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POSSIBILITY OF DERIVING KINETIC PARAMETERS FROM INTEGRATED DTA PEAKS

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Three DTA peaks (two endo and one exothermic) were replotted in the form of $\sum$ peak area. Δa, or $\sum$ peak magnitude, ΔT, as a function of temperature. The integral sigmoid curves were plotted in the form of $\log g(\alpha)$ *vs.* $1/T$ or $\log \frac{\log g(\alpha)}{T^2}$ *vs.* $1/T$. Both of the proposed summation methods gave satisfactory straight lines (F_1 function), characterized by the same activation energies, correlation coefficients and standard deviations. Integration of the peak areas by Simpson's rule resulted in the same values as obtained by the summation procedure. Analysis by the suggested integral method resulted in activation energies that show a logarithmic divergence relative to the magnitude of E_a estimated directly from the DTA peaks.

Analysis of DTA peaks is currently carried out with the object of deriving the associated activation energy and order of reaction. Most of the methods use the DTA peaks with the assumption of a certain order of reaction, the peak temperature, peak area and/or amplitude being correlated with the reaction temperature. In the present short report, a trial is made to employ the integrated DTA peak in association with some integral methods used in the analysis of nonisothermal TG traces. Integrated DTG peaks are also analyzed for the sake of comparison. The estimated activation energies are compared with those obtained from the original DTA and DTG peaks.

Analysis procedure

The DTA and DTG peaks of a previously investigated iron oxide hydrate [1, 2] were integrated by:

a) summation of each individual area strip (Δa) every 10 deg or 5 deg ($\sum \Delta a$) along the whole peak area; or

b) summation of the consecutive peak heights measured every 10 deg or 5 deg covering the whole peak ($\sum h$); or

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c) using the above measured peak heights (h_i) and applying Simpson's rule:

$$A_S = \frac{t}{3}[(h_0+h_n)+4(h_1+h_3\ldots h_{n-1})+2(h_2+h_4\ldots h_4)]$$

to obtain the peak area as a function of amplitude ($\sum h$). The calculated integrated peak areas or peak heights were plotted as the fraction reacted $\left(\alpha = \frac{\sum a_i}{A}\right)$ as a function of temperature. Here, α corresponds to the summated or integrated value up to the specified temperature referred to the integrated value. From the smoothed curve of α *vs.* T, values of T at intervals of 0.05 are selected for use in the next analysis. This involves plotting $\log g(\alpha)$ [3] or $\log\left[\frac{g(\alpha)}{T^2}\right]$ [4] *vs.* $1000/T$, and using a linear regression analysis based on the least squares method. The above-mentioned functions are denoted by (SS) and (CR) according to the methods proposed by Šatava and Škvára [3] or Coats and Redfern [4], respectively. An F_1 function ($n=1$) mechanism has been applied for the sake of simplicity as well as to allow comparison with the direct analysis of DTA or DTG peaks, which assumes essentially a first-order solid-state decomposition mechanism. In each case of analysis, the following parameters are estimated for the linear relationship: the correlation coefficient r, the standard error of the estimate S_e, and the activation energy E_a.

Results and conclusions

Table 1 summarized the results of analyzing two endothermic DTA peaks, an exothermic one, and two DTG peaks of the same material.

Analysis of the first dehydration step by both $\sum\Delta a$ and $\sum\Delta T$, using either the SS or the CR method, yields highly satisfactory straight lines. Thus, the linearity of the function tested by either method covers the whole range of fraction reacted (α = 0.05–0.95), and is characterized by a high mean correlation coefficient ($\bar{r}$ = 0.994423) and a low dispersion of the data ($\bar{S}_e = 4.63\times10^{-2}$). The mean activation energy, $\bar{E}$ = 38.6 kJ · mol^{-1}, is not much higher than the corresponding value estimated by direct analysis of modified CR method gives nearer values: while the integral area procedure yields the same E_a, the integrated amplitudes give a 20% higher value.

Analysis of the second dehydration peak by the proposed integral methods yields a better linear fit with the integrated amplitudes ($\bar{r}$ = 0.995044, $\bar{S}_e = 5.1\times10^{-2}$) than with the integrated area procedure ($\bar{r}$ = 0.961653, $\bar{S}_e$ = 12.9). A high mean activation energy is recorded, viz. 182.9 kJ · mol^{-1}, which is almost 70% higher

Table 1 Kinetic parameters obtained by applying the methods of Šatava and Škvára (SS), and modified Coats and Redfern (CR), on the integrated peaks of DTA and DTG

Procedure	Method	parameter	DTA 1	DTA 2	EXO	DTG 1	DTG 2
$\sum \Delta a$	SS	E_a (kJ·mol^{-1})	43.9	179.1	513.2	37.9	145.5
		$-r$	0.99356	0.96360	0.98974	0.99565	0.98938
		$S_e \times 10^2$	5.5	12.8	11.2	4.5	7.1
$\sum \Delta a$	CR	E_a (kJ·mol^{-1}	30.8	170.1	481.1	30.7	133.7
		$-r$	0.99091	0.95971	0.95378	0.97381	0.98236
		$S_e \times 10^2$	5.5	12.9	14.3	9.2	8.5
$\sum h$	SS	E_a (kJ·mol^{-1})	43.1	197.8	505.6	36.7	151.2
		$-r$	0.99629	0.99493	0.97247	0.99235	0.98654
		$S_e \times 10^2$	4.2	5.6	11.3	5.2	7.9
$\sum h$	CR	E_a (kJ·mol^{-1})	36.6	184.6	483.6	31.1	132.7
		$-r$	0.99414	0.99515	0.97665	0.98003	0.98846
		$S_e \times 10^2$	4.4	4.5	9.8	8.8	6.9
$\sum h$ Simpson	SS	E_a (kJ·mol^{-1})	45.6	214.2	506.8	46.4	156.2
		$-r$	0.99989	0.99545	0.95003	0.99968	0.98886
		$S_e \times 10^2$	0.74	4.6	17.5	1.2	7.2
$\sum h$ Simpson	CR	E_a (kJ·mol^{-1})	38.9	193.6	483.6	33.9	145.8
		$-r$	0.99561	0.98785	0.94805	0.99534	0.97853
		$S_e \times 10^2$	3.8	7.4	17.6	3.9	9.4
DTA DTG Peaks	Mean	E_a (kJ·mol^{-1})	30.9	115.1	219.8	36.4	101.9

than the estimate from direct analysis of the DTA peak. It should be mentioned that in addition to the first-order (F_1) mechanism, a diffusion-controlled D_3 mechanism equation was tested; it was found to exhibit a lower fit to the data (r = 0.943893, S_e = 20.7 × 10^{-2} and to yield a much higher activation energy, viz. 310 kJ·mol^{-1}.

As a means of comparison, the DTG peaks were replotted in the form of the suggested integrated peak area and amplitude method. These showed a satisfactory straight line fit ($\bar{r}$ = 0.986187, $\bar{S}_e$ = 7.19), with mean activation energies of 34.1 and 140.7 kJ·mol^{-1} for the first and second dehydration steps, respectively. The first value is in good agreement with whereas the second is ~40% higher than the values estimated from direct analysis of the DTG peak.

In conclusion:

a) Analysis by the proposed integrated peak method applies similarly to summation of either peak area or amplitude. This is true for both DTA and DTG peaks.

b) The suggested procedure leads to higher activation energies than the respective values calculated from the original DTA or DTG peaks. The difference between the two sets of values increases logarithmically as a function of the activation energy.

c) From the case subjected to this analysis, it seems unsuitable to apply the suggested procedure of peak integration to DTA, despite the fact that the data linearize satisfactorily to a straight line fit.

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