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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART VI

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It was previously indicated [1] that

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

where $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$, RH = constant heating rate, A = frequency factor, T = temperature (K), α = conversion, and $x = E/RT$.

For two TG curves obtained at different RHs, we may write from eqn. (1) (for T = constant)

$$\frac{(\text{RH})_2}{(\text{RH})_1} = \frac{g(\alpha_1)}{g(\alpha_2)} \tag{2}$$

where $g(\alpha) = -\ln(1-\alpha)$ for $n = 1$, and $[1-(1-\alpha)^{1-n}]/(1-n)$ for $n \neq 1$. This applies to an 'n-order' type reaction. By means of a computer, eqn. (2) can be employed to readily calculate values of reaction order, n, for various pairs of alpha values at any particular value of T [e.g. α_1 and α_2 from the $(\text{RH})_1$ and $(\text{RH})_2$ traces, respectively] using straightforward iteration. Thus, for instance, an initial value of n, say 0.10001, is chosen and from a pair of alpha values, the right-hand side (R.H.S.) of eqn. (2) is calculated [the left-hand side (L.H.S.) of eqn. (2) is known and is constant throughout the iteration]. Values of n are incremented until the R.H.S. becomes greater than the L.H.S. At this point, say $n = V_1$, if the absolute difference between the L.H.S. and the R.H.S. is less than the absolute difference between the L.H.S. and the immediately preceding value of the R.H.S., say at $n = V_2$, then $n = V_1$; otherwise, $n = V_2$. This iterative procedure is continued for the various pairs of α values and an average n value ($\bar{n}$) is calculated. The procedure may now be repeated using a smaller increment for n, say 0.01, and another initial value of n, say $n - 0.2$, in order to obtain a more refined $\bar{n}$ value.

From eqn. (2), it can be seen that for a constant value of $(\text{RH})_2/(\text{RH})_1$, the value of n is independent of temperature and only depends on the values of α_1 and α_2. In Fig. 1 is depicted a plot of values of α_1 and α_2 for various n values at a constant heating ratio of two. Values of α_2 ranged from 0.3 to 0.65 and corresponding values of α_1 ranged from 0.5 to 1. At lower values of α_2, the various curves become convergent. Thus, from eqn. (2), the slopes of the various curves in the figure can be written as

$$\text{Slope} = \frac{(\text{RH})_2}{(\text{RH})_1}\left[\frac{(1-\alpha_1)}{(1-\alpha_2)}\right]^n \tag{2a}$$

As the values of $\alpha \to 0$, the slope $\to (\text{RH})_2/(\text{RH})_1$, so that at relatively low α values it becomes very difficult to estimate n. The upper limit for α_2 is determined by the value of n. Thus, when $n = 1/3$, at $\alpha_2 = 0.628$, the value of $\alpha_1 = 0.994$. The utilization of Fig. 1 allows for a rapid estimation of n.

After the value of n has been determined, any one of the TG curves can be employed for the estimation of E. Thus, from eqn. (1)

$$\frac{g(\alpha_1)}{g(\alpha_2)}\,\frac{\text{T}_2}{\text{T}_1} = \frac{\text{Z}_1}{\text{Z}_2} \tag{3}$$

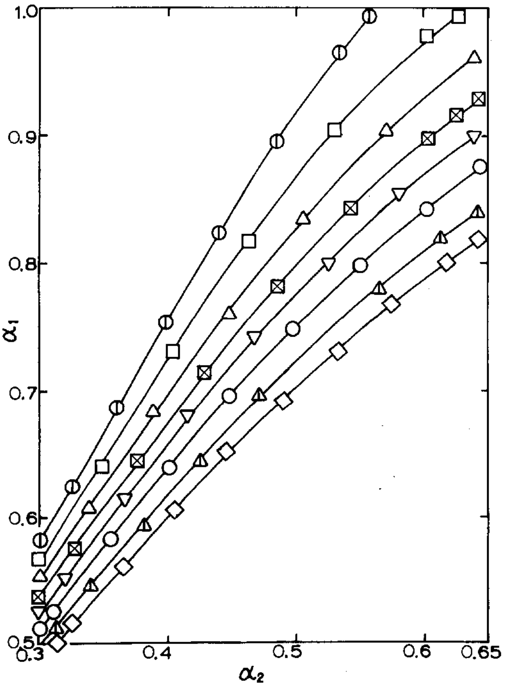

Fig. 1. Values of α_1 and α_2 at various TG isotherms for $(\text{RH})_2/(\text{RH})_1 = 2$. ⦶, $n = 1/6$; □, $n = 1/3$; △, $n = 1/2$; ⊠, $n = 2/3$; ▽, $n = 4/5$; ○, $n = 1$; ◬, $n = 5/4$; ◇, $n = 3/2$.

where $Z = [\exp(-x)/x]\ [1-(2/x)+(6/x^2)]$ and $x = E/RT$ [2,3]. Since values of E can vary over a wide range, a procedure previously described [2] was utilized whereby an approximate initial value of E can be estimated. At low values of α

$$E \sim [2T_1T_2/(T_1 - T_2)]\ \ln(\alpha_1/\alpha_2) \qquad (4)$$

Thus, two values of E can be initially calculated using low values of α corresponding to the initial three pairs of α–T values from one of the TG curves. An average E value was then determined and this value was rounded to the nearest kcal mole^{-1} (EA). The range of E values to be investigated was established as EA $-$ 2 to EA + 5 in increments of 0.1 kcal mole^{-1}. When the L.H.S. of eqn. (3) became greater than the R.H.S., a procedure similar to that described in the preceding was used to estimate the value of E for any pair of α–T values. This procedure was continued for the various α–T pairs and then an average E value ($\bar{E}$) was calculated.

TESTING THE METHOD

The preceding computer method for the estimation of n and E was tested using two sets of theoretical data. The first set was generated as described previously [1]. Using $n=1$, $E=30$ kcal mole^{-1}, $(\mathrm{RH})_1 = 1$, $(\mathrm{RH})_2 = 2$, $A = 3.30 \times 10^6$ min^{-1}, the following values of T and the corresponding values of α_1 and α_2 [from $(\mathrm{RH})_1$ and $(\mathrm{RH})_2$, respectively] are given in order: 720, 0.0892995, 0.0456937; 726, 0.106759, 0.0548859; 732, 0.127036, 0.0656746; 738, 0.150427, 0.0782771; 744, 0.177215, 0.0929252; 750, 0.207653, 0.109861; 756, 0.241938, 0.129332; 762, 0.280188, 0.151583; 768, 0.322415, 0.176845; 774, 0.368489, 0.205323; 780, 0.418108, 0.237182; 786, 0.470777, 0.272523; 792, 0.525786, 0.311368; 798, 0.582210, 0.353634; 804, 0.638930, 0.399109; 810, 0.694677, 0.447439; 816, 0.748103, 0.498107; 822, 0.797885, 0.550428; 828, 0.842837, 0.603562; 834, 0.882027, 0.656528; 840, 0.914884, 0.708254; 846, 0.941257, 0.757631; 852, 0.961424, 0.803592. In the following are given in order the average n value followed by its mean deviation, $\bar{E}$ followed by its mean deviation, and the number of significant figures (s.f.) used for α: 1.0000, 0, 30.0, 0, 6; 1.0004, 0.0017, 30.0, 0.02, 4; 1.004, 0.017, 30.05, 0.21, 3; 0.93, 0.18, 28.7, 2.4, 2.

From the preceding, it can be seen, as anticipated, that as the number of s.f. for α decreases, the mean deviation values increase and the deviations of E and n from their respective theoretical values also increase. For 2 s.f., the values of n ranged from ca. 0 to 1.4 (these limits correspond to the two lowest values of the α_1–α_2 pairs); similarly, the values of E (under these conditions) ranged from 24.4 to 33.5 kcal mole^{-1}. Thus, it is strongly recommended that at least 3 s.f. for α be employed for the iterative procedure or when using Fig. 1. Of course, the accuracy of the temperature values has been implicitly assumed.

The second set of data was generated [4] using a contracting volume model [$n = 2/3$, $E = 23.9$, $A = 1.8832 \times 10^{15}$ min^{-1}, $(RH)_1 = 0.257$, $(RH)_2 = 1$]. For this model, the preceding computer procedure is still applicable for the estimation of E and n. However, the data for the lowest three temperatures and the corresponding low values of α_1–α_2 pairs ($\alpha_2 = 0.008$–0.015 and $\alpha_1 = 0.03$–0.056) were not utilized (no value of n could be ascertained up to $n = 2$). Also, these low α values only possessed 1 and 2 s.f. Remaining values (2 and 3 s.f. for α) afforded the following values of E and n, respectively: 24.2 ± 0.2 kcal mole^{-1}, 0.68 ± 0.05.

This computer method was also applied to data for sodium bicarbonate (SB) at heating rates of 8.3 and 16.7 deg min^{-1} [5]. Values of α_2 used ranged from 0.36 to 0.65. By employing Fig. 1, $n = 0.72 \pm 0.05$; the computer procedure afforded $n = 0.70 \pm 0.05$ and $E = 21 \pm 3$ kcal mole^{-1} (these values are lower than those previously reported for SB (0.79–0.83 and 22–25) [2]). The present authors also subjected powdered SB (USP) to thermal analysis using TG. Similar values of n and E were obtained using the preceding computer method. However, since values of α were restricted to 0.3–0.65, eqn. (4) yielded very low EA values. Hence, values of E were tested from EA to an arbitrary EA + 20 kcal mole^{-1} (not as previously indicated for the theoretical data).

The preceding method has several severe limitations: at low α values it becomes very difficult to estimate n, as previously noted, due to convergence effects; values of α to be used are restricted to a relatively narrow range; and derived values are sensitive to small changes in α. Nevertheless, values of n can be rapidly estimated, irrespective of temperature (cf. Fig. 1).

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