Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART VIII

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For an 'n-order' reaction, we may write

$$Rt = A \exp(-E/RT)(1-\alpha)^n \tag{1}$$

where Rt = reaction rate, A = frequency factor, E = activation energy, T = temperature(K), α = conversion, n = reaction order and R = gas constant (2 cal mole^{-1} K^{-1} used).

From eqn. (1), it can be readily shown that for two TG curves obtained at different constant heating rates, (RH), [1,2]

$$n = \frac{ART}{AAT} \tag{2}$$

where ART = $\int_1^2 \ln(Rt/Rt, 1)dT$; AAT = $\int_1^2 \ln[(1-\alpha)/(1-\alpha_1)]dT$ and the temperature limits are identical for the two TG curves.

Similarly, it can be shown that

$$\frac{E}{R} = \frac{ARA}{ATA} \tag{3}$$

where ARA = $\int_1^2 \ln(Rt/Rt, 1)d\alpha$; ATA = $\int_1^2 [(1/T_1)-(1/T)]d\alpha$ and the conversion limits taken are identical for the two TG curves. From eqns. (2) and (3), It is readily apparent that values of the kinetic parameters, n and E, can be obtained by means of numerical integration. In this respect, a computer was employed using Simpson's One-Third Rule (SOTR) [3]. In previous determinations of n by eqn. (2), non-computer procedures were used to measure areas [1,2]. Such areas can be determined by a computer using SOTR in a matter of seconds.

TESTING THE METHOD

Equation (2) was tested for the evaluation of n by means of a computer and SOTR. To this end, theoretical data were generated using $n = 1$, $E = 30$ kcal mole^{-1}, $A = 3.30 \times 10^6$ min^{-1}, $(RH)_1 = 1$, $(RH)_2 = 2$. Thus, in the

following are given in order $T(K)$ and the corresponding α_1, α_2, and Rt, 1 and Rt, 2 ($\times 10^2$, min^{-1}): 720, 0.08930, 0.04569, 0.2692, 0.2821; 726, 0.1068, 0.05489, 0.3136, 0.3319; 732, 0.1270, 0.06567, 0.3631, 0.3886; 738, 0.1504, 0.07828, 0.4175, 0.4529; 744, 0.1772, 0.09293, 0.4763, 0.5152; 750, 0.2077, 0.1099, 0.5389, 0.6054; 756, 0.2419, 0.1293, 0.6043, 0.6941; 762, 0.2802, 0.1516, 0.6708, 0.7907; 768, 0.3224, 0.1768, 0.7365, 0.8948; 774, 0.3685, 0.2053, 0.7986, 1.005; 780, 0.4181, 0.2372, 0.8542, 1.120; 786, 0.4708, 0.2725, 0.8996, 1.237; 792, 0.5258, 0.3114, 0.9315, 1.353; 798, 0.5822, 0.3536, 0.9464, 1.464; 804, 0.6389, 0.3991, 0.9411, 1.566; 810, 0.6947, 0.4474, 0.9136, 1.654; 816, 0.7481, 0.4981, 0.8637, 1.721; 822, 0.7979, 0.5504, 0.7925, 1.763; 828, 0.8428, 0.6036, 0.7036, 1.774; 834, 0.8820, 0.6565, 0.6017, 1.751; 840, 0.9149, 0.7083, 0.4934, 1.691; 846, 0.9413, 0.7576, 0.3863, 1.595; 852, 0.9614, 0.8036, 0.2878, 1.464.

Using the preceding 23 data sets, ART = 63.526 and AAT = 63.601 so that, $n = 0.999$. Upon reducing the number of data sets to 15 (750–834K) (note that the number of data sets in SOTR should be an odd value, otherwise the SOTR usually employed requires additional terms), the value of $n = 1.000$. When the previous 15 data sets were used and the α and Rt values possessed 3 significant figures (s.f.), $n = 0.999$; for 2 s.f., $n = 1.019$. When all the preceding data were employed and the α and Rt values possessed 3 s.f., $n = 0.998$; for only 2 s.f., $n = 1.024$. It can be seen from the preceding [assuming $T(K)$ possesses an accurate value] that even for 2 s.f. for alpha and Rt, the value of n was reasonably close to the theoretical value.

In order to evaluate E/R from eqn. (3) by means of SOTR, theoretical data were generated for various values of α [$n = 1$, $E = 30$, $A = 3.30 \times 10^6$ min^{-1}, $(RH)_1 = 1$, $(RH)_2 = 2$]. Below are listed, in order, α and the corresponding values of $T_1(K)$ [at $(RH)_1$], $T_2(K)$ [at $(RH)_2$], Rt, 1 and Rt, 2 ($\times 10^2$, min^{-1}): 0.1, 723.8, 746.6, 0.2968, 0.5589; 0.15, 737.9, 761.6, 0.4165, 0.7840; 0.2, 748.6, 772.9, 0.5242, 0.9842; 0.25, 757.3, 782.2, 0.6186, 1.162; 0.3, 764.9, 790.3, 0.7029, 1.320; 0.35, 771.6, 797.5, 0.7739, 1.455; 0.4, 777.9, 804.1, 0.8362, 1.567; 0.45, 783.7, 810.3, 0.8841, 1.657; 0.5, 789.2, 816.2, 0.9184, 1.722; 0.55, 794.6, 822.0, 0.9405, 1.765; 0.6, 799.9, 827.6, 0.9474, 1.775; 0.65, 805.2, 833.3, 0.9379, 1.758; 0.7, 810.6, 839.0, 0.9101, 1.703; 0.75, 816.2, 845.0, 0.8611, 1.611; 0.8, 822.3, 851.5, 0.7895, 1.476; 0.85, 829, 858.7, 0.6862, 1.283; 0.9, 837.1, 867.4, 0.5450, 1.019.

Using the preceding 17 data sets, ARA = 0.50304 and ATA = 3.3536 $\times$ 10^{-5}, so that $E/R = 15000.1$ cal mole^{-1}. When only 11 data sets were used ($\alpha = 0.25$–0.75), $E/R = 15000.0$. Using all the preceding data sets and 3 s.f. for the Rt values, $E/R = 14997.0$; 2 s.f. for Rt values yielded $E/R = 15260.4$. Maintaining 2 s.f. for Rt values, the following gives, in order, the value of E/R (kcal mole^{-1}) and the corresponding changes in $T(K)$: 15.34, rounded to the nearest degree; 15.30, 1 degree too high; 15.34, 2 degrees too high; 15.36, 5 degrees too high. From the preceding, when both values of T_1 and T_2 were increased by the same 1–5 degrees above the theoretical values, the

corresponding values of E/R did not vary much (15.3–15.4 kcal mole^{-1}) or differ much from the theoretical value. Also, rounding $T(K)$ to the nearest degree still gave a satisfactory value of E/R (15.3). However, when T_1 and T_2 were not varied from the theoretical value by the same amounts, much larger deviations from the theoretical value were obtained. Thus, using all the 17 data sets and 4 s.f. for the Rt values, the E/R values (kcal mole^{-1}) obtained are listed along with the corresponding $T(K)$ changes: 14.48, T_1 maintained but T_2 increased by 1 degree above the theoretical value; 13.99, T_1 maintained but T_2 increased by 2 degrees; 12.71, T_1 maintained but T_2 increased by 5 degrees.

REFERENCES

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