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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XII

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INTRODUCTION

For an "n-order" unimolecular decomposition which involves isothermal TG (ITG), we can obtain

$$1-(1-\alpha)^{(1-n)}=k(1-n)t \tag{1}$$

where n = reaction order, α = conversion, t = reaction time, and k = reaction constant. A computer procedure was recently presented for the estimation of n and k [1], in which an n-order mechanism was assumed to be applicable. Several procedures have also been reported using ITG whereby one of various theoretically possible solid-state mechanisms could be ascertained [2–4].

The aim of this paper is to modify and thereby extend a computer procedure [5], previously presented for the estimation of n and activation energy (E) from non-isothermal TG (NITG) data, to the determination of n and k from ITG data utilizing eqn. (1).

RESULTS AND DISCUSSION

The main modifications of the previously reported computer procedure [5] for ascertaining n and E from NITG data were as follows. The dependent variable (Y) was now the left-hand side of eqn. (1) and the independent variable (X) was now set equal to t. Also, the number of data sets for a least-squares treatment was now one more than previously used (two data sets were previously used to determine Y and X). Otherwise, a similar approach was employed as in the previous computer procedure. Thus, in the expression

$$Y=A_1+A_2X \tag{2}$$

$A_2/(1-n)$ is equal to k and A_1 should possess a value of zero (theoretically). By utilizing successively increasing values of n and a least-squares treatment,

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TABLE 1

Results from the computer analysis of eqn. (1) for intercept, reaction constant, and reaction order, using theoretical ITG data [6]

500 Data 0.203,10, 0.377,20, 0.523,30, 0.645,40, 0.743,50, 0.822,60, 0.883,70, 0.928,80

Intercept	Rate const.	Reaction order
0.071704	0.014996	0.300001
0.069275	0.015145	0.310001
0.066863	0.015296	0.320001
0.064468	0.015449	0.330001
0.062091	0.015604	0.340001
0.059732	0.015761	0.350001
0.057393	0.01592	0.360001
0.055074	0.016081	0.370001
0.052776	0.016243	0.380001
0.0505	0.016408	0.390001
0.048246	0.016575	0.400001
0.046016	0.016744	0.410001
0.04381	0.016915	0.420001
0.041628	0.017088	0.430001
0.039473	0.017263	0.440001
0.037345	0.01744	0.450001
0.035244	0.01762	0.460001
0.033172	0.017802	0.470001
0.03113	0.017986	0.480001
0.029119	0.018173	0.490001
0.02714	0.018361	0.500001
0.025193	0.018553	0.510001
0.02328	0.018746	0.520001
0.021402	0.018942	0.530001
0.01956	0.019141	0.540001
0.017756	0.019342	0.550001
0.01599	0.019546	0.560001
0.014263	0.019752	0.570001
0.012577	0.019961	0.580001
0.010934	0.020172	0.590001
$9.333E-03$	0.020387	0.600001
$7.778E-03$	0.020604	0.610001
$6.268E-03$	0.020824	0.620001
$4.806E-03$	0.021046	0.630001
$3.393E-03$	0.021272	0.640001
$2.03E-03$	0.0215	0.650001
$7.19E-04$	0.021732	0.660001
$-5.39E-04$	0.021966	0.670001

Intercept, k and n are, respectively: $-5.39033339E-04$, 0.0219659954, 0.670001

Intercept	Rate const.	Reaction order
$7.19E-04$	0.021732	0.660001
$5.91E-04$	0.021755	0.661001
$4.63E-04$	0.021778	0.662001
$3.36E-04$	0.021802	0.663001
$2.09E-04$	0.021825	0.664001
$8.3E-05$	0.021848	0.665001
$-4.2E-05$	0.021872	0.666001

Intercept, k and n are, respectively: $-4.23281454E-05$, 0.0218718697, 0.666001 values of A_1 could readily be ascertained from ITG data. Values of n and k were considered to be final when the absolute values of A_1 was closest to zero. Thus, the starting value of n (0.100001, so that n cannot be exactly equal to unity, in which case eqn. (1) is no longer valid) was initially incremented (values of 0.01 were now used) until the value of A_1 changed sign. At this point, the value of n corresponding to the lower absolute value of A_1 was noted. Then a new starting value of n ($n - 0.01$) was incremented in steps of 0.001 until there was again a change in sign of A_1. Final refined values of n and k were taken as those values which corresponded to the lower absolute value of A_1. This method was tested using theoretical [6] as well as experimental [7] ITG data.

In Table 1 are presented theoretical ITG data (line No. 500) along with intercept (A_1), rate constant ($A_2/(1-n)$), and reaction order (n) (in order to conserve space, the starting value used for n was 0.300001). From this table it can be seen that final values of k and n were 0.0219 and 0.666, respectively (theor., 0.022 and 2/3). Also, by the preceding computer method, experimental ITG data for the hydrolysis of diacetone alcohol, using sodium hydroxide in excess, afforded the following values of k and n, respectively, 0.0172 and 0.97 (theor., 0.0175 and 1). From the preceding, it can be readily observed that the computer method, which was previously satisfactorily used for NITG data, could also be satisfactorily utilized for ITG data when appropriate modifications were instituted.

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