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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XX

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INTRODUCTION

For an "n-order" unimolecular decomposition involving isothermal TG (ITB), we can write [1]

$$\left[\left[1-(1-\alpha_1)^{1-n}\right]/\left[1-(1-\alpha_2)^{1-n}\right]\right]-(t_1/t_2)=0 \qquad (1)$$

which can be employed with two different pairs of α–t data, and where n is the reaction order, α is the degree of decomposition and t is the reaction time.

The aim of this paper is to employ a devised computer procedure which will ascertain the value of n (and subsequently rate constant k) from eqn. (1) and to determine the effect of changes in the number of significant figures of the data upon these values.

RESULTS AND DISCUSSION

Average values (AVG) of the left-hand side (LHS) of eqn. (1) were determined for the various pairs of ITG data for a particular value of n. Values of n were then initially incremented by 0.10001 and subsequently by smaller values (after an approximate value of n had been estimated). This procedure was carried out until a minimum AVG was obtained (which occurred either with a change in sign of the LHS, Tables 1 and 2, or without a sign change, Table 3). The value of n corresponding to the minimum AVG was considered to be the appropriate value for n. Once n had been

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TABLE 1

Results from a computer analysis of eqn. (1) for AVG and n using theoretical ITG data ($\alpha - t$) [2]

AVG	Reaction order (n)
550.59×10^{-4}	0.100
464.47×10^{-4}	0.200
373.54×10^{-4}	0.300
277.71×10^{-4}	0.400
176.92×10^{-4}	0.500
711.91×10^{-5}	0.600
$394.32 \times 10^{-5}(-)$	0.700
711.91×10^{-5}	0.600
603.47×10^{-5}	0.610
494.55×10^{-5}	0.620
385.13×10^{-5}	0.630
275.23×10^{-5}	0.640
164.84×10^{-5}	0.650
539.76×10^{-6}	0.660
$573.80 \times 10^{-6}(-)$	0.670
539.76×10^{-4}	0.660
428.60×10^{-6}	0.661
317.44×10^{-6}	0.662
206.19×10^{-6}	0.663
948.61×10^{-7}	0.664
$164.00 \times 10^{-7}(-)$	0.665

Minimum AVG $= 164.00 \times 10^{-7}(-)$ and $n = 0.665$
Value of $k = 2.185756 \times 10^{-2}$.

estimated, an average value of k was then obtained from the various data pairs using the expression

$$k = \left[1 - (1 - \alpha)^{1-n}\right]/(1 - n)t \tag{2}$$

In Tables 1–3, various final values of n and k obtained by the preceding computer procedure are shown. In Table 1, the ITG theoretical data [2] gave values of n and k of 0.665 and 0.0219 respectively (theoretical values are 2/3 and 0.022). When the number of significant figures (s.f.) for α was reduced to 2, the following values of n and k were obtained, respectively 0.648 and 0.0203.

In Tables 2 and 3, derived values of AVG and n along with their final values, utilizing various data sources, are shown [3,4]. In the former table, when the s.f. for α was reduced from 3 to 2, values of n and k changed to 0.945 and 0.00641 respectively. In the case of the latter table, when the s.f. for α was 3 or 4, there was no change in the values of n and k. However, when the s.f. was reduced to 2, although the value of n remained as 1.000, the value of k decreased to 0.007932 (dy^{-1}).

TABLE 2

Results from a computer analysis of eqn. (1) for AVG and n using isothermal data ($\alpha - t$) [3]

AVG	Reaction order (n)
820.21×10^{-4}	0.100
734.82×10^{-4}	0.200
645.05×10^{-4}	0.300
550.83×10^{-4}	0.400
452.15×10^{-4}	0.500
349.00×10^{-4}	0.600
241.46×10^{-4}	0.700
129.61×10^{-4}	0.800
136.03×10^{-4}	0.900
$106.03 \times 10^{-4}(-)$	1.000
136.03×10^{-5}	0.900
178.02×10^{-6}	0.910
$100.80 \times 10^{-5}(-)$	0.920
178.02×10^{-6}	0.910
595.20×10^{-7}	0.911
$586.56 \times 10^{-7}(-)$	0.912

Minimum AVG = $586.56 \times 10^{-7}(-)$ and $n = 0.912$
Value of $k = 0.0062886$.

TABLE 3

Results from a computer analysis of eqn. (1) for AVG and n using isothermal data ($\alpha - t$) [4]

AVG	Reaction order (n)
786.46×10^{-5}	0.100
730.09×10^{-5}	0.200
673.66×10^{-5}	0.300
617.25×10^{-5}	0.400
560.78×10^{-5}	0.500
504.16×10^{-5}	0.600
447.70×10^{-5}	0.700
391.11×10^{-5}	0.800
334.18×10^{-5}	0.900
0.00	1.000
221.72×10^{-5}	1.100
0.00	1.000
270.15×10^{-5}	1.010
0.00	1.000
267.66×10^{-5}	1.001

Minimum AVG = 0.00 and $n = 1.000$
Value of $k = 7.95756 \times 10^{-3}$.

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