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COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART IX

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ABSTRACT

By applying the restriction that α (conversion) = constant to non-isothermal TG (NITG), isothermal TG (ITG) and a combination of both (NITG/ITG), various corresponding expressions have been derived for the evaluation of the activation energy, E. By means of a computer, all the expressions developed were tested against data which was generated from theoretical equations. Also, changes were made in the number of significant figures (s.f.) of data in order to ascertain their effects on values of E. Data were generated and tested for the three theoretical mechanisms, A_2, F_1 and R_2.

INTRODUCTION

In Part VIII [1], numerical integration was employed to estimate the kinetic parameters, activation energy, E, and reaction order, n, from non-isothermal TG (NITG) data. In this paper, numerical integration will again be employed to estimate E using different expressions for NITG. Subsequently, expressions will be presented for the estimation of E from isothermal TG (ITG) data, and from ITG data in conjunction with NITG data.

NON-ISOTHERMAL TG

Generally, we may write

$$d\alpha/T^2 = \{Z\exp(-x)f(\alpha)/[T^2(\mathrm{RH})]\}dT \tag{1}$$

where $x = E/RT$; α = fractional conversion; Z = pre-exponential factor; RH = rate of heating; T = temperature (K); R = gas constant; and $f(\alpha)$ = some function of conversion. Utilizing two TG curves at different values of RH, and maintaining the same conversion limits for both curves (T values obtained using constant α values), eqn. (1) can be used to obtain the

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following expression, upon integration and the use of natural logarithms

$$\ln[A(\mathrm{RH})/A_1(\mathrm{RH})_1] = -(E/R)(1/T - 1/T_1) \qquad (2)$$

where A and A_1 denote $\int_0^{\alpha} \mathrm{d}\alpha/T^2$ for RH and $(\mathrm{RH})_1$, respectively. From eqn. (2), it is apparent that once values of A and A_1 are obtained by means of numerical integration [as was carried out in this paper using a computer and Simpson's One-Third Rule (SOTR)], the value of E can then be readily obtained.

TESTING THE NITG METHOD

Three data sets were generated to evaluate eqn. (2) based on the following theoretically possible expressions for f(α), i.e., $[1-\alpha][-\ln(1-\alpha)]^{1/2}$ (A_2), $[1-\alpha]^{1/2}$ (R_2), and $[1-\alpha]$ (F_1) [2–4]. For the generation of the A_2 data, the following expressions were employed

$$\alpha = 1 - \exp(-RS) \qquad (3a)$$

$$RS = [(1-n)ZT\exp(-x)Q/(x(\mathrm{RH}))]^2 \qquad (3b)$$

$$Q = 1 - (2/x) + (6/x^2) - (24/x^3) + (120/x^4) - (720/x^5) \qquad (3c)$$

Utilizing (RH) = 1 or 2 deg min^{-1}, $n = 1/2$, $R = 1.987$, $Z = 3 \times 10^{10}$ min^{-1} and $E = 23.90$ kcal mol^{-1}, along with eqn. (3), the following values of α, T_1(K) (at RH = 1), and T_2(K) (at RH = 2) were obtained, respectively: 0.0001, 393.95, 402.55; 0.05, 435.68, 446.13; 0.10, 441.05, 451.77; 0.15, 444.35, 455.22; 0.20, 446.79, 457,80; 0.25, 448.77, 459.85; 0.30, 450.45, 461.63; 0.35, 451.94, 463.18; 0.40, 453.29, 464.60; 0.45, 454.55, 465.92; 0.50, 455.75, 467.16; 0.55, 456.88, 468.36; 0.60, 458.00, 469.53; 0.65, 459.10, 470.69; and 0.70, 460.22, 471.87. These values (when RH = 1), where comparable, appear to be in good agreement with those obtained for the A_2 mechanism using a fourth-order Runge–Kutta procedure [2].

From the preceding data and eqn. (2), the values of E (kcal mol^{-1}) obtained, the number of significant figures (s.f.) for T(K) and the conversion range used are 23.87, 5, 0.0001–0.70; 23.87, 5, 0.0001–0.70; 23.77, 4, 0.0001–0.70; 23.17, rounded to nearest degree, 0.0001–0.70, respectively. When 5 s.f. were used and the T values arbitrarily increased, the following values of E were obtained: 23.99 (T values incremented by 1), 24.10 (T values incremented by 2), 24.31 (T values incremented by 4). From the preceding, as the number of s.f. was decreased, the value of E decreased; however, as the values of T were uniformly increased, the value of E increased. Thus, it may still be possible to attain reasonably satisfactory values of E using eqn. (2) and SOTR even when relatively inaccurate T values are used, i.e., T values rounded to nearest degree, provided that fortuitously all these T values used are uniformly higher than the theoretical T values.

Values of α and T(K) were generated for the R_2 mechanism using $Z = 3.6 \times 10^{13}$ min^{-1}, (RH) = 3 or 6, and $E = 28.00$ kcal mol^{-1}. Again, using eqn. (2) and SOTR, the values of E (kcal mol^{-1}) obtained, the number of s.f. used for T(K), and the conversion range employed are 28.01, 5, 0.0001–0.70; 28.08, 4, 0.0001–0.70; 27.18, rounded to nearest degree, 0.0001–0.70, respectively. Similarly, corresponding values from data generated for the F_1 mechanism, using $Z = 3.3 \times 10^6$ min^{-1}, (RH) = 1 or 2 and $E = 30.00$ kcal mol^{-1}, were 30.11, 4, 0.000001–0.90; 30.07, 4, 0.001–0.90; 30.08, 4, 0.0001–0.90; 30.04, 4, 0.001–0.50; 30.06, 4, 0.0001–0.50; 30.10, 5, 0.0001–0.90; 30.07, 5, 0.0001–0.80; 30.06, 5, 0.0001–0.70; and 30.36, rounded to nearest degree, 0.0001–0.90, respectively. From the preceding it can be seen that as in the case of the A_2 mechanism, deviations from the expected values of E were greatest for the R_2 and F_1 mechanisms when the number of s.f. for T(K) was decreased from 4 or 5, and the rounded nearest degree was used. Also, changes in the conversion range used did not appreciably affect E values indicating that the data used was self-consistent, as would be anticipated. Arbitrary changes in the low theoretical initial values used for conversion and T(K) also did not affect E values appreciably. Thus, for example, when the low initial theoretical data values for the F_1 mechanism were arbitrarily changed from 0.0001, 555.7, 569.26 to 0.0001, 500.7, 515.76, the corresponding E values were 30.09 and 30.08 kcal mol^{-1}. When the conversion range used was 0.05–0.85, the value of E was 30.04, a relatively small change. Further, although the use of the value of 2 rather than 1.987 for R can affect values of the data, the final E values obtained using $R = 2$ or 1.987 were very similar. Finally, an advantage of the procedure for NITG used in this work is that the value obtained for E is independent of $f(\alpha)$; however, because of the apparent sensitivity of E values toward changes in T(K), this method is only recommended when highly accurate T measurments are attainable.

ISOTHERMAL TG

As for non-isothermal TG, expressions follow which employ the $\alpha =$ constant concept. Thus, for several ITG curves, α vs. t (time) at various temperatures, we may write

$$g(\alpha) = kt = k_1 \cdot t_1 = \ldots = C \tag{4}$$

where $C =$ constant for any particular value of α. From eqn. (4), there follows

$$\ln(t) = E/RT + \ln(K) \tag{5}$$

where $K =$ constant $= C/Z$. It can readily be seen from eqn. (5) that a plot of $\ln(t)$ vs. $1/T$ should yield a linear relation whose slope will yield the value of E.

TESTING THE ITG METHOD

Two data sets were generated for the evaluation of eqn. (5) involving the A_2 and F_1 mechanisms. For the A_2 mechanism, isothermal data were obtained using the parameters $Z = 3 \times 10^{10}$ min^{-1} and $E = 24.90$ kcal mol^{-1}. Thus, the following give values of α ranging from 0.1 to 0.8. For each value of α are listed five values of t (min), corresponding to the T values (K) 430, 440, 450, 460 and 470, respectively: 0.1, 98.14, 50.61, 26.87, 14.67, 8.217; 0.2, 142.8, 73.65, 39.11, 21.35, 11.96; 0.3, 180.6, 93.11, 49.45, 26.99, 15.12; 0.4, 216.1, 111.4, 59.17, 32.30, 18.09; 0.5, 251.7, 129.8, 68.93, 37.63, 21.08; 0.6, 289.4, 149.2, 79.25, 43.26, 24.23; 0.7, 331.8, 171.1, 90.85, 49.59, 27.78; 0.8, 383.6, 197.8, 105.0, 57.34, 32.11.

The preceding data were employed in conjunction with eqn. (5) to afford the following range of E values (3 and 4 s.f. for t): 24.88–24.91 kcal mol^{-1}. The agreement with the theoretical E values is excellent. As for the A_2 mechanism, ITG data were generated for the F_1 mechanism using $Z = 9 \times 10^6$ min^{-1} and $E = 25.00$ kcal mol^{-1}. When t values were employed to the nearest tenth of a minute, values of E ranged from 24.98 to 25.01 kcal mol^{-1}. When values of t to the nearest minute were used, $E = 24.46$. When 0.5 min was arbitrarily added to each theoretical t value, the value of E became 24.81. Thus, as for the NITG case, the number of s.f. used can affect values of E. However, the ITG method would appear to be more reliable than the NITG method since accurate values of t can readily be measured and the use of isothermal procedures should allow more accurate T values to be attained. As in the case of NITG, the ITG method can afford values of E independent of mechanism.

ITG/NITG

By maintaining concurrently the same limiting condition for a NITG trace and an ITG trace as in the sections on non-isothermal and isothermal TG, i.e., $\alpha = \text{constant}$, the following approximate expression can be readily derived

$$t = \left[RT^2/E(\text{RH})\right] \exp\left[-E(1/T - 1/T_K)/R\right] \tag{6a}$$

where t and T denote time and temperature (K), respectively, corresponding to any particular arbitrary value of α chosen for the ITG/NITG curves, T_K = temperature (K) employed in obtaining the ITG trace. Equation (6a) was obtained assuming that $Q = 1$ [cf. eqn. (3c)]. From eqn. (6a)

$$\ln(t/T^2) = -E/RT + B \tag{6b}$$

where $B = \text{constant} = \ln[R/E(\text{RH})] + E/R(T_K)$. From eqn. (6b), a plot of the logarithmic term vs. $1/T$ should afford a linear relation from whose slope the value of E can be obtained.

TESTING THE METHOD

The following parameters were used to obtain the ITG/NITG data for an F_1 mechanism: $Z = 9 \times 10^6$ min^{-1}, $E = 25.00$ kcal mol^{-1}, RH = 1. Data for two theoretical ITG curves were obtained using $T_K = 600$ and 620. In the following are given, in order, the values of α, T(K), t for $T_K = 600$, t for $T_K = 620$: 0.1, 585.7, 14.98, 7.615; 0.3, 617.8, 50.70, 25.78; 0.5, 636.7, 98.53, 50.10; 0.7, 653.4, 171.1, 87.02; 0.8, 662.5, 228.8, 116.3. From the preceding data, the value of E obtained at $T_K = 600$ and 620 was 24.91 kcal mol^{-1} using a computer to carry out a least-squares routine. When 3 s.f. were used for t and the rounded nearest degree for T, the value of E for both T_K values was 25.15 kcal mol^{-1}.

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