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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES

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With the advent of and the ready access to programmable calculators and desk-size computers, previous laborious and time-consuming iterations can now be accomplished with facility. In this respect may be mentioned methods presented previously by the authors [1,2] for the estimation of kinetic parameters, i.e. activation energy, E, and reaction order, n, from TG and DTA traces. In these iteration procedures, the criterion used for acceptable values of E and n, under the conditions employed, was that the final value of n should yield values of E whose mean (or standard) deviation was the lowest calculable. Other criteria investigated for use in estimating E and n were: linearity or linear correlation coefficients (r) [3—7] and the minimum standard deviation from a least-squares fit of a best straight line [8,9]. In the present paper, an iteration method will be introduced wherein parameter values for E and n will be obtained by computer using another criterion.

THEORY

By assuming the validity of the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\mathrm{RH}} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

it was previously shown [1] that the following expression could be derived for TG traces

$$\ln \frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}}\left(\frac{T_2}{T_1}\right)^2 = -\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{2}$$

where α is the degree of conversion, T is the absolute temperature (K), A is a frequency factor, and RH is a constant heating rate. If we let Y equal the left-hand side of eqn. (2) and $X = 1/T_1 - 1/T_2$, then in the equation

$$Y = A_1 + A_2X \tag{3}$$

$-A_2$ is equal to E/R and A_1 should possess a value of zero. By employing successively increasing values of n and a least-squares treatment, values of

A_1 could readily be determined by computer using TG data. Values of n and A_2 ($-E/R$) were considered to be final when the absolute value of A_1 was closest to zero. This criterion disregards the value of r (thus, the final values of r may be high or low).

TESTING THE METHOD

The starting value of n (0.1) was initially incremented in steps of 0.1 (actually, 0.100001, so that n cannot be exactly equal to unity, in which case eqn. (1) is no longer valid) until the values of A_1 changed sign.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 ($n - 0.1$) was incremented in steps of 0.01 until there again was a change in sign of A_1. Final refined values of n and A_2 were taken as those values corresponding to the lower absolute value of A_1. This method was initially tested using theoretical data and, subsequently, TG data for sodium bicarbonate, teflon, and magnesium hydroxide.

In Table 1 are given values of A_1, $-A_2$, n, and r for theoretical TG data previously reported [1] (all subsequent TG data were obtained from this reference). From Table 1, it is evident that final values of n and E/R should be 0.50 and 13987, respectively (theoretical values, 0.50 and 14000). Although the absolute value of r was high for this final value of n, this may not apply for other cases, as will be observed in the following. TG data for sodium bicarbonate, teflon, and magnesium hydroxide will now be tested.

In the following are listed the last two values of A_1 used in the determination of parameter value, A_1, and the corresponding values of $-A_2$, n, and r:

TABLE 1

Values of A_1, $-A_2$, n, γ from theoretical TG data [1]

A_1	$-A_2$	n	$-r$
1.3941	60 570	0.1	0.948
1.1121	51 195	0.2	0.949
0.7886	40 408	0.3	0.954
0.4193	28 055	0.4	0.970
−0.0004	13 987	0.5	1.000
0.4193	28 055	0.40	0.970
0.3796	26 728	0.41	0.972
0.3395	25 384	0.42	0.975
0.2988	24 022	0.43	0.978
0.2577	22 642	0.44	0.982
0.2160	21 245	0.45	0.985
0.1738	19 830	0.46	0.989
0.1310	18 397	0.47	0.993
0.0878	16 945	0.48	0.996
0.0440	15 475	0.49	0.999
−0.0004	13 987	0.50	1.000

for sodium bicarbonate, 0.0266, —0.0011; 13186, 12258; 0.84, 0.85; —0.681, —0.648; for teflon, 0.0022, —0.0016; 33720, 33647; 1.08, 1.09; —0.996, —0.996; for magnesium hydroxide, 0.0007, —0.0005; 27350, 27301; 1.47, 1.48; —0.978, —0.978. From the preceding, final values of *E* ($\times 10^{-3}$) and *n* are: for sodium bicarbonate, 24.5 and 0.85 (lit. [1], 22—25 and 0.79—0.83); for teflon, 67.3 and 1.09 (lit. [1], 66—68 and 1); for magnesium hydroxide, 54.6 and 1.48 (lit. [1], 53 and 1.35—1.6).

The results indicate that the criterion used in this paper resulted in reasonably satisfactory values of *E* and *n* for the materials tested. By using a computer, such results can be readily obtained in a matter of seconds.

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