Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART III

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In Parts I and II [1,2], kinetic parameters, i.e. activation energy, E, and reaction order, n, were determined from TG data by means of a computer assuming that the following "n-order" expression was valid

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

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.

It is now further assumed that the integral of the Arrhenius function can be satisfactorily estimated by the 4th degree rational approximation (RA) [3]

$$T \cdot \exp(-x) \cdot \frac{(x^3 + 18x^2 + 88x + 96)}{(x^4 + 20x^3 + 120x^2 + 240x + 120)} \tag{2}$$

where $x = E/RT$. Upon integration of eqn. (1) and employment of eqn. (2)

$$LHS = RHS \tag{3}$$

where $LHS \equiv [1 - (1-\alpha_1)^{1-n}]/[1 - (1-\alpha_2)^{1-n}]$ and $RHS = (RA)_{T_1}/(RA)_{T_2}$.

An algorithm will now be developed for the estimation of E and n from TG data. For any particular value of E and for any particular value of n, various values of LHS and RHS can be obtained for the various α–T data pairs (NN). Denoting the sum of these values for LHS and RHS by TL and TR, respectively, we may define percent deviation (PD) as

$$PD = \frac{|TL - TR|}{(NN - 1)} \cdot 100 \tag{4}$$

Maintaining E constant and incrementing n over a range of values, various PD-values can be obtained. When the lowest value of PD is attained, corresponding values of E and n are stored, E is incremented and a range of n-values are used again to obtain additional values of PD. When another lowest value of PD is attained, corresponding E- and n-values are also stored. The two stored PD's are then compared and E- and n-values corresponding to the lowest PD [PD (min)] are considered as tentative final values [E(min) and n (min), cf. Table 1]. Final values of E and n are those

TABLE 1

Values of E, E(min), n(min), and PD(min) for theoretical TG data [4]

No	E-value compared	E (min)	n (min)	PD (min)
1	25	25	0.30	0 20
2	$25\frac{1}{2}$	25	0 30	0 20
3	26	26	0 35	0.11
4	$26\frac{1}{2}$	$26\frac{1}{2}$	0 40	0 074
5	27	$26\frac{1}{2}$	0 40	0 074
6	$27\frac{1}{2}$	$26\frac{1}{2}$	0 40	0 074
7	28	28	0 50	0 041
8	$28\frac{1}{2}$	28	0 50	0 041
9	29	28	0 50	0 041
10	$29\frac{1}{2}$	28	0 50	0 041
11	30	28	0 50	0 041
12	$30\frac{1}{2}$	28	0 50	0 041
13	31	28	0 50	0 041

which correspond to the lowest PD attainable over the entire E-range used.

In Fig. 1 is shown a plot of PD versus n for various E-values using theoretical TG data [4]. Values of n ranged from 0.1 (actually, 0.10001, so that n cannot be exactly equal to unity, in which case eqn. (3) is no longer valid) to 2.0 for various values of E (27 to 30 kcal mole^{-1}). From this figure, it can be observed that as the E-value is increased, the value of n, at which PD is at a minimum, either increases or remains virtually constant. Thus, for the following values of E, the corresponding values of n are given at the lowest attainable PD: 27, 0.4; 28, 0.5; 29, 0.6; 30, 0.6. Obviously, after a minimum PD has been attained for a certain pair of E and n values, there is no need to increment n for the particular value of E.

Since values of E can vary over a considerable range, it is necessary to introduce a method whereby an approximate initial value can be estimated. At low values of α, it can be readily shown that

$$E \cong \frac{RT_1T_2}{T_1 - T_2} \ln\left(\frac{\alpha_1}{\alpha_2}\right)$$ (5)

Thus, two values of E were initially calculated using low values of α corresponding to the initial 3 pairs of α–T values. An average E-value was then determined and this value was rounded to the nearest kcal mole^{-1} (E_A). The range of E-values to be investigated was then established as $E_A - 3$ to $E_A + 3$ kcal mole^{-1} in increments of 0.5 kcal mole^{-1}. The initial range of n-values to be employed was from 0.1 to 2 using increments of 0.05. However, the computer time was drastically reduced when after reaching the lowest value of PD for a particular value of E, E was incremented, and the new starting value of n was that attained at this value of PD (cf. Fig. 1). As
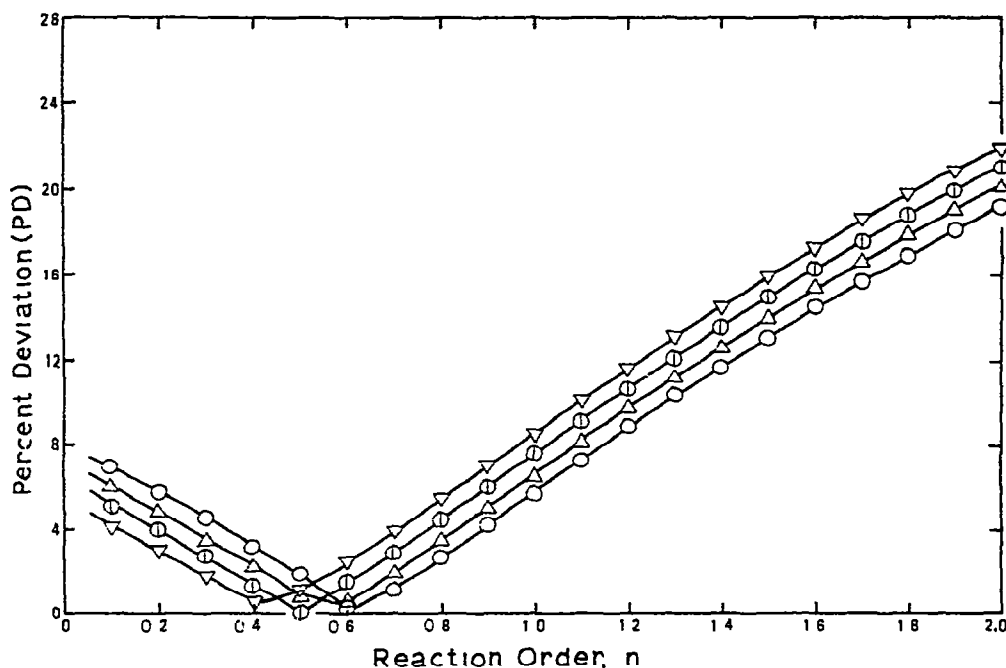
Fig 1 Percent deviation (PD) vs n for various E-values (kcal mole^{-1}) $\triangledown$, 27, $\oplus$, 28, $\triangle$, 29, $\bigcirc$, 30

previously indicated, final values of E and n were those corresponding to the lowest PD attainable over the entire range of E-values employed.

TESTING THE METHOD

In Table 1 are given values of E (min) and n (min) which correspond to the lowest value of PD as compared with PD's from various E-values over the range of 25–31 kcal mole^{-1} for theoretical data [4]. From this table, it can be readily seen that at the lowest attainable PD (0.041), the final values of E and n are, respectively, 28 kcal mole^{-1} and 0.50 (theoretical values, 28 and 0.50). In this manner, TG data [4] for sodium bicarbonate, teflon, and magnesium hydroxide were tested. The following gives, in order, the E-range used (0.5 kcal mole^{-1} increments), the final E- and n-values, and the corresponding lowest PD attained: for sodium bicarbonate, 20–26, 24, 0.80, 0.012 (ref. [4], 22–25 and 0.79–0.83); for teflon, 62–68, 65, 0.95, 0.015 (ref. [4], 66–68 and 1); for magnesium hydroxide, 51–57, 53, 1.35, 0.015 (ref. [4], 53–55 and 1.35–1.6.).

In order to refine the results, a program loop was established whereby the increments for E and n were reduced to 0.2 kcal mole^{-1} and 0.02, respectively. Further, the starting value of E was now equal to the "final" value of E less 0.8 kcal mole^{-1} and ranged over 1.6 kcal mole^{-1}; the starting value of n w s now the "final" value of n less 0.10. Under these conditions, the following value of E, n, and PD were obtained, respectively: for theoretical data, 28, 0.50, 0.041; for sodium bi-

carbonate, 24, 0.80, 0.012; for teflon, 64.6, 0.93, 0.00057, for magnesium hydroxide, 53.8, 1.41, 0.0018. These values of E and n are in good agreement with results previously obtained.

The preceding results indicate that the algorithm used in this paper afforded reasonably satisfactory values of E and n for the materials tested. For this reason and in view of the approximations involved in the method, further refinements (i.e. the use of smaller increments), at the expense of increased computer time, do not appear to be warranted.

OTHER APPROXIMATIONS

Finally, it may be mentioned that approximations other than eqn. (2) may be equally suitable. Thus, when the following approximation was employed ($9 < x < 174$) [5]

$$T \cdot \exp(-x) \cdot \frac{(x^3 + 6.055x^2 - 57.412x - 674.567)}{(x^4 + 8.02x^3 - 49.313x^2 - 841.655x - 1699.066)} \tag{6}$$

the following values of E, n, and PD were obtained, respectively (without any refinement): for theoretical data, 28, 0.50, 0.035; for sodium bicarbonate, 24, 0.80, 0.0026, for teflon, 65, 0.95, 0.018; for magnesium hydroxide, 53, 1.35, 0.014. These results for E and n are identical with those obtained (without refinement), using approximation (2). However, the lower PD for theoretical data obtained using eqn. (6) indicates that eqn. (6) may be a somewhat more suitable approximation than eqn. (2) for the algorithm utilized in this paper.

Recently, another approximation was presented ($x > 5$) [6] whereby

$$\text{RHS} \equiv \frac{\exp(-S/T_1)}{\exp(-S/T_2)} \tag{7}$$

where $S = f(E)$ (cf. ref 6). Based on the theoretical values obtained (no refinement) by this approximation for E, n, and PD, respectively, i.e., 28, 0.50, 0.044, it appears that eqn (7) is a less satisfactory approximation than eqns (2) or (6). (The theoretical data afforded refined values of 27.2, 0.44, 0.044, respectively.)

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