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Note

Kinetic parameters from DTA curves

LEO REICH AND S. S. STIVALA
Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030 (U.S.A.)
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Recently, the authors presented[1] a novel method for the estimation of kinetic parameters, activation energy (E) and reaction order (n), from thermogravimetric (TG) traces. In the present paper this method is extended to DTA traces for the evaluation of E and n. Materials studied were sodium bicarbonate, calcium oxalate monohydrate, and benzenediazonium chloride.

THEORY

Utilizing the well-known TG rate expression

$$\frac{d\alpha}{dT} = \frac{A}{(\mathrm{RH})} e^{-E/RT} (1 - \alpha)^n \tag{1}$$

it was previously shown[1] that the following equation can readily be derived for TG traces

$$\ln \frac{1 - (1 - \alpha_1)^{1-n}}{1 - (1 - \alpha_2)^{1-n}} \left(\frac{T_2}{T_1}\right)^2 = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2}$$

where, α is the degree of conversion, T is the absolute temperature (K), A is a frequency factor, and RH is a constant rate of heating. By assuming that the heat evolved in a small temperature interval is directly proportional to the weight of material reacting during that temperature rise, and that heat capacity terms are negligible in comparison with other terms, the following approximate expression can be obtained[2, 3]

$$(1 - \alpha) = \frac{a_T}{A_T} \tag{3}$$

where

$$a_T = \int_T^{T\infty} \Delta T \mathrm{d}T; \; A_T = \int_{T0}^{T\infty} \Delta T \mathrm{d}T \; (\Delta T \text{ is obtained experimentally from DTA curves}).$$

Substituting eqn. (3) into (2), there is obtained

$$\ln \frac{1-\left(\frac{\bar{a}_{T,1}}{A_T}\right)^{1-n}}{1-\left(\frac{\bar{a}_{T,2}}{A_T}\right)^{1-n}}\left(\frac{T_2}{T_1}\right)^2 = \frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{4}$$

For two pairs of given values of $\bar{a}_T/A_T$ and T, values of E/R can be calculated from eqn. (4) for various arbitrarily selected values of n. However, assuming uniqueness, only one pair of E,n values will be pertinent. By using other pairs of $\bar{a}_T/A_T$ and T values, other sets of values of E and corresponding n will be obtained. In all these sets, there should only be one pair of E,n values in common. However, such values would rarely, if ever, be expected to be exactly equal in practice, due to experimental limitations, impurities present in the sample, etc. Therefore, these values were taken as those whose standard deviation (SD) was the least of all the SD's obtained for all the sets of values obtained (in the previous paper[1], the least mean deviation was employed). Although eqn. (4) does not apply when n is exactly equal to unity it is rare in practice for reactions to be exactly first-order and hence this equation is considered to be of general validity. Further, once E and n have been evaluated the pre-exponential factor (or frequency factor), A, may be evaluated from the expression,

$$\ln K = \ln \frac{1-\left(\frac{\bar{a}_T}{A_T}\right)^{1-n}}{T^2} + \frac{E}{RT} \tag{5}$$

where, $K = A(1-n)R/(\mathrm{RH})E$.

TESTING OF THE METHOD

The present method was tested using data for the thermal decomposition of sodium bicarbonate[4], calcium oxalate monohydrate[5], and benzenediazonium chloride (in aqueous solution)[6]. In the following, derived data was readily obtained using a programmable calculator (HP-97).

Table 1 lists derived values for E and n obtained from data reported for the thermal decomposition of sodium bicarbonate[4], (RH) = 3.5 deg min^{-1}. From Table 1, values of n, (E/R) ave., and SD are given in the following in the order mentioned: 0.3, 9.100, 1.196; 0.4, 9.399, 1.109; 0.5, 9.710, 1.077; 0.6, 10.03, 1.118; 0.7, 10.37, 1.238; 0.8, 10.72, 1.428. From the preceding, it can be seen that the least SD corresponds to an (E/R) ave. of 9.71 kcal mole^{-1} and $n = 0.5$. Values of $n = 0.45$ and $n = 0.55$ afforded SD's of 1.085 and 1.088, respectively. Therefore, final values were considered to be, $n = 0.5$ ($\pm$.05), E ave. = 19.4 $\pm$ 2 kcal mole^{-1}. Values for sodium bicarbonate have been reported[1, 4, 7] to range as follows: n = 0.68–0.83 and E = 22–25 kcal mole^{-1}.

Table 2 gives derived data for E and n obtained from data reported for the

TABLE 1

VALUES OF E/R AND n FROM SODIUM BICARBONATE DECOMPOSITION[4]

				E/R ($\times 10^{-3}$) for n-values of					
$T_1(K)$	$\frac{\bar{a}_{T,1}}{A_T}$	$T_2(K)$	$\frac{\bar{a}_{T,2}}{A_T}$	0.3	0.4	0.5	0.6	0.7	0.8
390.6	0.915	403.7	0.82	8.427	8.491	8.555	8.620	8.685	8.750
403.7	0.82	412.3	0.68	10.82	10.99	11.16	11.33	11.51	11.68
412.3	0.68	423.2	0.44	8.991	9.294	9.604	9.921	10.25	10.58
423.2	0.44	433.6	0.155	8.163	8.823	9.522	10.26	11.04	11.85

TABLE 2

VALUES OF E/R AND n FROM DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE[5]

				E/R ($\times 10^{-3}$) for n-values of						
$T_1(K)$	$\frac{\bar{a}_{T,1}}{A_T}$	$T_2(K)$	$\frac{\bar{a}_{T,2}}{A_T}$	0.85	0.9	0.95	1.0	1.05	1.1	1.15
423.2	0.98	443.2	0.925	11.76	11.77	11.78	11.80	11.81	11.83	11.84
443.2	0.925	463.2	0.795	10.06	10.09	10.13	10.17	10.21	10.25	10.29
463.2	0.795	473.2	0.695	8.953	9.026	9.099	9.172	9.246	9.320	9.395
473.2	0.695	483.2	0.558	9.467	9.590	9.714	9.839	9.965	10.09	10.22
483.2	0.558	493.2	0.393	9.622	9.825	10.03	10.24	10.45	10.66	10.88
493.2	0.393	503.2	0.227	9.485	9.808	10.14	10.48	10.82	11.17	11.53

TABLE 3

VALUES OF E/R AND n FROM THERMAL DECOMPOSITION OF CALCIUM CARBONATE[5]

				E/R ($\times 10^{-3}$) for n values of					
$T_1(K)$	$\frac{\bar{a}_{T,1}}{A_T}$	$T_2(K)$	$\frac{\bar{a}_{T,2}}{A_T}$	0.4	0.5	0.55	0.6	0.65	0.7
981.2	0.95	1008.2	0.925	13.06	13.11	13.13	13.16	13.18	13.20
1008.2	0.925	1035.7	0.84	27.43	27.61	27.70	27.79	27.88	27.97
1035.7	0.84	1064.7	0.685	25.09	25.46	25.65	25.83	26.02	26.21
1064.7	0.685	1095.2	0.515	16.22	16.71	16.96	17.22	17.47	17.73
1095.2	0.515	1127.7	0.26	17.67	18.73	19.28	19.84	20.40	20.98

dehydration of calcium oxalate monohydrate[5] in air. From Table 2, the following values for n, (E/R) ave., and SD were obtained, respectively: 0.85, 9.89, 0.98; 0.9, 10.02, 0.93; 0.95, 10.15, 0.89; 1.0, 10.28, 0.87; 1.05, 10.42, 0.86; 1.1, 10.55, 0.88; 1.15, 10.69, 0.91. Therefore, final values were considered to be, $n = 1.05$ (± 0.05) and E ave. $= 20.8 \pm 1.7$ kcal mole^{-1}. Reported[7, 8] values range from $n = 0.74$–1.0 and $E = 17.8$–22 kcal mole^{-1}. Calcium oxalate decomposes in two stages, the final stage involving the decomposition of calcium carbonate[5] to calcium oxide and carbon

TABLE 4

VALUES OF E/R AND n FROM THERMAL DECOMPOSITION OF BENZENEDIAZONIUM CHLORIDE IN AQUEOUS SOLUTION AT HEATING RATES OF 1 AND 2 DEG MIN^{-1} [6]

	$\bar{a}_{T,1}$		$\bar{a}_{T,2}$	E/R ($\times 10^{-3}$) for n-values of						
$T_1(K)$	A_T	$T_2(K)$	A_T	0.8	0.9	0.95	1.0	1.05	1.1	1.2
$(RH) = 1$ deg min^{-1}										
306.3	0.962	310.6	0.926	14.46	14.50	14.53	14.55	14.57	14.59	14.63
310.6	0.926	314.9	0.877	11.42	11.48	11.51	11.54	11.57	11.60	11.66
314.9	0.877	319.2	0.775	14.59	14.74	14.81	14.88	14.95	15.03	15.17
319.2	0.775	323.5	0.614	14.39	14.67	14.80	14.94	15.08	15.23	15.51
323.5	0.614	327.8	0.424	12.39	12.83	13.05	13.28	13.51	13.74	14.21
327.8	0.424	332.1	0.231	11.41	12.14	12.51	12.89	13.28	13.67	14.49
332.1	0.231	336.4	0.078	11.09	12.36	13.04	13.72	14.45	15.18	16.73

	$\bar{a}_{T,1}$		$\bar{a}_{T,2}$	E/R ($\times 10^{-3}$) for n-values of						
$T_1(K)$	A_T	$T_2(K)$	A_T	0.7	0.8	0.85	0.90	0.95	1.0	1.1
$(RH) = 2$ deg min^{-1}										
314.9	0.93	319.2	0.87	14.37	14.45	14.49	14.52	14.56	14.60	14.68
319.2	0.87	323.5	0.76	15.17	15.33	15.41	15.49	15.57	15.65	15.81
323.5	0.76	327.8	0.605	13.44	13.71	13.85	13.99	14.13	14.27	14.55
327.8	0.605	330.2	0.49	13.76	14.21	14.44	14.67	14.91	15.14	15.62
330.2	0.49	334.7	0.245	13.59	14.37	14.77	15.17	15.59	16.01	16.87

dioxide. Data for this final stage was compiled in Table 3. From Table 3, the following values for n, (E/R) ave., and SD were obtained, respectively: 0.4, 19.90, 6.10; 0.5, 20.33, 6.066; 0.55, 20.54, 6.055; 0.60, 20.77, 6.051; 0.65, 20.99, 6.053; 0.70, 21.22, 6.062. From the preceding, final values were taken as, $n = 0.60$ (± 0.05) and E ave. $= 41.5 \pm 12$ kcal mole^{-1}. Reported[7, 9, 10] values range from $n = 0.4$–0.7 and $E = 39$–54 kcal mole^{-1}. It should be noted here that the E-value SD was relatively large indicating possible data inconsistency and/or inaccuracy (also cf. Table 3). (Nevertheless, the final values were in reasonably good agreement with reported values.

In Table 4 are listed derived values for E and n from the thermal decomposition of benzenediazonium chloride in aqueous solution[6] at heating rates of ca. 1 and 2 deg min^{-1}. For (RH) $= 1$ deg min^{-1}, the following values for n, (E/R) ave., and SD were obtained, respectively: 0.8, 12.82, 1.60; 0.9, 13.25, 1.36; 0.95, 13.46, 1.28; 1.0, 13.69, 1.245; 1.05, 13.92, 1.240; 1.1, 14.15, 1.29; 1.2, 14.63, 1.55. From these values, it can be seen that the least SD affords values of $n = 1.05$ ($\pm .05$) and E ave. $= 27.8 \pm 2.5$ kcal mole^{-1}. For (RH) $= 2$ deg min^{-1}, the following values for n, (E/R) ave., and SD were obtained, respectively: 0.7, 14.06, 0.71; 0.8, 14.41, 0.585; 0.85, 14.59, 0.565; 0.9, 14.77, 0.582; 0.95, 14.95, 0.635; 1.0, 15.13, 0.718; 1.1, 15.51, 0.945. From the preceding, final values are seen to be, $n = 0.85$ ($\pm$ 0.05) and E ave. $= 29.2 \pm 1.1$ kcal mole^{-1}. Reported[6, 7, 11, 12] values range from $n = 1$–1.1 and $E =$

28–29 kcal mole^{-1}. It may be mentioned here that cases may arise where there does not appear to be any minimum SD. In such cases, the raw data may not be sufficiently accurate or eqn. (1) and/or (3) may not be applicable.

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