Thermochimica Acta, 81 (1984) 377–380
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XI *

LEO REICH and S.S. STIVALA

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

(Received 15 June 1984)

In a previous publication [1], the present authors presented a computer algorithm (and program) whereby one of ten theoretically possible solid-state decomposition mechanisms could be discerned using non-isothermal TG data. Further, the corresponding value of activation energy could be determined concurrently. In the present paper, isothermal TG data will be analyzed, using a similar computer algorithm, to again distinguish one of ten theoretically possible solid-state decomposition mechanisms and to simultaneously obtain the corresponding value of the rate constant (k).

THEORY

For an isothermal decomposition reaction, we may write

$$g(\alpha)/t = k \tag{1}$$

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), for any particular possible mechanism postulated, various values of k can be obtained from various α–t data pairs. Thus, an average k value ($\bar{k}$) can be readily calculated for each mechanism postulated along with its mean deviation (MD). We may then define the percent deviation (PD) as

$$\text{MD} \times 100/\bar{k} = \text{PD} \tag{2}$$

The mechanism which possesses the lowest value of PD is then considered to be the most probable mechanism (its $\bar{k}$ value has already been determined).

RESULTS AND DISCUSSION

The following ten theoretical mechanisms were examined to ascertain which one of them conformed best to the isothermal TG data: A4, A3 and

* For Part X see ref. 2.

0040-6031/84/$03.00

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).

In the Appendix is given a computer printout of the various isothermal TG data employed (cf. lines 500–540) along with results of their computer analysis. The most probable mechanisms are listed with corresponding values of $\bar{k}$ and PD. From the Appendix, it can readily be observed that the agreement between calculated and expected results is excellent. It may also be noted here that the data, with the exception of those in line 520, were generated by theoretical means.

APPENDIX

A computer printout of various isothermal TG data (α–t) used (lines 500–540) and the results of their computer analysis for the most probable mechanisms and corresponding average rate constants.

```
500  DATA .4124,10,.5613,20,.6664,30,.7475,40,.8133,50,.8676,60,.9127,70,.
     9500,80: REM   D2, K=.010, 8-PRS.

MECHSM   K-VALUE              %-DEVN
---------------------------------------

A4====>.0338952968====>18.9911878
A3====>.0340216939====>17.2654217
A2====>.0345137944====>13.909139
R2====>.0135595156====>9.02079859
R3====>.0100310131====>7.73949864
F1====>.0381143822====>4.93793298
D1====>.01381104====>2.89291754
D2====>9.99894344E-03====>2.6934621E-03
D4====>2.60105988E-03====>1.19533117
D3====>3.64051596E-03====>3.44233729

THE MOST PROBABLE MECHANISM IS: D2, WITH K= .01, AND %-DEVN.= 2.7E-03

510  DATA  .203,10,.377,20,.523,30,.645,40,.743,50,.822,60,.883,70,.928,80
     : REM   BROWN, R3, K=.0073, 8PRS.

MECHSM   K-VALUE              %-DEVN
---------------------------------------

A4====>.0300664678====>16.1936974
A3====>.0291535619====>13.6515201
A2====>.0278199407====>8.90285136
R2====>9.96465117E-03====>.953987643
R3====>7.29269758E-03====>.0142080549
F1====>.0270494522====>2.01454737
D1====>9.36890034E-03====>7.00188943
D2====>6.70486861E-03====>8.36863233
D4====>1.73422147E-03====>8.86106603
D3====>2.39428878E-03====>9.7297303

THE MOST PROBABLE MECHANISM IS: R3, WITH K= 7.3E-03, AND %-DEVN.= .0142
```

```
520  DATA .153,10,.283,20,.4,30,.5,40,.58,50,.65,60,.71,70,.755,80: REM
     FROST/PEARSON, F1, K=.0175, 8 PRS.

MECHSM   K-VALUE              %-DEVN
------------------------------------------

A4====>.0272067152====>16.8289571
A3====>.025467354====>14.4780037
A2====>.0225812939====>10.0572745
R2====>7.15196691E-03====>1.42518514
R3====>5.05763082E-03====>.80848164
F1====>.0172134763====>.441527509
D1====>5.75313638E-03====>7.41386123
D2====>3.69726118E-03====>8.32401447
D4====>9.04671116E-04====>8.63745683
D3====>1.10250522E-03====>9.21253905

THE MOST PROBABLE MECHANISM IS: F1, WITH K= .0172, AND %-DEVN.= .4415
```

```
530  DATA .007968,10,.061995,20,.19426,30,.4007,40,.63212,50,.82236,60,.93
     569,70: REM    A3, K=.02, 7-PRS.

MECHSM   K-VALUE              %-DEVN
------------------------------------------

A4====>.0223460729====>4.8335898
A3====>.0199999614====>2.35637539E-05
A2====>.0172209765====>6.8660057
R2====>5.60100019E-03====>13.267537
R3====>4.15554843E-03====>13.3702135
F1====>.0160000145====>13.5714369
D1====>5.32008239E-03====>14.2686659
D2====>3.97754937E-03====>14.2742826
D4====>1.05348142E-03====>14.2761147
D3====>1.53335036E-03====>14.2791069

THE MOST PROBABLE MECHANISM IS: A3, WITH K= .02, AND %-DEVN.= 0
```

```
540  DATA  .06059,10,.2212,20,.4302,30,.6321,40,.7904,50,.8946,60,.9532,70
     : REM  A2, K=.025, 7-PRS.

MECHSM   K-VALUE              %-DEVN
------------------------------------------

A4====>.0286990473====>10.6034405
A3====>.0270701192====>6.65762921
A2====>.0249995949====>6.04068104E-04
R2====>8.607793E-03====>9.17932069
R3====>6.41371E-03====>9.69312326
F1====>.0249985669====>10.7138947
D1====>8.25491498E-03====>13.6503961
D2====>6.22286092E-03====>13.8555464
D4====>1.65733214E-03====>13.9242951
D3====>2.44659808E-03====>14.0374755

THE MOST PROBABLE MECHANISM IS: A2, WITH K= .025, AND %-DEVN.= 6E-04
```

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 73 (1984) 165.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 80 (1984) 185.