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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XVI

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In a previous communication [1], expressions were developed which were utilized to analyze data from non-isothermal TG (NITG) curves, at relatively low conversions, for activation energy (E). Such an analysis led to the estimation of E alone, virtually independent of reaction order (n) values. In this paper, expressions have been developed with the same goal in mind, to determine values of E irrespective of the n-values. To this end, rational approximations and an iterative computer procedure were employed.

THEORY

It was previously reported [2–4] that the integral of the Arrhenius function could be satisfactorily represented by rational expressions such as,

$$T\exp(-x)\frac{(x^2+10x+18)}{(x^3+12x^2+36x+24)} \tag{1}$$

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

as well as the equation which was derived using integration by parts,

$$T\exp(-x)\frac{1}{x}\left[1-\frac{2!}{x}+\frac{3!}{x^2}+\ldots+\frac{(-1)^N(N+1)!}{x^N}\right],\ N=2 \tag{3}$$

where $x=E/RT$. The suitability of eqns. (1)–(3) as well as of other expressions for the estimation of E and n has been reported [2,3]. By employing any of eqns. (1)–(3), we may readily write for an n-type unimolecular or pseudo-unimolecular decomposition by means of NITG, at relatively low conversions [1]

$$\ln\left[\frac{(\alpha/T)}{(RA)}\right]=-\frac{E}{RT}+\ln\left(\frac{A}{\beta}\right) \tag{4}$$

where A = pre-exponential factor, β = constant heating rate, and α = degree

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of conversion. The term RA can denote any of the moieties in eqns. (1)–(3) which follow the term $T \exp(-x)$.

RESULTS AND DISCUSSION

A computer program was devised which allowed the determination of E/R from eqn. (4) by means of iteration. Since values of x are invariably larger than 5, an initial value of $x = 5$ was arbitrarily assumed. Using a least squares treatment (LSQ), where the left-hand side of eqn. (4) was the dependent variable and the independent variable $-1/T$, $\alpha-T$ data provided an initial value of E/R. This value of E/R was then used in the RA-term so that another value of E/R could be obtained by means of LSQ. This iterative procedure was rapid and continued until the absolute value of the difference between a value of E/R and its previous value divided by the value of E/R was less than 0.0001. When this limiting condition was met, the value of E/R was considered to be the proper value (generally, less than 4 iterations were required). Along with E/R, a correlation coefficient (CR) was obtained. The preceding method was applied to low conversion data for octamethylcyclotetrasiloxane (OMCS) [5], teflon [5], magnesium hydroxide [6], as well as theoretical data [7].

In the case of OMCS, 5 pairs of $\alpha-T$ data were used where α varied from 0.005 to 0.106. A value of $E = 10.3$ kcal mol^{-1} was obtained along with CR = 0.9955 (lit. [5,8], $E = 11.7$ and 12.7 ± 1.5). For teflon, 5 pairs of data afforded values of $E = 65.1$ kcal mol^{-1}, CR = 0.9997 (lit. [5], $E = 66$–68 kcal mol^{-1}). The procedure was also applied to NITG data for magnesium hydroxide to test the effect of an apparent high value of n, ca. 1.5. For 7 α-values ranging from 0.03 to 0.12 (trace 1), $E = 58.4$ kcal mol^{-1} and CR = 0.9967 (lit. [2,3,6,8–11], $E = 53$–57 kcal mol^{-1}). Finally, employing 12 pairs of theoretical $\alpha-T$ data where α ranged from 0.007 to 0.1001, $E = 29.8$ and CR = 0.9999 (lit. [7], $E = 30$ kcal mol^{-1}). From the preceding, it can be seen that the method employed was rapid and provided reasonably satisfactory values of E even though n-values ranged from ca. 0.3 to 1.5.

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