Thermochimica Acta, 75 (1984) 405–407
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

COMPUTER ANALYSIS OF NON-ISOTHERMAL TG DATA FOR MECHANISM AND ACTIVATION ENERGY. PART II

LEO REICH and S.S. STIVALA

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030 (U.S.A.)

(Received 22 November 1983)

In Part I [1], the authors presented a computer program (in BASIC) whereby one of ten theoretically possible mechanisms for solid-state decomposition could be distinguished and its corresponding activation energy (E) determined from TG data. Also, in Part I, a so-called $p(x)$ function was employed in order to establish an algorithm [2,3]. This $p(x)$ function involved the integral of the Arrhenius function (which cannot be solved in closed form). In the present paper, another algorithm is presented which involves integration by parts of the Arrhenius function in an attempt to achieve the same goals as in Part I.

THEORY

Employing integration by parts [3], it can be shown that

$$\ln\left[g(\alpha)(T5/T)^2\right] = \ln\left[g(\alpha 5)\right] - (E/R)(1/T - 1/T5) \quad (1)$$

where $g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$; α = conversion; and $T5$ = temperature (K) at 50% conversion ($\alpha 5$). For each of ten different possible decomposition mechanisms, the corresponding slope and intercept of eqn. (1) can be obtained from TG data using a least squares treatment. The mechanism whose intercept value affords the lowest percent deviation (PD) from the corresponding theoretical value of $g(\alpha 5)$ is considered to be the most probable mechanism. The corresponding E-value can then be calculated from the value of the slope.

RESULTS AND DISCUSSION

Theoretical and experimental TG data [α vs. T (K)] [1] are presented in the Appendix. The following ten mechanisms were tested: A4, A3, A2, R2,

0040-6031/84/$03.00

R3, F1, D1, D2, D3, and D4 [1]. Results are summarized in tables in the Appendix (DIFF = PD/100). From these results, it can be ascertained that the computer algorithm employed has a limited potential. Thus, whereas it can be used successfully for theoretical TG data (cf. lines 530 and 540), it cannot distinguish D3 from R3 using experimental data (see lines 550 and 560). (Although values of DIFF for D3 and R3 were different using experimental data, the difference was considered to be too small to be significant.) Further, small changes in $T5$ can greatly affect final values of DIFF. From the preceding, it can be concluded that the computer procedure employed in this paper possessed limited capability.

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 73 (1984) 165.
2 J. Szako, J. Phys. Chem., 72 (1968) 2406.
3 L. Reich and S.S. Stivala, Elements of Polymer Degradation, McGraw-Hill, New York, 1971, pp. 91–92.

APPENDIX

Results of a computer algorithm, to distinguish one of ten theoretical mechanisms, which involves integration by parts of the Arrhenius function.

```
530  DATA .07197,620,.10695,640,.15439,660,.21661,680,.29533,700,.39099,72
     0,.50186,740,.62308,760,.74587,780,.85746,800,.94279,820: REM  REICH,
     TA,34,287(1979);DATA-->29.9K/M FOR D3-MECH.(11PRS.), T5=739.7(K)
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.11822	1.7
A3/(-LN(1-A))^(1/3)	.13544	3.2
A2/(-LN(1-A))^(1/2)	.15268	6.3
R2/1-(1-A)^(1/2)	.02478	12.7
R3/1-(1-A)^(1/3)	2E-03	13.5
F1/-LN(1-A)	.16989	15.4
D1/A^2	.12886	23.9
D2/A+(1-A)LN(1-A)	.05945	26.5
D4/1-(2A/3)-(1-A)^(2/3)	.02288	27.6
D3/(1-(1-A)^(1/3))^2	3E-05	29.9

```
PROB. MECHNSM.: D3/(1-(1-A)^(1/3))^2 WITH DIFF.= 3.1E-05 & E= 29.9 KCAL/MOL
```

```
540  DATA   .1319,405,.20195,410,.30251.415,.44105,420,.61869,425,.81878,4
     30,.97883,435: REM      THEOR.DATA->28K/M, R2-MECH. (7 PRS.), TS=421.7
     (K)
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.32366	7.7
A3/(-LN(1-A))^(1/3)	.32514	10.8
A2/(-LN(1-A))^(1/2)	.32664	17.1
R2/1-(1-A)^(1/2)	5.29E-03	28
R3/1-(1-A)^(1/3)	.01856	30.3
F1/-LN(1-A)	.32811	35.9
D1/A^2	.11741	45.4
D2/A+(1-A)LN(1-A)	.04585	52.9
D4/1-(2A/3)-(1-A)^(2/3)	.01227	55.9
D3/(1-(1-A)^(1/3))^2	.01877	62.4

PROB. MECHNSM.: R2/1-(1-A)^(1/2) WITH DIFF.= 5.291E-03 & E= 28 KCAL/MOL

```
550  DATA    .011736,413.2,.022472,423.2,.039326,433.2,.078652,443.2,.191,
     453.2,.3427,463.2,.58427,473.2,.8764,483.2,.97191,493.2: REM   ZSAKO
     DATA, CMPLX.II, TS=469.7->R3/D3 MECHS., E=->26/54 K/M (9 PRS.)
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.06025	5.7
A3/(-LN(1-A))^(1/3)	.06466	8.2
A2/(-LN(1-A))^(1/2)	.06911	13.3
R2/1-(1-A)^(1/2)	.10249	25.1
R3/1-(1-A)^(1/3)	.05214	26.1
F1/-LN(1-A)	.0735	28.3
D1/A^2	.31434	47
D2/A+(1-A)LN(1-A)	.13144	49.9
D4/1-(2A/3)-(1-A)^(2/3)	.08302	51.2
D3/(1-(1-A)^(1/3))^2	.05159	52.9

CAN'T DISTINGUISH D3/R3 MECHANISMS!

```
560  DATA   .208,408.2,.3,413.2,.403,418.2,.528,423.2,.667,428.2,.806,433.
     2,.917,438.2: REM   SOD.BIOASS., TS=422.1->R3/D3 MECHS., E=22/46 KCAL
     /MOL (7 PRS.)
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.05617	5.3
A3/(-LN(1-A))^(1/3)	.05768	7.6
A2/(-LN(1-A))^(1/2)	.05922	12.2
R2/1-(1-A)^(1/2)	.02645	20.5
R3/1-(1-A)^(1/3)	.01078	22.3
F1/-LN(1-A)	.06072	26.2
D1/A^2	.09804	33.8
D2/A+(1-A)LN(1-A)	.05234	39.1
D4/1-(2A/3)-(1-A)^(2/3)	.02326	41.5
D3/(1-(1-A)^(1/3))^2	.01017	46.2

CAN'T DISTINGUISH D3/R3 MECHANISMS!