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A NEW ITERATIVE METHOD FOR DETERMINING KINETIC PARAMETERS FROM TG DATA

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ABSTRACT

An iterative method is described which computes n and E from nonisothermal TG data. The method which requires only three (α,T) data pairs as input, involves successive iterations of E/R and n using data pairs where $\Delta\alpha$ is first small, then large. A complete algorithm for implementation of the method on a programmable calculator is presented as well as results of analysis of calculated and experimental (α,T) data.

INTRODUCTION

Reich and Stivala have utilized a kinetic analysis of TG data that makes use of an approximate rate equation in a two point form

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

These workers have shown that constant E/R values are obtained for pairs of (α,T) data when n has the correct value [1]. Subsequently, Reich and Stivala described an iterative method that determines the correct n when the values of

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right]=y$$

and

$$\left(\frac{1}{T_{i+1}}-\frac{1}{T_i}\right)=x$$

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are related by linear regression yielding an intercept closest to zero for the correct value of n [2]. In later work, other approximate rate laws were used that were based on other ways of approximating the temperature integral [3,4].

Reich and Stivala have also utilized a technique of minimization of the difference between the left-hand side and right-hand side of eqn. (1) as E and n are varied using various pairs of (α, T) data [5]. Finally, these workers have developed a method that makes use of (α, T) data obtained at different heating rates [6]. Thus, a number of recent iterative techniques have been described.

In the present paper, we present a somewhat different iterative technique for computing n and E. This method requires only three (α_i, T_i) data pairs and is adaptable to programmable calculators of intermediate capacity. The implementation of the method is described for the Hewlett-Packard HP-34C machine.

METHOD

The method of determining n and E described in this paper makes use of the two point approximate equation

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = \frac{E}{R}\left(\frac{1}{T_{i+1}} - \frac{1}{T_i}\right) \tag{2}$$

While other forms are possible when other approximations to the temperature integral are used, they offer no distinct advantages [3,4]. The first step in the analysis is to compute an approximate value of E/R. This is performed using two data pairs, (α_1, T_1) and (α_2, T_2), where α_1 and α_2 are small since E/R is nearly constant for any value of n under these conditions. The first value assigned to the reaction order, n_0, is zero, and a reasonably good value of E/R results with $n_0 = 0$ as long as α_1 and α_2 are small (see rows 1 and 2 of E/R values shown in Table 1).

After getting an approximate first iterate value for E/R, two data points (α_2, T_2) and (α_3, T_3) are considered where $\alpha_3 \gg \alpha_2$. If $\alpha_3 \gg \alpha_2$, the maximum variation in the function of α occurs as n' is iterated. Under these conditions, a recalculation of E/R using these data will give a value close to the test value of E/R only when n has the correct value. Using the first iterate E/R value, the function

$$F_1 = \exp\left[\frac{E}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)\right] \div \left(\frac{T_3}{T_2}\right)^2 \tag{3}$$

is calculated using T_2 and T_3. Then, the function

$$F_2 = \left[\frac{1-(1-\alpha_2)^{1-n}}{1-(1-\alpha_3)^{1-n}}\right] \tag{4}$$

TABLE 1

Values of (α, T) and E/R computed using $n = 5/3$, $E = 100$ kJ mole^{-1} and $A/\beta = 3 \times 10^{10}$ min^{-1}

Point [a]	T_1 (K)	α_1	T_2 (K)	α_2	$n = 0.4$	$n = 0.8$	$n = 1.2$	$n = 5/3$	$n = 2.0$	$n = 2.4$
1	390	0.01414	400	0.03177	11894	11951	12007	12073	12120	12177
2	400	0.03177	410	0.06740	11646	11768	11891	12036	12140	12265
3	410	0.06740	420	0.13369	11210	11461	11715	12016	12233	12498
4	420	0.13369	430	0.24365	10452	10929	11419	12009	12441	12973
5	430	0.24365	440	0.39894	9238	10062	10931	12003	12807	13813
6	440	0.39894	450	0.57706	7559	8825	10216	12000	13378	15142
7	450	0.57706	460	0.73851	5619	7320	9311	11999	14150	16966
8	460	0.73851	470	0.85531	3751	5762	8321	11997	15039	19076
9	470	0.85531	480	0.92584	2220	4355	7371	11995	15916	21120
10	480	0.92584	490	0.96354	1104	3199	6539	11991	16668	22804
11	490	0.96354	500	0.98235	347	2302	5857	11994	17258	24047

[a] Point numbers refer to the left-hand (α, T) data pair.

is computed with $n_0 = 0$ and the result is compared with the value of F_1. It is easily shown that if $F_2 > F_1$, then the iterated value of the order, n', is smaller than the "correct" n ($n' < n$ when $F_2 > F_1$).The process continues by incrementing n' by 0.100001 (so that n' is never exactly one) and repeating the calculations. At the point where $F_1 > F_2$, n' is greater than n by an amount less than 0.1 for the first iterate value of E/R. This fixes an approximate upper limit of n', usually within 0.1 of the "correct' n. At this point, the value of n' calculated from (α_2, T_2) and (α_3, T_3) using the first iterate E/R value is reduced by 0.1 ($n' \rightarrow n' - 0.1$) and $\Delta n'$ is reduced from 0.1 to 0.01. The resulting n', the first iterate to n, is used in recalculating a second iterate E/R value using the first two data pairs. This E/R value is very nearly correct because the value of n' used is correct to within approximately 0.1. Having a very nearly exact second iterate to E/R, the function F_1 is calculated using points (α_2, T_2) and (α_3, T_3). Processing continues by computing the function F_2 iterating with $\Delta n = 0.01$. When $F_2 < F_1$ occurs, computation ends and n' has been determined with an upper limit within 0.01 of the "correct" value. If desired, the entire process can be repeated to provide a third iterate to E from which n' can be obtained using iterations of 0.001. The flow chart shown in Fig. 1 illustrates the logic of processing and the complete program for the HP-34C calculator is shown in the Appendix.

TESTING THE METHOD

Using the program

Implementing the program shown in the Appendix on the HP-34C programmable calculator uses the entire capacity of the machine with partitioning for 105 program lines and 15 registers. The computation can easily be adapted to other advanced calculators and microcomputers. As written, the program utilizes the following locations (given as register number, use): R_0 and $R_{.4}$, α_1; R_1, α_2; R_2, α_3; R_3 and $R_{.2}$, T_1; R_4, T_2; R_5, T_3; R_6, n'; R_7, R_8, $R_{.0}$ and $R_{.1}$, computed results; R_9, E/R; $R_{.3}$, Δn. The α_i, T_i, n_0, and Δn values are entered and processing is initiated by pressing label A. The first stop displays the first iterate n'. Pressing R/S restarts processing which ends with the second iterate n', etc. The value of E/R after each iteration is stored in R_9.

Testing the method with calculated (α, T) data

The iterative method was tested using the calculated values of α shown in Table 1 for which $n = 1.666...$ and $E = 100$ kJ mole^{-1}. Since the method involves using three values of α, it was necessary to determine the effects produced by the nature of that selection. In order to show the trends and effects that changing α has on E/R, values for the latter were calculated and they are also shown in Table 1.

One of the first factors to be studied was the effects produced by choosing different points for use in the calculations. For example, E/R is approximately constant for small values of α_1 and α_2. It would appear, then, that the first iterate n' should depend on which points are chosen. Table 2 shows the results obtained when various combinations of three points were chosen. In each case, the (α_3, T_3) point was the same (point 10) although when other points for which $\alpha_3 > 0.7$ are used similar results are obtained.

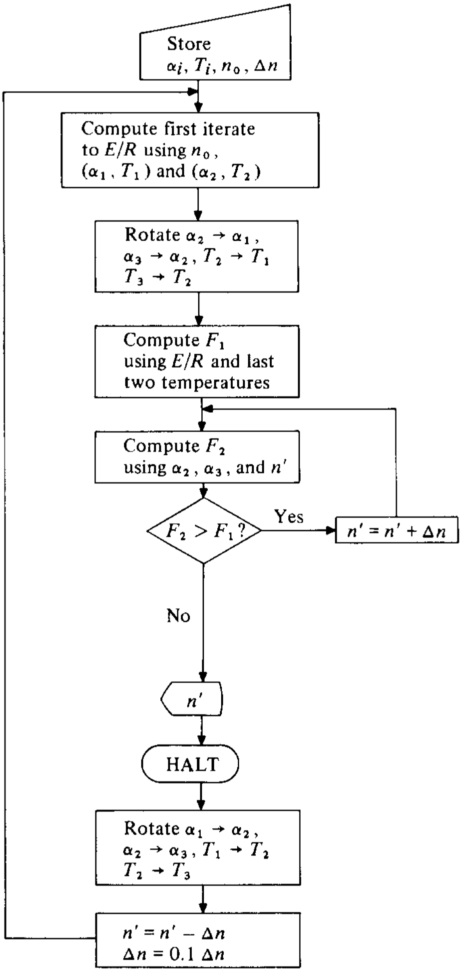

Fig. 1. Flowchart for the three-point iterative method.

From the data shown in Table 2, it is immediately obvious that as the second point represents successively larger values of α, the first iterate n' and

TABLE 2

Kinetic parameters obtained for (α,T) data calculated using $n = 1.66667$, $E = 100$ kJ mole^{-1}, and $A/\beta = 3\times10^{10}$ min^{-1}

Points used [a]	First iteration		Second iteration	
	n'	E (kJ mole^{-1})	n	E (kJ mole^{-1})
1, 2, 10	1.7	98.430	1.69	100.300
1, 3, 10	1.6	97.159	1.67	99.918
1, 4, 10	1.6	95.256	1.67	99.628
1, 5, 10	1.6	92.425	1.66	99.268
1, 6, 10	1.5	88.417	1.64	98.043
3, 4, 10	1.5	91.157	1.64	98.468
4, 5, 10	1.4	83.060	1.60	95.982

[a] Numbers refer to points in Table 1.

E/R become less accurate. This is expected since the first value of E/R is established using $n_0 = 0$ and assuming that E/R is constant for all n' values. Obviously, this approximation is worse for larger values of α. The second iteration largely removes this error since E/R is established using the first iterate n'. If the results obtained using points (1, 5, 10), where $\alpha_2 = 0.24365$, are considered, the second iterate n' is 1.66 and $E = 99.268$ kJ mole^{-1}. Clearly, even though α_2 is hardly "small", the results are as accurate as the five-decimal α values will allow. However, when points (1, 6, 10) are used, the second iterate values $n' = 1.64$ and $E = 98.043$ are probably outside the accepted tolerance for these parameters. However, in the case of the computation using points (1, 6, 10), the third iterate values are $n' = 1.667$ and $E = 99.740$ kJ mole^{-1}. In the case of the computation using points (4, 5, 10), the third iterate values are $n' = 1.653$ and $E = 99.030$ kJ mole^{-1}. Certainly in this case neither α_1 nor α_2 fit the criterion of "small" α. The results of three iterations appear to exhibit sufficient accuracy in the derived n and E values as long as both α_1 and α_2 values are less than about 0.25 with better accuracy resulting when $\alpha_1 < 0.1$. Because $\Delta n = 0.001$ during the third iteration, performing three iterations greatly increases computing time.

Numerical solutions of rate equations are available for various values of n from 0 to 2 [7] and they have been analyzed by the method of Reich and Stivala [2]. These data have also been used as a test of the present method with the results shown in Table 3. These results show that as long as α_1 and α_2 fit the criterion of being small, two iterations produce n' and E values that are as accurate as can be expected. This is especially true when it is recalled that the value for n' represents the value which first produces $F_2 < F_1$ so that the actual n is smaller than the value shown by less than 0.01.

TABLE 3

A comparison of results obtained using the Reich and Stivala and present methods with calculated (α, T) data

n			E (kJ mole^{-1})[a]	
Actual	Reich–Stivala[b]	Present[c]	Reich–Stivala[b]	Present[c]
0	0.02	0.01	100.231	99.999
1/3	0.34	0.34	100.848	99.842
1/2	0.50	0.51	101.526	100.069
2/3	0.67	0.67	100.912	99.713
1	1.00	1.01	101.065	100.065
4/3	1.34	1.34	99.621	99.956
5/3	1.67	1.67	99.323	99.628
2	2.00	2.01	100.707	100.071

[a] Actual $E = 100$ kJ mole^{-1} used in numerical solution of rate equation.

[b] Using the Reich and Stivala method [2].

[c] Using two iteration cycles. These data were calculated using $\alpha_1 < 0.05$, $\alpha_2 < 0.15$, and $\alpha_3 > 0.85$ (usually $\alpha_3 > 0.95$).

Testing the method with TG data

In order to test the described method using actual TG data, the data for decomposition of NH_4HCO_3 were used [9]. In each case, α_1 was in the range 0.04–0.10, α_2 in the range 0.15–0.20, and α_3 was > 0.67. Table 4 shows the results of the analysis. Again, it is clear that the present method gives satisfactory agreement with established methods.

TABLE 4

A comparison of n and E values for the decomposition of NH_4HCO_3 obtained by two iterative methods

Run	Reich and Stivala[a]		Present method	
	n	E (kJ mole^{-1})	n	E (kJ mole^{-1})
1	1.20	99.97	1.16	98.70
2	1.32	90.68	1.61	95.71
3	1.33	99.11	1.58	103.20
4	1.06	80.62	0.93	75.80
5	1.66	94.57	1.52	89.67
Ave	1.31	92.99	1.36	92.96
σ	0.22	7.86	0.30	10.61

[a] Computed [8] using the method of Reich and Stivala [2].

It must be cautioned that in TG studies α is determined by comparison of an observed mass loss with that corresponding to the complete reaction. If a given reaction is accompanied by only a few per cent mass loss, α is generally not determined as accurately as when a larger mass loss is involved. The present method, and those based on other computations, will not generally give kinetic parameters of high accuracy for such cases.

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APPENDIX

HP-34C Program listing for the three-point iterative method

Line	Display	Keys
000-		
001-	25 13 11	h LBL A
002-	24 0	RCL 0
003-	13 0	GSB 0
004-	23 7	STO 7
005-	24 1	RCL 1
006-	13 0	GSB 0
007-	23 8	STO 8
008-	24 7	RCL 7
009-	24 8	RCL 8
010-	71	÷
011-	23 7	STO 7
012-	24 4	RCL 4
013-	24 3	RCL 3
014-	71	÷
015-	15 3	g X^2
016-	24 7	RCL 7
017-	61	x
018-	14 1	f LN
019-	23 8	STO 8
020-	24 4	RCL 4
021-	25 2	h 1/X
022-	24 3	RCL 3
023-	25 2	h 1/X
024-	41	–
025-	23 7	STO 7
026-	24 8	RCL 8
027-	24 7	RCL 7
028-	71	÷
029-	23 9	STO 9
030-	24 1	RCL 1
031-	23 0	STO 0
032-	24 2	RCL 2
033-	23 1	STO 1
034-	24 4	RCL 4
035-	23 3	STO 3
036-	24 5	RCL 5
037-	23 4	STO 4
038-	25 2	h 1/X
039-	24 3	RCL 3
040-	25 2	h 1/X
041-	41	–
042-	24 9	RCL 9
043-	61	x
044-	15 1	g e^x
045-	24 4	RCL 4
046-	24 3	RCL 3
047-	71	÷
048-	15 3	g X^2
049-	71	÷
050-	23 .1	STO .1
051-	25 13 12	h LBL B
052-	24 0	RCL 0
053-	13 0	GSB 0
054-	23 7	STO 7
055-	24 1	RCL 1
056-	13 0	GSB 0
057-	23 8	STO 8
058-	24 7	RCL 7
059-	24 8	RCL 8
060-	71	÷
061-	23 .0	STO .0
062-	24 .1	RCL .1
063-	24 .0	RCL .0
064-	14 51	f $X > Y$
065-	22 2	GTO 2
066-	22 3	GTO 3
067-	25 13 0	h LBL 0
068-	32	CHS

Line	Display	Keys
069-	1	1
070-	51	+
071-	1	1
072-	24 6	RCL 6
073-	41	–
074-	25 3	h Y^X
075-	32	CHS
076-	1	1
077-	51	+
078-	25 12	h RTN
079-	25 13 2	h LBL 2
080-	24 .3	RCL .3

Line	Display	Keys
081-	23 51 6	STO+6
082-	22 12	GTO B
083-	25 13 3	h LBL 3
084-	24 6	RCL 6
085-	74	R/S
086-	24 4	RCL 4
087-	23 5	STO 5
088-	24 3	RCL 3
089-	23 4	STO 4
090-	24 1	RCL 1
091-	23 2	STO 2
092-	24 0	RCL 0
093-	23 1	STO 1

Line	Display	Keys
094-	24 .4	RCL .4
095-	23 0	STO 0
096-	24 .2	RCL .2
097-	23 3	STO 3
098-	24 .3	RCL .3
099-	23 41 6	ST0 – 6
100-	24 .3	RCL .3
101-	1	1
102-	0	0
103-	71	÷
104-	23 .3	STO .3
105-	22 11	GTO A