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Note

COMPUTER ANALYSIS OF NON-ISOTHERMAL AND ISOTHERMAL TG DATA FOR MECHANISM

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In previous publications [1,2], methods were presented for the graphical analysis of non-isothermal as well as isothermal TG data for mechanism. By means of the preceding analysis, it was possible to distinguish one out of 12 theoretically possible solid-state decomposition mechanisms. In this paper, a computer program is presented (see Appendix) which can readily be employed to supplement the preceding graphical analysis as well as to afford a more quantitative analysis of the TG data.

For two TG curves obtained at different heating rates (RH), we may write for $T =$ constant [1]

$$(\mathrm{RH})2/(\mathrm{RH})1 = \mathrm{g}(\mathrm{AA}1)/\mathrm{g}(\mathrm{AA}2) \quad (1)$$

where, AA1 and AA2 denote degree of conversion; and $\mathrm{g}(\mathrm{AA}) = \int_0^{\mathrm{AA}} \mathrm{d}(\mathrm{AA})/\mathrm{f}(\mathrm{AA})$. Using $(\mathrm{RH})2/(\mathrm{RH})1 = 2$, various values of AA1 and AA2 could be calculated from eqn. (1) for the 12 theoretical solid-state mechanisms previously listed [1] (also see line numbers (LN) 290–300 of the computer program in the Appendix). These values of AA1 and AA2 for the various mechanisms were then correlated using the cubic equation (cf. LN 70 of computer program)

$$\mathrm{AA1} = A + B(\mathrm{AA2}) + C(\mathrm{AA2})^2 + D(\mathrm{AA2})^3 \quad (2)$$

Values of the constants A, B, C, and D for the various mechanisms may be gleaned from the BASIC computer program in the Appendix. (It may be noted here that the As in LNs 170–280 denote constants, whereas in LNs 290–300, the As denote degree of conversion in the listed mechanisms.) Thus, in LN 290, the first mechanism listed, i.e., A4, corresponds to values of constants in LN 170; the next mechanism listed in LN 290, A3, corresponds to values in LN 180, etc. These values of the constants were obtained by means of regression procedures. With the exception of mechanisms A4 and A3, the correlation coefficients for the other mechanisms were about 0.99999 or greater; corresponding values for A4 and A3 were about 0.9994 (these relatively low values were probably due to the steepness of the plots of

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AA1 vs. AA2). Equation (2) was employed rather than theoretical expressions in order to expand the range of the experimental values of AA1 and AA2 that could be utilized.

The BASIC computer program in the Appendix for the analysis of non-isothermal and isothermal TG data for mechanism employs the standard error of estimate (S.E.E.) as a criterion. Thus, the mechanism which afforded the lowest value of S.E.E. was considered to be the most probable mechanism. For illustrative purposes, two computer analyses were carried out (for six data pairs, the time of a run was ca. 10 sec). The first data set in LN 310 represented a pseudo-first-order reaction in solution. For such an 'n-type' reaction, the analysis previously presented [3] would be more appropriate; nevertheless, based upon the mechanisms employed in the computer program, an F1 mechanism would be anticipated. Following the computer program are depicted values of S.E.E. for the first data set for the 12 different mechanisms. From these values, the F1 mechanism is the most probable. (It should be noted here that the first and second data sets used were not obtained using eqn. (1), but were obtained from isothermal data employing a reaction time ratio of two [2].) Theoretical TG data were then employed which represented an R3 mechanism [2]. The second data set consists of four data pairs of conversion values and is shown in LN 310. Following this data set are shown values of S.E.E. for the 12 mechanisms. As expected, the most probable mechanism was R3, based upon the lowest value of S.E.E. It may be noted here that at the lower conversion values (less than 0.5) it becomes very difficult to differentiate the mechanisms denoted by D2, D3 and D4. Thus, for the preceding mechanisms, conversion values above 0.5 become more meaningful in the determination of mechanism.

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 59 (1982) 247.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 60 (1983) 251.
3 L. Reich and S.S. Stivala, Thermochim. Acta, 58 (1982) 383.

APPENDIX

A BASIC computer program for analysis of isothermal and non-isothermal TG data for mechanism

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LIST
 10 L = 6: REM PRS OF CONVERSION DATA IN LN# 310
 20 DIM ST$(40), AA(40), D(40), TT(40)
 30 D(0) = 200
 40 FOR J = 1 TO 12: READ ST$(J): NEXT
 50 FOR J = 1 TO 2 * L: READ AA(J): NEXT
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```
60 FOR CC=1 TO 12: ON CC GOSUB 170, 180, 190, 200, 210, 220, 230, 240, 250, 260,
   270, 280
70 DEF FN I(AA)=A+B * AA+C * AA * AA+D * AA * AA * AA
80 FOR K=1 TO 2 * L-1 STEP 2: D(CC)=(AA(K+1)-FN I(AA(K))) ∧ 2+D(CC)
90 NEXT K
100 TT(CC)=(D(CC)/L) ∧ (1/2): REM TT(CC)=STD.ERROR. OF ESTIMATE
110 PRINT "S.E.E.=";TT(CC);" FOR "ST$(CC): REM S.E.E.=STD.ERROR OF
   ESTIMATE
120 IF D(CC)<=D(CC-1) THEN 140
130 D(CC)=D(CC-1): ST$(CC)=ST$(CC-1)
140 NEXT CC
150 PRINT: PRINT "MOST PROBABLE MECHANISM IS: "ST$(CC-1)
160 END
170 A=.0361132: B=13.1773653: C=-62.9731296: D=100.325: RETURN
180 A=.02594: B=6.7498946: C=-15.71297: D=11.968909: RETURN
190 A=-1.406115E-08: B=4: C=-4.7212058E-06: D=1.17281664E-05: RETURN
200 A=5.608611E-03: B=3.875975: C=-5.28328584: D=2.5131608: RETURN
210 A=-1.2126606E-03: B=2.8531885: C=-2.6952913: D=.858267584: RETURN
220 A=.010826499: B=1.84068145: C=.161684084: D=-1.14163135: RETURN
230 A=1.82090839E-03: B=1.97104275: C=-.523903255: D=-.472076202: RE-
   TURN
240 A=-1.07320249E-07: B=2: C=-1: D=4.49602E-06: RETURN
250 A=3.6122111E-03: B=1.41421338: C=4.728793E-09: D=2.59372575E-07: RE-
   TURN
260 A=.016712702: B=1.23409591: C=0.46808098: D=-0.61113475: RETURN
270 A=.0228394788: B=1.1796683: C=.57508252: D=-.737157136: RETURN
280 A=7.95141778E-08: B=1.33679679: C=.0456124356: D=-.34176826: RETURN
290 DATA "A4: (-LN(1-A))∧(1/4)","A3: (-LN(1-A))∧(1/3)","P3: A∧(1/2)","A2:
   (-LN(1-A))∧(1/2)","A1.5: (-LN(1-A))∧(2/3)","R2: 1-(1-A)∧(1/2)","R3: 1-(1-A)
   ∧(1/3)","F1: -LN(1-A)","D1: A∧2","D2: A+(1-A)LN(1-A)"
300 DATA"D4: 1-(2A/3)-(1-A)∧(2/3)","D3: (1-(1-A)∧(1/3))∧2"
310 DATA .4,.650,.455,.71,.5,.755,.545,.795,.795,.58,.83,.65,.86: REM DATA FROM
   'GRAPH. ANAL. ISOTH. TG DATA FOR MECHSM.'

]RUN
S.E.E.=4.64964318 FOR A4: (-LN(1-A))∧(1/4)
S.E.E.=.231063193 FOR A3: (-LN(1-A))∧(1/3)
S.E.E.=1.34477746 FOR P3: A∧(1/2)
S.E.E.=.174463225 FOR A2: (-LN(1-A))∧(1/2)
S.E.E.=.100415939 FOR A1.5: (-LN(1-A))∧(2/3)
S.E.E.=.0771002011 FOR R2: 1-(1-A)∧(1/2)
S.E.E.=.0474720219 FOR R3: 1-(1-A)∧(1/3)
S.E.E.=9.36016153E-03 FOR F1: -LN(1-A)
S.E.E.=.0529886287 FOR D1: A∧2
S.E.E.=.075028241 FOR D2: A+(1-A)LN(1-A)
S.E.E.=.0845576288 FOR D4: 1-(2A/3)-(1-A)∧(2/3)
S.E.E.=.110702103 FOR D3: (1-(1-A)∧(1/3))∧2

MOST PROBABLE MECHANISM IS: F1: -LN(1-A)

310 DATA .203,.377,.377,.645,.523,.822,.645,.928
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]RUN
S.E.E. = 4.49415076 FOR A4: (-LN(1-A))^(1/4)
S.E.E. = .304924535 FOR A3: (-LN(1-A))^(1/3)
S.E.E. = 1.14847754 FOR P3: A^(1/2)
S.E.E. = .164843774 FOR A2: (-LN(1-A))^(1/2)
S.E.E. = .0730312195 FOR A1.5: (-LN(1-A))^(2/3)
S.E.E. = .0249866815 FOR R2: 1-(1-A)^(1/2)
S.E.E. = 4.07454649E-04 FOR R3: 1-(1-A)^(1/3)
S.E.E. = .0406762638 FOR F1: -LN(1-A)
S.E.E. = .0798643405 FOR D1: A^2
S.E.E. = .108641841 FOR D2: A+(1-A)LN(1-A)
S.E.E. = .117558311 FOR D4: 1-(2A/3)-(1-A)^(2/3)
S.E.E. = .140783636 FOR D3: (1-(1-A)^(1/3))^2

MOST PROBABLE MECHANISM IS: R3: 1-(1-A)^(1/3)
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