases 1 and 2, all the nine α ratios in LN 10 of the CP were tested and the average n-values and their corresponding mean deviations were, respectively: 0.50 ± 0.00 and 1.01 ± 0.00. In case 3, six α ratios were tested for BDC and afforded an average value of $n = 0.98 \pm 0.02$ (lit. [3–5,7], 1–1.1). In case 4, four α ratios were utilized from data for the dehydroxylation of MH to afford a value of $n = 1.8 \pm 0.05$ for Trace 1 and $n = 1.7 \pm 0.22$ for Trace 2 (lit. [8], 1.5–1.7). Finally, in case 5, four α ratios were tested for PP and yielded $n = 0.81 \pm 0.02$ (lit. [3], 0.88 ± 0.11).

From the preceding, it can be seen that the calculated values of n for the various cases were in reasonably good agreement with anticipated or reported values. A possible limitation of the method in the case of TG is the difficulty of measuring accurately large values of slope from a primary thermogram (RT). (However, where available, DTG equipment should be able to manage such measurements.) On the other hand, DTA (or DSC) can afford accurate values of slope (ΔT can be used since ratios are employed) but much interpolation would probably be needed since specified values of α, determined by area measurements, would be difficult to obtain readily. Of course, once values of n are determined, values of E can then be obtained.

APPENDIX

A computer program to calculate reaction order (n) using a cubic equation.

```
2 '***CALCN. OF 'N' USING CUBIC EQU.***
3 '
5 CLS
8 '
10 INPUT"WHICH RATIO: 2/8 (1), 2/9 (2), 2.5/7.5 (3), 3/6 (4), 3/7 (5), 3/8 (6),
4/7 (7), 4/8 (8), 5/8 (9) ";A
15 '
20 ON A GOSUB 110,120,130,140,150,160,170,180,190
25 '
30 PRINT:INPUT"ENTER IN ORDER: T1, RT1, T2 & RT2 ";T1,R1,T2,R2
35 '
40 LH=(R1/R2)*(T1/T2)^2
45 '
50 N=A0+ A1*LH+A2*(LH)^2+A3*(LH)^3
55 '
60 PRINT:PRINT"THE VALUE OF REACTION ORDER= ";CSNG(N)
65 '
70 END
100 '
110 A0=-1.21469:A1=5.88051:A2=-4.29979:A3=1.63847:RETURN
115 '
120 A0=-.554837:A1=2.96582:A2=-1.50471:A3=.36425:RETURN
125 '
130 A0=-1.6883:A1=6.280628:A2=-4.068854:A3=1.47885:RETURN
135 '
140 A0=-3.89949:A1=10.41649:A2=-6.60883:A3=2.75432:RETURN
145 '
150 A0=-2.35935:A1=7.02524:A2=-4.17492:A3=1.51003:RETURN
155 '
160 A0=-1.361512:A1=4.431316:A2=-2.306174:A3=.672883:RETURN
165 '
170 A0=-2.9409:A1=6.80851:A2=-3.634:A3=1.27719:RETURN
175 '
180 A0=-1.59965:A1=3.9671:A2=-1.73755:A3=.462325:RETURN
185 '
190 A0=-2.00998:A1=4.1452:A2=-1.79115:A3=.499774:RETURN
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