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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART VII

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In Part V [1], it was shown that for two TG curves at different heating rates (RH) and for constant alpha values

$$\frac{(\mathrm{RH})_2}{(\mathrm{RH})_1} = \frac{Z_2}{Z_1} \tag{1}$$

where, the Z ratio can be satisfactorily expressed by employing the equation

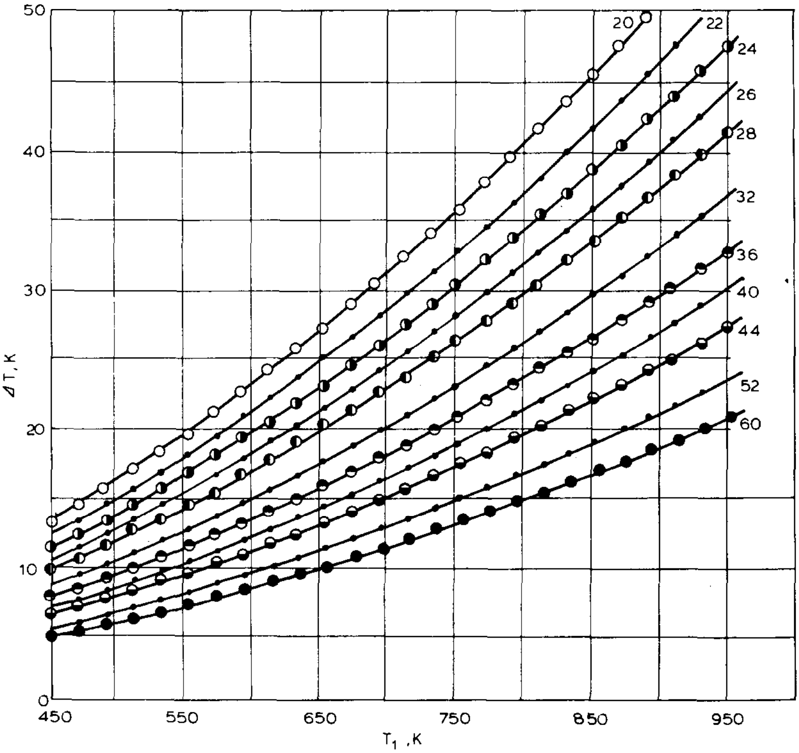

Fig. 1. $T_2 - T_1$ (ΔT) vs. T_1 for various activation energies. The activation energies (kcal mole^{-1}) are given on the curves.

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[2,3]

$$Z = (T\exp(-x)/x)(1 - (2/x) + (6/x^2)) \tag{2}$$

where, $x = E/RT$. By arbitrarily maintaining a heating rate ratio of two, various values of T_2 and T_1 [corresponding to $(\mathrm{RH})_2$ and $(\mathrm{RH})_1$, respectively] could be calculated for various values of E (kcal mole^{-1}). In Fig. 1 are depicted plots of ΔT $(T_2 - T_1)$ versus T_1 (K). Values of E ranged from 20 to 60 kcal mole^{-1} while T_1 ranged from 450 to 950 K. In order to maintain clarity, not all the values of E employed in the calculations were represented in the plots. From these plots, it can be seen that the separation of the curves becomes smaller with decreasing T_1 values and with increasing E values. Thus, it is not recommended that low T_1 and/or high E values be utilized in the procedure described later for the estimation of E.

Values of T_2 and T_1 at the various E values were correlated by means of the cubic equation

$$T_2 = A + BT_1 + CT_1^2 + DT_1^3 \tag{3}$$

Values of the constants in eqn. (3) for various E values are given in Table 1. In all cases, the correlation coefficient was higher than 0.999999 (26 pairs of

TABLE 1

Constants in eqn. (3) for various values of E

E (kcal mole^{-1})	A	B	$C \times 10^5$	$D \times 10^9$
20	−2.49540449	1.01150631	5.10587775	1.96830341
22	−0.993727586	1.00574693	5.20762182	0.147132375
24	1.31542339	0.994176101	6.58784782	−9.05107922
26	0.428040928	0.99752277	5.76787103	−7.17588724
28	−1.24951292	1.00594173	3.98819772	1.01715051
30	−1.9651116	1.00895833	3.29083517	2.83323962
32	−0.503973469	1.00207428	4.01749238	−1.53544816
34	−1.05680301	1.00463219	3.39241893	0.525413668
36	0.684422269	0.99695089	4.27632949	−4.44706011
38	1.9515379	0.99086589	4.99536542	−8.62678114
40	−2.45869118	1.0128685	1.36622113	8.77843284
42	0.768967635	0.996817824	3.69999064	−3.4397402
44	−3.34885624	1.0162094	0.690480017	10.2156143
46	1.52261879	0.993002447	4.02084119	−6.20999426
48	1.11545327	0.995361023	3.51579808	−4.2627996
50	−2.19498921	1.00980971	1.33818597	5.48166097
52	−0.506360535	1.00189453	2.43103692	−0.340082271
54	−0.923650033	1.00424133	1.93090191	1.92479696
56	0.0208466326	1.00028414	2.39343854	−0.575469922
58	0.357977211	0.998692345	2.53282272	−1.47900473
60	0.71003422	0.996557347	2.84298561	−3.6103537

$T_1 - T_2$ values were utilized in most cases). By entering experimental values of T_1 and T_2 into a computer and employing values of the constants in Table 1, it became relatively simple and rapid to estimate corresponding values of the standard error of estimate (S.E.E.), That value of E was chosen whose corresponding value of S.E.E. was the lowest.

TESTING THE METHOD

Theoretical values of T_1 and T_2 at various constant alpha values and $(RH)_2/(RH)_1 = 2$ have already been presented [1]. Ten arbitrarily selected pairs of $T_1 - T_2$ values were utilized (T_1 ranged from 750 to 804 and T_2 from 774 to 832 K). In the following are listed in order the values of E (kcal mole^{-1}) and corresponding S.E.E., respectively: 20, 12.02; 22, 8.803; 24, 6.135; 26, 3.774; 28, 1.736; 30, 0.02712; 32, 1.549; 34, 2.923; 36, 4.148; 38, 5.231; 40, 6.290; 42, 7.178; 44, 7.993; 46, 8.753; 48, 9.465; 50, 10.12; 44, 7.993; 46, 8.753; 48, 9.465; 50, 10.12; 52, 10.72; 54, 11.27; 56, 11.78; 58, 12.27; 60, 12.70. From the preceding, it is apparent that $E = 30$ (within 1 kcal mole^{-1}), which agrees well with the theoretical value of E. When the theoretical values of T_2 were rounded to the nearest degree and the resulting data analyzed, the lowest value of S.E.E. (0.3669) was attained again at a value of $E = 30$ kcal mole^{-1}.

Ozawa [4,5] presented TG data for the decomposition of nylon 6 at various RHs and at various constant alpha values (T_1 ranged from 592 to 621 and T_2 from 605 to 640 K for the data utilized in the present paper). Data were selected wherein $(RH)_2/(RH)_1 = 1.96$ and were analyzed by computer. In the following are listed in order values of E (kcal mole^{-1}) and S.E.E., respectively: 20, 7.496; 22, 5.519; 24, 3.922; 26, 2.643; 28, 1.772; 30, 1.583; 32, 2.000; 34, 2.614; 36, 3.273; 38, 3.916; 40, 4.419; 42, 5.031; 44, 5.401; 46, 5.994; 48, 6.385; 50, 6.761; 52, 7.144; 54, 7.468; 56, 7.776; 58, 8.089; 60, 8.362. From the preceding, $E = 30$ within 1 kcal mole^{-1} (reported value, 29.7 ± 1.5).

An advantage of the preceding computer method is that E values can be obtained independent of mechanism. However, due to limitations already described and to the need for highly accurate TG temperature data, this method may perhaps be best utilized for corroborative purposes.

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 55 (1982) 385.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 52 (1982) 337.
3 L. Reich and S.S. Stivala, Thermochim. Acta, 53 (1982) 121.
4 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
5 L. Reich and S.S. Stivala, Elements of Polymer Degradation, McGraw-Hill, New York, 1971, pp. 106–107.