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KINETIC PARAMETERS FROM THERMOGRAVIMETRIC CURVES

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ABSTRACT

A novel procedure is presented for the evaluation of kinetic parameters, activation energy (E) and reaction order (n), from thermogravimetric (TG) traces. From given values of conversion (α) and corresponding temperatures (T) are calculated values of E corresponding to various arbitrary values of n. Then, the resulting arbitrary E-values may be plotted against respective n-values and the region bounded by intersecting curves used to simultaneously estimate E and n. This procedure was tested against theoretical data, teflon, sodium bicarbonate, and magnesium hydroxide, and was found to be satisfactory. Some advantages of this method are: it is relatively simple to use; it allows the user to readily discern whether the data are homogeneous and, if not, at what conversions the data deviate. A less sensitive ancillary procedure is also described which can dispense with plotting in the estimation of E and n.

INTRODUCTION

Many procedures have been reported during thermal decomposition of solids by TG (reviews are given in refs. 1–3). Thus, E and n have been estimated using maximization of rate, multiple heating rates, variable heating rate, expressions involving double logarithm terms, approximate integration of the rate equation, etc. In this paper, we present a novel procedure wherein values of E corresponding to various arbitrarily selected values of n are calculated for each two given pairs of values of α and T. The resulting arbitrary values of E may be plotted against corresponding n-values, and the region bounded by intersecting curves used to simultaneously estimate actual values of E and n. This procedure was tested against theoretical data, as well as data for the thermal decomposition of teflon, sodium bicarbonate, and magnesium hydroxide. Some distinct advantages of this method are: its relative simplicity; it allows the user to readily discern whether the data are homogeneous and, if not, at what conversions the data deviate from uniformity. A less sensitive ancillary procedure is also described which can dispense with plotting in the estimation of E and n.

THEORY

In this analysis, the following well-known rate expression is used,

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

where, A denotes a frequency factor; (RH) is a constant rate of heating. Upon integrating (1), there is obtained (except for $n = 1$),

$$1-(1-\alpha)^{1-n} = \frac{A(1-n)}{(\mathrm{RH})} \int_0^T e^{-E/RT}\, dT \tag{2}$$

When eqn (2) is expanded in an asymptotic series (1–4) and higher order terms ignored there is obtained,

$$1-(1-\alpha)^{1-n} = \frac{A(1-n)RT^2}{(\mathrm{RH})E} \left(1 - \frac{2RT}{E}\right) e^{-E/RT} \tag{3}$$

Since $(1 - 2RT/E)$ is approximately unity (or constant) during solid pyrolysis, and taking natural logarithms of both sides of (3),

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] = \ln K - \frac{E}{RT} \tag{4}$$

where, K = constant. For two pairs of values of α and T, eqn (4) becomes

$$\ln \frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}} \left(\frac{T_2}{T_1}\right)^2 = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

For two pairs of given values of α and T, i.e., α_1, T_1 and α_2, T_2, values of E/R can be calculated from eqn (5) 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 α 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. This pair can be ascertained by plotting the various sets of E, n values. The region bounded by the intersecting curves will be common to all (or most) of the curves and from this region can be determined values of E and n, simultaneously. "Average" values of E and n, were calculated by taking the means of the extreme values of the bounded region. Although eqn (5) 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 by use of eqn (4). Thus, from this expression, we can write

$$\ln K = \ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] + \frac{E}{RT} \tag{4a}$$

where,

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

Various values of K (and hence of A) can be evaluated from values of α and corresponding values of T. From these values of K, an average value of A may then be estimated.

After derived data (E and n) have been tabulated, data which are non-uniform may readily be detected. These non-uniform derived data should not be included in subsequent plots since each curve is used in the estimation of a bounded region and the use of even one erratic curve may cause relatively large deviations in values of E and n. Justification for the omission of non-uniform data can usually be found from plots of the raw data (α versus T). Such plots often indicate that values of α and T, which afforded non-uniform derived data, do not lie on a smooth curve drawn through the remaining α, T values, and probably represent inaccurate data.

TESTING OF THE METHOD

The present method was tested using theoretical data as well as data for the thermal decomposition of teflon[5], sodium bicarbonate[6], and magnesium hydroxide[7]. Thus, using the following values: $A = 3.6 \times 10^{13}$ (min^{-1}), (RH) $= 3$ deg min^{-1}, $E = 28$ kcal mol^{-1}, and $n = 1/2$, eqn (3) can be solved for α for various values of T. In this manner were obtained the following values of T (K) and corresponding $\alpha(\times 10^2)$: 405, 13.1895; 410, 20.1953; 415, 30.2608; 420, 44.1051; 425, 61.8692; 430, 81.8781; 435, 97.8827. These values were employed in eqn (5) to calculate values for E/R from corresponding arbitrary values of n, as shown in Table 1. [Values in this and other tables were readily obtained by the use of a programmable calculator (HP-65)].

From the table, it can be seen that E/R values tend to change uniformly for different sets of α and T values for a particular value of n. However, E/R does not change for $n = 0.5$ and is thus common to all the sets of data. In this case, no plots

TABLE 1

VALUES OF E/R AND n FROM THEORETICAL DATA

α_1	T_1(K)	α_2	T_2(K)	E/R ($\times 10^{-3}$) for n-values of:				
				0.1	0.3	0.5	0.7	0.9
0.13190	405	0.20195	410	13.463	13.729	13.998	14.271	14.547
0.20195	410	0.30261	415	13.146	13.569	14.001	14.442	14.892
0.30261	415	0.44105	420	12.626	13.301	14.000	14.723	15.470
0.61869	425	0.81878	430	10.202	11.991	14.000	16.240	18.717
0.81878	430	0.97883	435	7.007	10.006	14.000	19.195	25.759

TABLE 2

VALUES OF E/R AND n FROM TEFLON DECOMPOSITION[5]

				E/R ($\times 10^{-3}$) for n-values of:			
α_1	$T_1(K)$	α_2	$T_2(K)$	0.5	0.7	0.9	1.1
0.016	773.2	0.087	803.2	33.86	34.01	34.17	34.32
0.087	803.2	0.216	823.2	29.64	30.14	30.63	31.14
0.216	823.2	0.489	843.2	29.98	31.38	32.82	34.30
0.489	843.2	0.663	853.2	26.07	28.72	31.54	34.53
0.663	853.2	0.826	863.2	22.51	26.47	30.88	35.75

TABLE 3

VALUES OF E/R AND n FROM SODIUM BICARBONATE DECOMPOSITION[6]

				E/R ($\times 10^{-3}$) for n-values of:			
α_1	$T_1(K)$	α_2	$T_2(K)$	0.5	0.7	0.9	1.1
0.208	408.2	0.300	413.2	12.50	12.90	13.31	13.72
0.300	413.2	0.403	418.2	10.59	11.11	11.65	12.20
0.403	418.2	0.528	423.2	10.47	11.24	12.03	12.86
0.528	423.2	0.667	428.2	10.06	11.17	12.36	13.62
0.667	428.2	0.806	433.2	9.523	11.16	12.99	14.99
0.806	433.2	0.917	438.2	8.271	10.63	13.41	16.64

are necessary since the constancy of E/R may be readily perceived. Therefore, $n = 0.5$, $E = 2 \times 14 = 28$ kcal mol^{-1}, and $A = 3.6 \times 10^{13}$ (min^{-1}) (from (4a)), which were used in deriving the theoretical data. In actual practice, however, it is usually necessary to make plots to ascertain E and n since heterogeneous decompositions may occur, e.g., due to impurities present, or raw data may not be accurate due to errors or to equipment limitations. In the following, plots have been carried out for teflon, for sodium bicarbonate, and magnesium hydroxide.

In order to facilitate the plotting and since values of n for teflon and sodium bicarbonate are expected to be above 0.5, values of n of 0.5 and above were arbitrarily selected for these materials. Results obtained for teflon and sodium bicarbonate are given in Tables 2 and 3, respectively. In Table 2, it can be observed that the values of E/R for the pair of α-values, 0.087 and 0.216, do not show the uniform trend that the other values possess, and hence these values were not included in the teflon plots in Fig. 1. The shaded area in Fig. 1 represents a region which is common to all the curves. From this region, the following average values were obtained: $E = 67 \pm 1.5$ kcal mol^{-1} and $n = 1.0 \pm 0.05$. Assuming first-order kinetics, Doyle[5] utilized the same data for teflon and indicated that the TG curve for teflon could be best described using values of E between 66–68 kcal mol^{-1}.

In Table 3, it can be observed that with the exception of the first value under

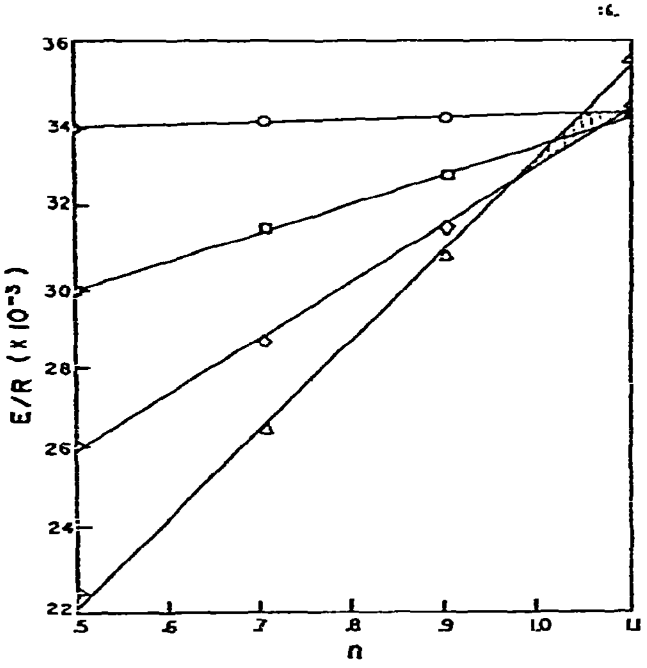

Fig. 1. Plots of E/R versus n from teflon decomposition. Values of α; ○, 0.016 and 0.087; □, 0.216 and 0.489; ◇, 0.489 and 0.663; △, 0.663 and 0.826.

n = 0.7, the other values of E/R are relatively constant. Thus, there does not appear to be any need to make a plot for the bicarbonate data. Taking an average value of E/R (omitting the first value), the following values are obtained: n = 0.7, E = 22 ± 0.4 kcal mol^{-1} (an actual plot gave average values, n = 0.69 ± 0.08 and E = 23 ± 1 kcal mol^{-1}). Using the same raw data for the bicarbonate decomposition but different procedures, values of n = 0.79–0.83 and E = 22–25 kcal mol^{-1} have been reported[6]. Assuming a first-order reaction, Wendlandt[8] reported a value of E = 20 kcal mol^{-1} for sodium bicarbonate. Others[9, 10] have reported that the decomposition of sodium bicarbonate is complex. Thus, it has been reported[10] that the thermal decomposition proceeded from an initial rate-controlling unimolecular reaction to a two-thirds molecular reaction in the later stages. It has also been reported[9] that the bicarbonate decomposition involves an initial stage during which E = 71 kcal mol^{-1} and a later stage during which E = 23 kcal mol^{-1}. The preceding may be a possible explanation as to why the data for α-values, 0.208 and 0.300 in Table 3, did not fit in with data obtained for α-values involving higher conversions.

It is possible to dispense with plots entirely in the estimation of E and n. For example, from Table 2 for teflon decomposition, it can be observed that the pertinent n-value lies near 1.1. Then, calculating E/R values for n = 0.95, 0.99, 1.05, and 1.1 (except for α_1 = 0.087 and α_2 = 0.216) and averaging, the following values of E/R (× 10^{-3}) are obtained, respectively, 32.93 ± 0.77, 33.40 ± 0.46, 34.12 ± 0.27, and 34.73 ± 0.51. From the preceding, the smallest mean deviation is for the E/R value

TABLE 4

VALUES OF E/R AND n FROM THERMAL DEHYDROXYLATION OF MAGNESIUM HYDROXIDE (TRACE I)[7]

					E/R ($\times 10^{-3}$) for n-values of:					
No.	α_1	$T_1(K)$	α_2	$T_2(K)$	0.9	1.1	1.3	1.5	1.7	1.9
1	0.0478	625	0.0797	632	28.45	28.64	28.83	29.03	29.22	29.42
2	0.0797	632	0.1162	638	25.27	25.54	25.82	26.09	26.37	26.65
3	0.1162	638	0.1777	645	25.54	25.97	26.39	26.83	27.26	27.71
4	0.1777	645	0.2620	652	24.82	25.47	26.13	26.80	27.48	28.18
5	0.2620	652	0.3485	657	27.62	28.69	29.78	30.90	32.05	33.22
6	0.3485	657	0.4100	660	28.06	29.49	30.97	32.50	34.07	35.68
7	0.4100	660	0.4715	664	18.84	20.05	21.30	22.60	23.94	25.34
8	0.4715	664	0.5308	667	23.06	24.82	26.66	28.58	30.58	32.66
9	0.5308	667	0.5900	670	22.10	24.11	26.23	28.46	30.80	33.24
10	0.5900	670	0.6538	674	17.33	19.24	21.27	23.43	25.71	28.10
11	0.6538	674	0.7107	677	21.10	23.83	26.77	29.91	33.26	36.81
12	0.7107	677	0.7563	680	17.23	19.87	22.73	25.82	29.14	32.67

at $n = 1.05$ (within an error of $\pm$ 0.05). Thus, $n = 1.0$ and $E = 68 \pm 0.5$ kcal mol^{-1} by this procedure. Similarly, from the sodium bicarbonate data in Table 3, the following E/R ($\times 10^{-3}$) values were obtained for n = 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, respectively (excluding the α-values 0.208 and 0.300): 10.41 $\pm$ 0.44, 10.73 $\pm$ 0.29, 11.06 $\pm$ 0.17, 11.40 $\pm$ 0.11, 11.76 $\pm$ 0.20, and 12.12 $\pm$ 0.36. From the preceding, the smallest mean deviation leads to values of $n = 0.75$ and $E = 23 \pm 0.2$ kcal mol^{-1} for sodium bicarbonate. When all values in the tables were used, the following values for teflon and sodium bicarbonate were obtained, respectively, $n = 0.99$ and $E = 66 \pm 1.6$ kcal mol^{-1}; $n = 0.80$ and $E = 24 \pm 0.8$ kcal mol^{-1}. Thus, the inclusion of all data did not appreciably change previous values of n and E obtained with data exclusion. In the following, both of the preceding described methods (graphical and non-graphical) are applied.

Table 4 lists derived values for E and n obtained from data reported for the thermal dehydroxylation of magnesium hydroxide (trace 1)[7]. From this table, relatively many inconsistencies can be observed. Thus, for example, in the column under $n = 0.9$, there is a decrease in values until sets of data numbered 5 and 6 are reached. Because of the relatively slow decrease in values, 7 also appears to be inconsistent along with 10 and 12 (we can now see that the first value under $n = 0.9$ appears to be too high). From the preceding, inconsistencies (as far as the graphical method is concerned) appear between 625–632K, 652–664K, 670–674K, and 677–680K, and should be omitted in the previously described plots of E versus n. Close scrutiny of a plot of α versus T for trace I data revealed that α values at temperatures (K) of 625, 652, 654, 660, and 674 did not lie on a smooth curve drawn through the remaining values. Such data may have arisen due to equipment limitations as well as to the nature of the dehydroxylation itself (heterogeneity, heat transfer effects, etc.). At any rate, if we disregard the sets of data numbered 1, 5–7, 10, and 11, and plot the

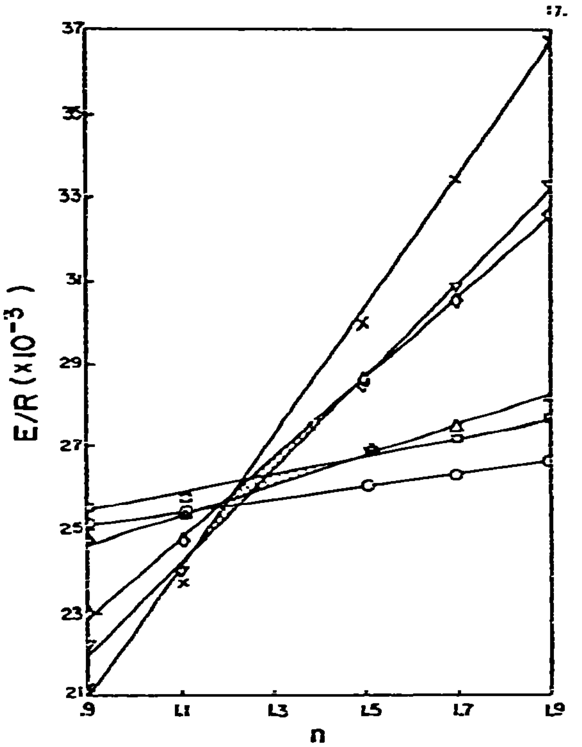

Fig. 2. Plots of E/R versus n from thermal dehydroxylation of magnesium hydroxide. Values of α: ○, 0.0797 and 0.1162; □, 0.1162 and 0.1777; △, 0.1777 and 0.2620; ◇, 0.4715 and 0.5308; ▽, 0.5308 and 0.5900; ×, 0.6538 and 0.7107.

remaining data (Fig. 2), the following average values can be obtained: $E = 53 \pm 4$ kcal mol^{-1} and $n = 1.3 \pm 0.2$. When all the data were employed in the non-graphical method previously described, the following average values of E/R ($\times 10^{-3}$) were obtained for values of n = 1.2, 1.25, 1.3, 1.35, 1.4, 1.45, 1.5, 1.55, 1.6, 1.65, and 1.7, respectively: 25.35 ± 2.36, 25.71 ± 2.24, 26.07 ± 2.20, 26.44 ± 2.19, 26.82 ± 2.23, 27.20 ± 2.27, 27.58 ± 2.32, 27.97 ± 2.36, 28.36 ± 2.41, 28.75 ± 2.46, and 29.16 ± 2.51. For the lowest mean deviation, the following values are obtained: $E = 53 \pm 4$ kcal mol^{-1} and $n = 1.35$ (within ± 0.05). Thus, the agreement between the graphical method (which involves data bias) and the non-graphical method (in which all data are employed) is very satisfactory. Using all the values of trace 1, and refining the derived data using sophisticated computer procedures, the following values were arrived at[7]: $E = 53.0$ kcal mol^{-1} and $n = 1.6$. It should also be noted here that the trace 1 TG data were also subjected to analysis[7] using methods of Freeman and Carroll (FC), Coats and Redfern (CR), and Satava (S). The FC method afforded plots which should have been linear but were not. Also, CR and S methods could not distinguish (based on correlation coefficients) between an order of 1.5 and 2. Further, many forms of the rate equation gave results with correlation coefficients higher than 0.995 which made it difficult to decide what the correct mechanism should be. The relatively large number of difficulties encountered using the α, T data of trace 1 could have been predicted from the relatively large number of inconsistencies observed in Table 4.

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