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COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XXI

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ABSTRACT

The utilization of thermogravimetry should allow an estimate of the extent of reaction for consecutive equations such as

$A \xrightarrow{k_1} B + \text{gas}$, and $B \xrightarrow{k_2} C + \text{gas}$

based on the amount of gas liberated.

An expression was developed for the concurrent determination of the rate constants, k_1 and k_2, for the above two consecutive irreversible first-order reactions, which required the measurement of reaction rates (slopes). Then a computer algorithm was presented to implement this expression. This algorithm involved a modification of an algorithm previously reported by the authors, and was tested for the cases of theoretical and experimental data. Values of k_1 and k_2 obtained for these cases are compared with assumed and previously reported values.

INTRODUCTION

Thermal decompositions of various materials by means of TG (or DSC) often involve one-step irreversible unimolecular or pseudounimolecular reactions. A mechanism of higher complexity which is not reducible to a simple one-step process is one involving two consecutive irreversible first-order reactions

$$A \xrightarrow{k_1} B + \text{gas} \tag{1a}$$

$$B \xrightarrow{k_2} C + \text{gas} \tag{1b}$$

In the preceding expressions, A, B and C denote starting material, intermediate product and final product, respectively; k_1 and k_2 represent the rate constants for the two steps.

The concentrations of A, B and C as a function of time can readily be estimated once the rate constants are known. In this respect, the following pertinent equations were derived as far back as the 19th century [1–4] (a denotes the initial concentration of A).

$$[\mathrm{A}] = a \exp(-k_1 t) \tag{2}$$

$$[\mathrm{B}] = [ak_1/(k_1 - k_2)][-\exp(-k_1 t) + \exp(-k_2 t)] \tag{3}$$

$$[\mathrm{C}] = a\{1 + [1/(k_1 - k_2)][k_2 \exp(-k_1 t)] - k_1 \exp(-k_2 t)\} \tag{4}$$

The converse and more practical problem of determining the rate constants rapidly and accurately from experimental data has been previously attempted using tables, and manual and graphical methods [5–7]. Although such procedures have been successful, they employ non-computer methods. The manual method used [6] is of a tedious and slow nature and only utilized two pairs of data. The use of tables and graphs did allow a rapid and accurate determination of the rate constants. However, some of these procedures employed only three pairs of data and involved displacement measurements between experimental and theoretical curves.

The utilization of TG should allow the estimation of the extent of the reactions depicted in eqns. (1), based on the amount of gas liberated. Thus, it appeared of practical and theoretical interest to investigate these reactions further. The aim of this paper is to develop a computer algorithm for the series first-order irreversible reactions which will allow a relatively rapid and accurate determination of values of rate constants k_1 and k_2.

THEORETICAL ASPECTS

Although the following derived expressions are of a general nature, they will be applied to the case where the gas is the same in steps (1a) and (1b). It can be shown that the extent of reaction based on the amount of gas liberated is equal to $([\mathrm{A}] + 2[\mathrm{C}])/2a$. Letting $F = [\mathrm{A}] + 2[\mathrm{C}]$, we may write using eqns. (2) and (4)

$$F = a\{2 - [(k_1 - 2k_2)/(k_1 - k_2)] \exp(-k_1 t) \\ - [k_1/(k_1 - k_2)] \exp(-k_2 t)\} \tag{5}$$

From the preceding, $F = 2a\alpha$, where α is the extent of overall reaction based on the amount of gas liberated. Then eqn. (5) becomes

$$2(1 - \alpha) = K_1 \exp(-k_1 t) + K_2 \exp(-k_2 t) \tag{6}$$

where $K_1 = (k_1 - 2k_2)/(k_1 - k_2)$ and $K_2 = k_1/(k_1 - k_2)$. Upon differentiation of eqn. (6) and substitution of the expression for $K_2 \exp(-k_2 t)$ from eqn. (6) into the resulting expression, we can obtain employing natural logarithms

$$\ln[\rho - k_2(1 - \alpha)] = -k_1 t + \ln[K_1(k_1 - k_2)/2] \tag{7}$$

where $\rho = d\alpha/dt$. If we now let the subscript 0 refer to an initial set of data values, there is finally obtained

$$\ln\{[\rho - k_2(1-\alpha)]_0/[\rho - k_2(1-\alpha)]\} = k_1(t - t_0) \tag{8}$$

From eqn. (8), it can readily be seen that if we let the left-hand side of eqn. (8) equal Y then

$$Y = A_2X + A_1 \tag{9}$$

where $A_2 = k_1$, $X = t - t_0$ and $A_1 = 0$.

Using eqn. (9), we can now employ the concepts of a computer algorithm previously devised and reported by the authors [8,9]. However, this algorithm will be slightly modified (to be discussed later on), and values of k_1 and k_2 will again be determined via an iteration procedure wherein a minimum value of A_1 will be obtained for the conditions employed.

APPLICATIONS OF THE METHOD

The procedure was initially tested using two sets of theoretical data. Thus, in the first case, values of $k_1 = 0.0444$ and $k_2 = 0.00123$ were assumed. The following eight data triads in the order t, α and $\rho \times 10^3$ were calculated and used, respectively: 70, 0.5065, 1.544; 100, 0.5395, 0.8137; 130, 0.5602, 0.6062; 160, 0.5772, 0.5372; 190, 0.5928, 0.5054; 220, 0.6076, 0.4838; 310, 0.6488, 0.4320; 340, 0.6615, 0.4164. The values at $t = 70$ were taken as the initial values. Then employing a modified version of the algorithm previously mentioned, values of $k_1 = 0.0452$ and $k_2 = 0.00123$ were obtained. When an additional data triad was used, i.e., 370, 0.6738 and 0.4013, values of $k_1 = 0.0429$ and $k_2 = 0.00123$ were obtained. Averages of the preceding values were $k_1 = 0.0441$ and $k_2 = 0.00123$ in excellent agreement with assumed values. (The computer run time using BASICA (IBM) was ca. 3 min; however, this time can be greatly reduced using QuickBASIC 3.0 (Microsoft) or Turbo BASIC (Borland).)

It should be noted here that for the algorithm employed, eqn. (9) did not act as a well-behaved function. Thus, in Table 1 are shown values of k_1, k_2 and intercept for various k_2 values. Owing to space limitations, only portions of the results obtained are depicted. As values of k_2 increased from an initial value of 0.0001 in increments of 0.00001, values of A_1 actually increased (see Table 1). It was only when k_2 began to approach its proper value that A_1 began to decrease. This can be observed from the table for values of $k_2 = 0.00121$ and greater. However, as the k_2 value kept increasing, an error message appeared and the program aborted. (This was due to the appearance of the logarithm of a negative number.) Thus, it was necessary to modify the previously mentioned algorithm, as previously indicated. An 'error trap' was instituted so that if the positive A_1 values

TABLE 1

Values of k_1, k_2 and intercept from theoretical data

X	Y	X	Y	X	Y
30	0.6663135	30	0.669023	30	0.6717582
60	0.9777541	60	0.9823001	60	0.9868974
90	1.10504	90	1.11032	90	1.115653
120	1.168298	120	1.173793	120	1.179354
150	1.212562	150	1.218121	150	1.223748
180	1.251483	180	1.257057	180	1.262701
240	1.326013	240	1.331594	240	1.337245
270	1.362788	270	1.368369	270	1.374018
$k_2 = 0.0001$		$k_2 = 0.00011$		$k_2 = 0.00012$	
$k_1 = 2.385181\text{E-}03$,		$k_1 = 2.393715\text{E-}03$		$k_1 = 2.402383\text{E-}03$	
$A_1 = 0.7938945$		$A_1 = 0.7977176$		$A_1 = 0.8015822$	
30	0.6745191	30	1.089987	30	1.098402
60	0.9915468	60	1.842628	60	1.864705
90	1.121052	90	2.216448	90	2.249364
120	1.184985	120	2.370017	120	2.407659
150	1.229445	150	2.441778	150	2.48095
180	1.268414	180	2.487673	180	2.527241
240	1.342964	240	2.565046	240	2.604776
270	1.379737	270	2.601598	270	2.641314
$k_2 = 0.00013$		$k_2 = 0.00100$		$k_2 = 0.00101$	
$k_1 = 2.411183\text{E-}03$		$k_1 = 4.986339\text{E-}03$		$k_1 = 5.093883\text{E-}03$	
$A_1 = 0.8054891$		$A_1 = 1.491344$		$A_1 = 1.508423$	
30	1.106969	30	1.306047	30	1.318938
60	1.887497	60	2.548523	60	2.604533
90	2.283729	90	3.606192	90	3.780615
120	2.447151	120	4.312487	120	4.694289
150	2.522115	150	4.656368	150	5.224177
180	2.568837	180	4.786401	180	5.432524
240	2.64655	240	4.900394	240	5.584894
270	2.683075	270	4.934016	270	5.615345
$k_2 = 0.00102$		$k_2 = 0.00121$		$k_2 = 0.00122$	
$k_1 = 5.208578\text{E-}03$		$k_1 = 1.356853\text{E-}02$		$k_1 = 1.673725\text{E-}02$	
$A_1 = 1.526018$		$A_1 = 1.947788$		$A_1 = 1.896856$	
30	1.332136	30	1.332149	30	1.332163
60	2.664511	60	2.664573	60	2.664636
90	3.994508	90	3.994748	90	3.994986
120	5.328824	120	5.329716	120	5.330608
150	6.704555	150	6.707978	150	6.711412
180	7.929853	180	7.941132	180	7.95254
240	10.56589	240	10.72346	240	10.90888
270	9.941309	270	10.01909	270	10.1042
$k_2 = 0.00123$		$k_2 = 1.23001\text{E-}03$		$k_2 = 1.23002\text{E-}03$	
$k_1 = 3.895993\text{E-}02$		$k_1 = 3.947419\text{E-}02$		$k_1 = 4.006167\text{E-}02$	
$A_1 = 0.5059085$		$A_1 = 0.4640336$		$A_1 = 0.4161396$	

TABLE 1 (continued)

X	Y	X	Y	X	Y
30	1.332176	30	1.332189	30	1.332203
60	2.664697	60	2.66476	60	2.664822
90	3.995227	90	3.995469	90	3.995706
120	5.331501	120	5.332396	120	5.333291
150	6.714859	150	6.718317	150	6.721787
180	7.964081	180	7.975756	180	7.987569
240	11.13884	240	11.43797	240	11.86676
270	10.19639	270	10.29888	270	10.41206
k_2 =1.23003E-03		k_2 =1.23004E-03		k_2 =1.23005E-03	
k_1 = 4.075427E-02		k_1 = 0.0416083		k_1 = 4.274274E-02	
A_1 = 0.3597374		A_1 = 0.2902856		A_1 = 0.1984344	
30	1.332216	30	1.332218	30	1.332219
60	2.664884	60	2.664891	60	2.664897
90	3.995948	90	3.995974	90	3.995997
120	5.334186	120	6.334289	120	5.334378
150	6.72527	150	6.725632	150	6.725994
180	7.999523	180	8.00082	180	8.002024
240	12.63333	240	12.75469	240	12.90526
270	10.54088	270	10.55508	270	10.56948
k_2 =1.23006E-03		k_2 =1.230061E-03		k_2 =1.230062E-03	
k_1 = 4.457655E-02		k_1 = 4.485062E-02		k_1 = 0.0451822	
A_1 = 5.112028E-02		A_1 = 2.923489E-02		A_1 = 2.818585E-03	
30	1.33222				
60	2.664904				
90	3.996024				
120	5.334468				
150	6.726356				
180	8.003323				
240	13.08259				
270	10.5841				
k_2 =1.230063E-03					
k_1 = 4.556659E-02					
A_1 = −2.774143E-02					

k_1 = 0.0451822, k_2 =1.230062E-03 and intercept = 2.818585E-03. The preceding are the final values!

became too negative (thereby causing an error message), this trap redirected the computer to recover the k_2 value associated with the positive A_1 value (prior to becoming negative) and to then employ smaller increments (reduced by a factor of ten) for k_2. This allowed k_2 to increase very slowly and in this manner final values of k_1 and k_2 could be obtained even when A_1 became slightly negative, without any error messages or program abort. This can be seen from the table, beginning with a value of $k_2 = 0.00121$. As the value of k_2 increased to 0.00123, there was a sharp drop in A_1 from 1.897 to

0.506. A further increase in k_2 to a value of 0.00124 would result in an error message and an aborted program unless the program, via an error trap, caused $k_2 = 0.00123$ to increase in much smaller increments. Thus, increments of 1×10^{-9} were finally employed, leading to final values for k_1 and k_2. From the table, the absolute value of A_1 at $k_2 = 1.230062 \times 10^{-3}$ was smaller than the absolute value of the negative A_1 value at $k_2 = 1.230063 \times 10^{-3}$ so that the final values of k_1 and k_2 were those previously noted for the eight data triads. (It should also be noted here that although the value of k_2 changes very slowly, the corresponding value for k_1 changes much more rapidly.)

In the second case where theoretical values were employed to test the algorithm, values of $k_1 = 0.0167$ and $k_2 = 0.00265$ were assumed. It may be mentioned here that these values are close to the values obtained from experimental data (in min^{-1}) which will be treated subsequently. Contrary to the procedure used in the first case, a plot of α vs. t was now constructed using the theoretical values in order to determine values of ρ at various times. In this manner, the following values of t, α and $\rho \times 10^3$ (calcd.) are given, respectively: 60, 0.344, 3.60; 90, 0.442, 2.70; 150, 0.568, 1.55; 180, 0.612, 1.24; 240, 0.679, 1.00; 300, 0.730, 0.720; 390, 0.789, 0.580; 450, 0.821, 0.475; 510, 0.847, 0.408. In order to obtain accurate slopes, the theoretical plot of α vs. t was varied from about $\alpha = 0.2$ to 0.9 (initial and final points cannot be used), and values at $t = 60$ were used as initial values. The nine data triads afforded values of $k_1 = 0.0174$ and $k_2 = 0.00265$, in good agreement with assumed values. (It cannot be overemphasized that many values of α and t are necessary to obtain the required accurate slopes: the experimental data to be discussed next had relatively few such values.)

The algorithm was finally tested using experimental data previously reported [6] for the hydrolysis of 2,7-dicyanonaphthalene. Ammonia was liberated and titrated to obtain values of α and t. A plot of the experimental data is shown in Fig. 1. From this figure, it can be seen that the early values are undoubtedly too low, probably because of the time lag for quantitatively sweeping the ammonia formed from the reaction vessel [5]. Thus, if the initial data is neglected, there can be at best only five data triads available for testing, which is a relatively small number for obtaining accurate slopes. From the smooth plot, the following values of t (min), α and $\rho \times 10^3$ (min^{-1}) were obtained, respectively: 90, 0.432, 3.39; 120, 0.518, 2.25; 180, 0.621, 1.32; 240, 0.692, 0.900; 300, 0.738, 0.688. Values at $t = 90$ min were employed as the initial values. From the five data triads used, values of $k_1 = 1.12\ \text{h}^{-1}$ and $k_2 = 0.150\ \text{h}^{-1}$ were calculated by the authors (RS). When additional approximate data triads were extracted from the smooth curve ($t = 150$, 210 and 270 min), values of $k_1 = 1.08\ \text{h}^{-1}$ and $k_2 = 0.147\ \text{h}^{-1}$ were obtained.

By utilizing a manual method, Kaufler (K) reported [6] corresponding values of $k_1 = 1.007\ \text{h}^{-1}$ and $k_2 = 0.161\ \text{h}^{-1}$ whereas, using tables and

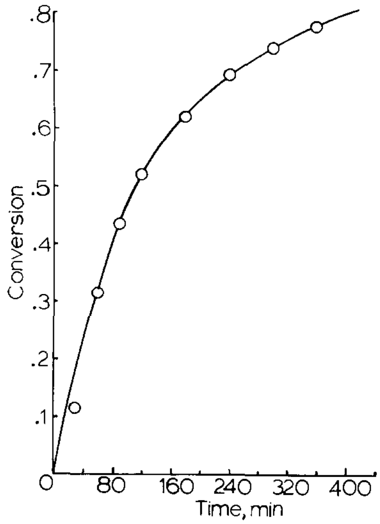

Fig. 1. Conversion vs. time for the hydrolysis of 2,7-dicyanonaphthalene [6].

graphs, Swain (S) reported [5] values of $k_1 = 0.937\ \text{h}^{-1}$ and $k_2 = 0.180\ \text{h}^{-1}$. In order to estimate the best fit to the experimental data, a standard error of estimate (*SEE*) was defined as

$$SEE = \left[\Sigma(y - y_e)^2/n\right]^{1/2} \tag{10}$$

where n = number of data sets used for the comparison, y = values from assuming the calculated values of k_1 and k_2, and y_e = corresponding experimental α values. In this manner, the following approximate values were calculated using values at $t = 90$–360: $SEE(\text{S}) = 0.008$, $SEE(\text{K}) = 0.009$ and $SEE(\text{RS}) = 0.014$. From the preceding, it is apparent that the best fit was obtained by (S). While the next best fit was obtained by (K), as mentioned previously, (K) used a tedious manual procedure which utilized only two pairs of data (α and t) and involved successive approximations which must have required hours of calculation. As indicated previously, one possible reason for the relatively high *SEE* value for (RS) lies in the poor accuracy of values obtained for slopes due to the relatively small number of experimental values available (in this regard, it may be stressed that none of the other procedures utilized slopes). However in view of the success of the computer algorithm when employing theoretical data, we conclude that this procedure is promising and look forward to its being utilized in the future. Finally, it may be mentioned that eqn. (8) also can be applied for the case of two parallel first-order reactions, each yielding a common product.

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