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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART II.

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In Part I [1], kinetic parameters, i.e. activation energy, E, and reaction order, n, were determined from TG data by means of a computer using an expression

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

which was obtained by integration, where α is the degree of conversion and T is the absolute temperature (K). An algorithm was employed whereby values of E and n, obtained by iteration, were considered to be final when the absolute value of the intercept was closest to zero. The results obtained indicated that the utilization of such an algorithm gave satisfactory values of E and n for several materials tested. In the present paper, the same algorithm will be applied to TG data using the more exact expression

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

where $R_T \equiv \mathrm{d}\alpha/\mathrm{d}T$.

Values of E and n calculated from eqn. (2) were found to be sensitive to small changes in R_T. Thus, it was necessary to determine R_T with a high degree of accuracy as a function of α. To this end, a multiple regression analysis was carried out with α as a function of temperature. Polynomials of 6-, 14-, and 20-degree were employed. It was necessary that the correlation coefficient be 0.99999 or higher in order to achieve reasonably satisfactory results. Thus, in Table 1, it can be seen that when a 6-degree polynomial was employed for theoretical TG data (this data plus that for sodium bicarbonate and teflon were obtained from ref. 2), a correlation coefficient (r) of only 0.9997+ was obtained; the resulting values of E and n, i.e. 31 kcal mole^{-1} and 0.65, respectively, were not in good agreement with the corresponding theoretical values, 28 and 0.5. Upon increasing the polynomial degree to 14 and 20, the values of r, E, and n obtained were 1.00000+, 28.5, 0.51 for 14-degree, and 0.99999+, 27.5, 0.49 for 20-degree. These results were in satisfactory agreement with the theoretical values. However, the use of 14- or 20-degree polynomials does not ensure the desired value of r. For example, when all the data for teflon were used, the 14- and 20-degree poly-

TABLE 1

Summary of results using polynomials

Data pair used	Material	Polynomial degree	r	E (kcal mole^{-1})		n	
				Calcd.	Reptd.	Calcd.	Reptd.
All	Theoretical	6	0.9997+	31	28	0.65	0.5
All	Theoretical	14	1.00000+	28.5	28	0.51	0.5
All	Theoretical	20	0.99999+	27.5	28	0.49	0.5
8/12	Teflon	14	1.00002+	63	66—68	0.88	1—1.1
8/12	Teflon	20	0.99999+	63	66—68	0.86	1—1.1
6/7	Sodium bicarbonate	14	0.99999+	23	22—25	0.74	0.79—0.85
6/7	Sodium bicarbonate	20	0.99999+	23	22—25	0.73	0.79—0.85
All	OMCS	14	0.99999+	13	11.7—12.7	0.38	0—0.17
All	OMCS	20	0.99999+	12	11.7—12.7	0.20	0—0.17

nomials afforded the values of r of 0.99989 and 0.99947, respectively. In order to raise the value of r, four pairs of α—T end-values were omitted from the final calculations. In this manner, the preceding values of r were increased to 1.00002 and 0.99999, respectively. Table 1 indicates that 8 out of 12 original data pairs were employed in the final calculations of kinetic parameters for teflon and that 6 out of 7 were used for sodium bicarbonate. In reducing the amount of data to raise r to an acceptable level, it is important to maintain data both before and after the inflection point of the TG curve in order to maintain TG curve characteristics.

When the acceptable value of r has been attained, R_T values may be calculated using a delta procedure, i.e. $\Delta\alpha/\Delta T$. Such a procedure was employed whereby values of α were calculated over a 0.1 degree temperature range, using the polynomial expressions, i.e. $T + 0.05$ and $T - 0.05$. After estimating values of R_T for the data, the data extremities were then not included in the final calculations, otherwise, calculations are involved which extend beyond the validity of the polynomial expressions.

From Table 1, it can be seen that 14- and 20-degree polynomials afford values of E and n for teflon which are lower than reported values. In the case of octamethylcyclotetrasiloxane (OMCS), the n value, using the 14-degree polynomial, appears to be too high in comparison with reported values [3,4] (data for OMCS was obtained from ref. 3). Values of E and n for sodium bicarbonate appear to be satisfactory.

The preceding indicates that, although eqn. (2) is more exact than eqn. (1), the use of the latter leads to more satisfactory values of E and n, to less computer time consumption, and does not involve data omission (in order to reach acceptable levels of r values).

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