Thermochimica Acta, 94 (1985) 413–416
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XIV

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(Received 3 April 1985)

The present authors recently presented computer programs which could be used to analyze isothermal TG (ITG) data. In this regard, computer procedures were devised for the estimation of: activation energy (E) [1], and mechanism and rate constant [2–5]. None of the preceding ITG procedures allowed for the determination of both E and mechanism concurrently. In this paper, a computer procedure (CP) will be presented which will allow both E and mechanism to be estimated simultaneously. This CP was tested utilizing theoretical ITG data generated by means of a computer.

THEORY

For an isothermal unimolecular solid-state decomposition, we may write

$$g(\alpha) = kt \tag{1}$$

where t = reaction time, $g(\alpha) = \int_0^\alpha d\alpha / f(\alpha)$, α = fractional conversion, and $f(\alpha)$ = some function of α which is theoretically possible. From eqn. (1), the following can be readily obtained

$$\ln[g(\alpha)/t] = -E/RT + \ln(Z) \tag{2}$$

where Z = pre-exponential factor, and T = temperature (K).

In order to employ eqn. (2) for the purposes previously mentioned, several ITG runs are carried out at various temperatures. Then for various time periods (t), various values of α are obtained for each temperature. In this paper, ten possible theoretical mechanisms will be tested by means of a computer. Equation (2) was employed, and for each mechanism, a least-squares procedure carried out for each particular value of t to afford corresponding values of slope (E/R) and intercept ($\ln(Z)$). Then for all the t-values utilized, averages of E/R and $\ln(Z)$ are estimated for each mechanism. Futher, the mean deviation (DIFF) for $\ln(Z)$ is obtained for each mechanism. The most probable mechanism (and E-value) is considered to be the one whose DIFF possesses the lowest value.

0040-6031/85/$03.30

RESULTS AND DISCUSSION

The following ten theoretical mechanisms were examined to ascertain which one of them best conformed to the isothermal TG data: A4, A3, and A2 (random nucleation, Avrami–Erofeev equations); R2 and R3 (phase boundary reaction, cylindrical and spherical symmetry, respectively); F1 (random nucleation, one nucleus per particle); D1, D2, D3, and D4 (corresponding to 1-dimensional diffusion; 2-dimensional diffusion, cylindrical symmetry; 3-dimensional diffusion, Jander spherical symmetry; and 3-dimensional diffusion, Ginstling–Brounshtein spherical symmetry).

Theoretical computer values of alpha were generated for various t- and T-values for the mechanisms: A2, F1, R2 and D3. Thus, for example, for the R2-mechanism, values were obtained from the expression; $\alpha = 1 - B^2$ where $B = 1 - 0.5Zt\ \exp(-E/RT)$ (0.5 is an integration factor). For the four preceding mechanisms, the following values of Z and E (kcal mol^{-1}) were employed, respectively: 3×10^{10}, 24.9; 1×10^{13}, 30.0; 1×10^{13}, 30.0; 1×10^{14}, 35.0.

The seven specific t-values of 20, 30, 40, 50, 60, 70, and 80 were employed for all the mechanisms tested. In the Appendix a computer printout of the various ITG data employed is shown along with results of their computer analysis. In each of lines 525, 540, 550, and 560 are listed the five T-values (K) used in testing for the four mechanisms. In each of lines 535, 545, 555, and 565 are listed corresponding values of α. Thus, for example, in line 535, each of the first five α values correspond to each of the T-values listed in line 525 for the particular value of $t = 20$. Then, the next group of five α values also corresponds to each of the T-values in line 525, but for the particular value of $t = 30$, etc., up to $t = 80$.

From the Appendix, it can be observed that there is good agreement between calculated and expected results, i.e., probable mechanism and E, when values of α possess four significant figures (SF). This agreement was still good when three SF were used for α. However, when only two SF were employed for α, there was little agreement; thus, the probable mechanism and its corresponding value of E (kcal mol^{-1}) are given in the following for the mechanisms A2, F1, R2, D3, respectively: A4, 12.5; A2, 14.9; R2, 30.0; A4, 5.6. From the preceding, it can be perceived that there were changes in mechanism (and E) for all but the R2-mechanism. Thus, in utilizing the computer procedure described above, it is necessary that α-values possess an accuracy of 3 or more SF to obtain reliable results.

APPENDIX

A computer printout of various theoretical ITG data (lines 525-565, see the text for explanation) and the results of their computer analysis for the most probable mechanisms and corresponding E-values.

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525  DATA   440,445,450,455,460: REM   TEMPS. USED (K) FOR A2-MECH. AND DA
     TA IN #535

535  DATA  .01632,.03073,.05668,.1020,.1779,.03635,.06781,.1230,.2150,.356
     4,.06370,.1174,.2082,.3498,.5431,.09774,.1772,.3056,.4896,.7059,.1377
     ,.2449,.4085,.6204,.8284,.1826,.3177,.5107,.7324,.9092,.2315,.3931,.6
     069,.8213,.9564
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.1495	12.4
A3/(-LN(1-A))^(1/3)	.12215	16.6
A2/(-LN(1-A))^(1/2)	1.06E-03	24.9
R2/1-(1-A)^(1/2)	4.15988	43
R3/1-(1-A)^(1/3)	2.92352	45.3
F1/-LN(1-A)	.40485	49.8
D1/A^2	12.08173	78.6
D2/A+(1-A)LN(1-A)	8.94984	84.4
D4/1-(2A/3)-(1-A)^(2/3)	7.43564	86.8
D3/(1-(1-A)^(1/3))^2	4.26744	91.7

PROB. MECHNSM.: A2/(-LN(1-A))^(1/2) WITH DIFF.= 1.056E-03 & E= 24.9 KCAL/MOL

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540  DATA  430,435,440,445,450: REM   TEMPS. USED (K) FOR F1-MECH. AND DAT
     A IN #545

545  DATA  .1066,.1553,.2215,.3080,.4154,.1556,.2237,.3131,.4244,.553,.201
     9,.2865,.394,.5212,.6582,.2456,.3443,.4653,.6017,.7387,.287,.3973,.52
     82,.6687,.8002,.3261,.4461,.5838,.7244,.8472,.363,.4909,.6327,.7707,.
     8832
```

MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.22383	7.5
A3/(-LN(1-A))^(1/3)	.24343	10
A2/(-LN(1-A))^(1/2)	.20637	15
R2/1-(1-A)^(1/2)	2.14328	25
R3/1-(1-A)^(1/3)	1.46174	26.7
F1/-LN(1-A)	1.65E-03	30
D1/A^2	5.77323	42.9
D2/A+(1-A)LN(1-A)	4.29803	47.7
D4/1-(2A/3)-(1-A)^(2/3)	3.57993	49.7
D3/(1-(1-A)^(1/3))^2	2.10612	53.6

PROB. MECHNSM.: F1/-LN(1-A) WITH DIFF.= 1.648E-03 & E= 30 KCAL/MOL

```
550  DATA  425,430,435,440,445: REM   TEMPS. USED (K) FOR R2-MECH. AND DAT
     A IN #555

555  DATA .0732,.1096,.1617,.2347,.3343,.1088,.162,.2372,.3404,.4761,.1436
     ,.2128,.3091,.4381,.6009,.1778,.262,.3775,.5281,.7087,.2113,.3096,.44
     23,.6102,.7996,.244,.3557,.5035,.6844,.8735,.2761,.4001,.5612,.7508,.
     9305
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MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.4581	9
A3/(-LN(1-A))^(1/3)	.71193	11.9
A2/(-LN(1-A))^(1/2)	1.28469	17.8
R2/1-(1-A)^(1/2)	2.24E-03	30
R3/1-(1-A)^(1/3)	.97828	31.7
F1/-LN(1-A)	2.98112	35.1
D1/A^2	3.42727	51.9
D2/A+(1-A)LN(1-A)	1.27576	56.9
D4/1-(2A/3)-(1-A)^(2/3)	.24055	58.9
D3/(1-(1-A)^(1/3))^2	1.93794	63

PROB. MECHNSM.: R2/1-(1-A)^(1/2) WITH DIFF.= 2.245E-03 & E= 30 KCAL/MOL

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560  DATA  455,460,465,470,475: REM  TEMPS. USED (K) FOR D3-MECH. AND DATA
      IN #565

565  DATA  .3711,.4421,.5203,.604,.6905,.4393,.519,.6045,.6929,.78,.4929,.
     5781,.6674,.7567,.8404,.5371,.6259,.7169,.8049,.8835,.5749,.666,.7572
     ,.8426,.9151,.6077,.7002,.7907,.8727,.9385,.6367,.7298,.819,.897,.956
     1
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MECHNSM.	DIFF.	E (K/M)
A4/(-LN(1-A))^(1/4)	.06045	5.6
A3/(-LN(1-A))^(1/3)	.16462	7.5
A2/(-LN(1-A))^(1/2)	.43694	11.2
R2/1-(1-A)^(1/2)	.83375	15.5
R3/1-(1-A)^(1/3)	.21249	17.5
F1/-LN(1-A)	1.26885	22.1
D1/A^2	2.98315	21.7
D2/A+(1-A)LN(1-A)	2.06962	27.1
D4/1-(2A/3)-(1-A)^(2/3)	1.42718	29.7
D3/(1-(1-A)^(1/3))^2	3.95E-03	35

PROB. MECHNSM.: D3/(1-(1-A)^(1/3))^2 WITH DIFF.= 3.955E-03 & E= 35 KCAL/MOL

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 71 (1983) 281.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 60 (1983) 251.
3 L. Reich and S.S. Stivala, Thermochim. Acta, 80 (1984) 185.
4 L. Reich and S.S. Stivala, Thermochim. Acta, 81 (1984) 377.
5 L. Reich and S.S. Stivala, Thermochim. Acta, 88 (1985) 485.