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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART V

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It can be readily shown [1] that

$$g(\alpha) = [A/(\mathrm{RH})] \int_0^T \exp(-x)\, \mathrm{d}T \tag{1}$$

where $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$, RH = constant heating rate, A = frequency factor, T = temperature (K), α = conversion, and $x = E/RT$. Denoting the integral on the right-hand-side (R.H.S.) of eqn. (1) by Z, and for two runs at different RHs, we may write (for constant alpha values)

$$\frac{(\mathrm{RH})_1}{(\mathrm{RH})_2} = \frac{Z_1}{Z_2} \tag{2}$$

Further, it was previously indicated [2–3] that the Z ratios could be satisfactorily expressed by employing either of the equations for Z

$$Z = (T\exp(-x)/x)[1 - (2/x) + (6/x^2)] \tag{3}$$

or

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

Using eqns. (2) and (3) or (4), the value of E can readily be estimated for various values of alpha by means of an iteration procedure using a computer. Thus, if we let the L.H.S. = $(\mathrm{RH})_1/(\mathrm{RH})_2$ and T_1 and T_2 correspond to temperatures obtained from TG curves using $(\mathrm{RH})_1$ and $(\mathrm{RH})_2$, respectively, at any particular alpha value, then the initial value of E can be incremented until Z_1/Z_2 becomes greater than the L.H.S. in eqn. (2) (say at a value of $E = V_1$). At this point, if the absolute value of (Z_1/Z_2 − L.H.S.) is less than the corresponding value obtained for the previous E value (say at $E = V_2$), then the preferred E value is simply V_1; otherwise, $E = V_2$. This procedure is then continued for the various selected values of alpha. The final E value may be expressed as an average value (EA) plus or minus the mean deviation.

After establishing a value of EA, the value of the reaction order, n, can be estimated as follows for an "n-order" type reaction. Thus, for any one of the TG traces

$$\frac{Z_1}{Z_2}=\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}} \tag{5}$$

Since E is now known, we can employ the TG data to estimate Z_1/Z_2 for any pair of values of T_1 and T_2. The corresponding values, α_1 and α_2, are then used in the R.H.S. of eqn. (5). Now, an arbitrarily selected initial value of n (say 0.10001) is incremented until the R.H.S. is greater than the L.H.S. The final value of n is selected in a manner previously described for E. Thus, an average value of n is obtained for the TG data. Another set of n-values can then be obtained from the second TG curve. An overall average value of n can then be estimated.

TESTING THE METHOD

Theoretical data was generated using the values $n = 1$, $E = 30$ kcal mole^{-1}, $(\mathrm{RH})_1 = 1$ deg min^{-1} (for run 1), $(\mathrm{RH})_2 = 2$ (for run 2), $A = 3.30 \times 10^6$ min^{-1}, and the expression

$$\alpha = 1-\exp(-(AT\exp(-x)/((\mathrm{RH})x))\cdot(1-(2!/x)+(3!/x^2) \\ -(4!/x^3)+(5!/x^4)-(6!/x^5)) \tag{6}$$

In this manner, values of $\alpha - T$ were obtained for $(\mathrm{RH})_1$ and $(\mathrm{RH})_2$. In order to obtain corresponding values of T at any particular value of alpha [using $(\mathrm{RH})_1$ data as a basis], the data obtained using $(\mathrm{RH})_2$ was subjected to interpolation. Thus, in the following are given values of alpha and the corresponding values of T(K) [for $(\mathrm{RH})_1$ and $(\mathrm{RH})_2$, respectively]: 0.0892995, 720, 739.25; 0.106759, 726, 748.90; 0.127036, 732, 755.29; 0.150427, 738, 761.69; 0.177215, 744, 768.08; 0.207653, 750, 774.44; 0.241938, 756, 780.81; 0.280188, 762, 787.18; 0.322415, 768, 793.57; 0.368489, 774, 799.96; 0.418108, 780, 806.36; 0.470777, 786, 812.76; 0.525786, 792, 819.17; 0.582210, 798, 825.59; 0.638930, 804, 832.01; 0.694677, 810, 838.43; 0.748103, 816, 844.84; 0.797885, 822, 851.25; 0.842837, 828, 857.66; 0.882027, 834, 864.06; 0.914884, 840, 870.53; 0.941257, 846, 877.00; 0.961424, 852, 883.49.

Since values of E can vary over a considerable range, a method previously described [2] was employed whereby an approximate initial value of E can be estimated. At low values of alpha

$$E \sim \frac{2T_1T_2}{T_1-T_2}\ln(\alpha_1/\alpha_2) \tag{7}$$

Thus, two values of E were initially calculated using low values of alpha corresponding to the initial 3 pairs of $\alpha - T$ values [from the data using $(RH)_1$]. An average E value was then determined and this value was then rounded to the nearest kcal mole^{-1} (EV). The range of E values to be investigated was then established as EV $-$ 2 to EV $+$ 2 kcal mole^{-1} in increments of 0.050. When either eqn. (3) or (4) was used, identical results were obtained. In the following are listed the value or range of alpha and the corresponding values of E, respectively: 0.150427–0.241938, 30.01; 0.280188 –0.368489, 30.06; 0.418108–0.582210, 30.01; 0.63893–0.882027, 29.96; 0.914884, 29.91; 0.941257, 29.86; 0.961424, 29.81. The average E and its mean deviation was 29.98 ± 0.05 kcal mole^{-1} (for 20 values of alpha).

Now that E is known, the L.H.S. of eqn. (5) can be estimated for various values of T for any particular TG curve. The corresponding alpha values can be inserted in the R.H.S. of eqn. (5). By varying n from 0.10001 [so that n cannot be exactly equal to unity in which case eqn. (5) would not be valid] to 2 in increments of 0.01 until the R.H.S in greater than the L.H.S., values of n could be determined as previously described. The following n values were obtained [(RH) = 1]: 1.0000 (19 times); for (RH) = 2, 1.040 (once), 0.9400 (once), 0.9700 (twice), 1.0000 (six times), 1.0100 (eight times), 0.9900 (once). The latter (RH) value afforded n (ave.) $= 0.9995 \pm 0.0135$.

The preceding computer method was also applied to TG data presented by Brown and Phillpotts [1] and Ozawa [4]. In the following are given, in order, average values of E calculated from Brown's theoretical data along with the number of significant figures used for the interpolated values of T: 24.05 ± 0.095, 5; 24.01 ± 0.13, 4; 24.00 ± 0.66, integral values (theoretical value of $E = 23.90$). Average values of n were then estimated for the two (RH)s used: 0.66 ± 0.02 and 0.69 ± 0.02 (theoretical value of $n = 2/3$). Ozawa presented TG data for the decomposition of nylon 6. In the following are listed, in order, average values of E followed by the two (RH) values (deg h^{-1}) used in the calculation: 29.0 ± 2.7, 14.3, 28; 32.2 ± 2.9, 28, 48; 28.9 ± 1.4, 48, 140. Using a graphical procedure, a value of E equal to 29.7 ± 1.5 kcal mole^{-1} was obtained [5].

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