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# A GENERAL ITERATIVE METHOD FOR OBTAINING KINETIC PARAMETERS FROM TG DATA

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## ABSTRACT

An iterative method is described for determining the reaction order and activation energy from TG curves. The method makes use of equations to represent the temperature integrals which are derived using numerical relationships in terms of $E$, $T$, and empirical constants. Like the method of Reich and Stivala, the computation involves varying the value of $n$ until the appropriate linear relationship gives an intercept of zero. The slope of the line is $YE^X$, where $Y$ and $X$ are constants in the equation

$$-\log I = YE^X(1/T) + \log E^W + U$$

The method is tested using data obtained by means of a fourth order Runge–Kutta solution of the rate law for both Arrhenius and non-Arrhenius cases.

## INTRODUCTION

Most of the methods of analyzing TG data are based on the rate law

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

where $\alpha$ is the fraction of reaction completed, $T$ is the temperature (K), $\beta$ is the heating rate, $E$ is the activation energy, $n$ is the order, and $R$ is the molar gas constant. Owing to the fact that the temperature integral

$$I = \int_0^T e^{-E/RT}\, dT \tag{2}$$

has no analytical closed from, approximations based on

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)} = \frac{A}{\beta}\int_0^T e^{-E/RT}\, dT \tag{3}$$

abound [1–13]. Most of these methods make use of a truncated series approximation of the integral. It has also been suggested that non-linear heating rates be used to make the direct integration possible [14] and thus avoid errors introduced by approximations of the integral.

Recently, Reich and Stivala described a compact computer method that is based on the approximate equation

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)}=\frac{ART^2}{\beta E}\left(1-\frac{2RT}{E}\right)\mathrm{e}^{-E/RT} \tag{4}$$

in which the temperature integral is represented by a truncated series [2,15] Since $E>>2RT$, $(1-2RT/E)$ is approximately constant and the two point form of eqn. (4) is

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right]=-\frac{E}{R}\left(\frac{1}{T_i}-\frac{1}{T_{i+1}}\right) \tag{5}$$

Thus, when

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

and

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

eqn. (5) represents a linear equation with a slope of $-E/R$ and an intercept of zero. Linear regression is then performed iteratively to find the value of $n$ resulting in an intercept of zero [16]. One of the deficiencies of this method is that it is valid only for reactions obeying the rate law of eqn. (1). For this case, only the Arrhenius temperature integral [eqn. (2)] is approximated by a truncated series and the method thus represents a special case. Further, the truncated series and the approximation that $(1-2RT/E)$ is a constant are not equally valid for all values of $E$ and $T$. What is needed is a general iterative method that is not limited to a rate law of the form of eqn. (1) but one that will be valid for

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{A}{\beta}(1-\alpha)^n T^m\,\mathrm{e}^{-E/RT} \tag{6}$$

where $m=0$, $\pm 1/2$, $\pm 1, \ldots$ This paper describes such a method where the temperature integrals

$$I=\int_0^T T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T$$

are approximated by numerical relationships [17,18].

## THEORY

If we start with the rate law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}(1-\alpha)^n T^m\,\mathrm{e}^{-E/RT} \tag{6}$$

integration when $n \neq 1$ leads to

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)}=\frac{A}{\beta}\int_0^T T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{7}$$

For two different temperatures, $T_i$ and $T_{i+1}$, there will be two different fractions of reaction, $\alpha_i$ and $\alpha_{i+1}$, respectively. Taking the ratio of these two gives

$$\frac{\left[1-(1-\alpha_i)^{1-n}\right]/(1-n)}{\left[1-(1-\alpha_{i+1})^{1-n}\right]/(1-n)}=\frac{\frac{A}{\beta}\int_0^{T_i} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T}{\frac{A}{\beta}\int_0^{T_{i+1}} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T} \tag{8}$$

Simplifying and taking logarithms yields

$$\log\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\right]=\log\frac{\int_0^{T_i} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T}{\int_0^{T_{i+1}} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T} \tag{9}$$

which can be written as

$$\log\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\right]=\log\int_0^{T_i} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T-\log\int_0^{T_{i+1}} T^m\,\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{10}$$

We have recently shown that an accurate representation for the temperature integral is afforded by empirical relationships in the form

$$-\log I=N(1/T)+D \tag{11}$$

or, more precisely

$$-\log I=YE^X(1/T)+\log E^W+U \tag{12}$$

where $X$, $Y$, $W$, and $U$ are constants that have been tabulated for integrals involving several values of $m$ [17,18]. Therefore, we can write

$$\log\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\right]=-\left(YE^X(1/T_i)+\log E^W+U\right)+\left(YE^X(1/T_{i+1})+\log E^W+U\right) \tag{13}$$

Since the last two terms of eqn. (12) are not functions of temperature, eqn.

(13) simplifies to

$$\log\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\right] = YE^X\left(\frac{1}{T_{i+1}} - \frac{1}{T_i}\right) \tag{14}$$

and, therefore, values of only $Y$ and $X$ are required for the particular value of $m$ used. In the method developed in this work, the left-hand side of eqn. (14) and $(1/T_{i+1} - 1/T_i)$ are subjected to linear regression starting with $n = 0.1$. The iterative variation of $n$ is carried out until the intercept is closest to zero as before [16,19]. Then

$$-\text{Slope} = YE^X \tag{15}$$

or

$$\log(-\text{Slope}) = \log Y + X \log E \tag{16}$$

from which $E$ is readily determined using the tabulated values of $Y$ and $X$ previously reported [18,20].

## TESTING THE METHOD

In order to test the method, values of $\alpha$ are needed at various temperatures for known values of $E$, $A/\beta$, $n$, and $m$ as they appear in eqn. (6). Since the purpose was to determine if the iterative method would yield accurate computed values of $n$ and $E$, these parameters were given values of $n = 1.000$ and $E = 100$ kJ mole$^{-1}$ to compute the ($\alpha$, $T$) data. The values of $\alpha$ at various temperatures were then computed by means of a fourth order Runge–Kutta program using a TI-59 programmable calculator. This method has been shown to yield extremely accurate results [21]. The ($\alpha$, $T$) data resulting from numerical solution of eqn. (6) using values of $E$, $A/\beta$, and $n$ given above and using values of $m = 0$, $\pm 1/2$, $\pm 1$, $\pm 3/2$, and $\pm 2$ are shown in Table 1. To analyze these ($\alpha$, $T$) data, a program was written to perform the iterative method described by eqn. (14). Details of the program and its use will be reported elsewhere. Because this program produces an iterative evaluation of the intercept nearest zero for the correct $n$, the procedure starts with $n = 0.1$ and $n$ is incremented by 0.100001 (so that $n$ is never exactly 1) until the intercept becomes negative. At this point, the value of $n$ is reduced to that of the previous iteration and incrementing by 0.01 occurs so that the "correct" $n$ is determined to two decimal places [16,19]. It is then necessary to evaluate $E$ from the slope of this regression relationship for the "correct" $n$. Thus, the values of $Y$ and $X$ used to determine $E$ as a function of $1/T$ in eqn. (12) are required and these are shown in Table 2 for each value of $m$.

TABLE 1

Values of ($\alpha$, $T$) computed by means of a fourth order Runge–Kutta method[a]

| $m=2$[b] | | $m=2$[c] | | $m=3/2$[c] | | $m=1$ | | $m=1/2$ | |
|---|---|---|---|---|---|---|---|---|---|
| $T$ (K) | $\alpha$ | $T$ (K) | $\alpha$ | $T$ (K) | $\alpha$ | $T$ (K) | $\alpha$ | $T$ (K) | $\alpha$ |
| 570 | 0.054955 | 430 | 0.029768 | 460 | 0.029157 | 330 | 0.008671 | 370 | 0.045544 |
| 580 | 0.117828 | 440 | 0.083931 | 470 | 0.070741 | 340 | 0.035013 | 380 | 0.110434 |
| 590 | 0.237259 | 450 | 0.213322 | 480 | 0.160892 | 350 | 0.107524 | 390 | 0.244707 |
| 600 | 0.434910 | 460 | 0.465500 | 490 | 0.333240 | 360 | 0.279202 | 400 | 0.475456 |
| 610 | 0.691163 | 470 | 0.792193 | 500 | 0.596244 | 370 | 0.585616 | 410 | 0.759829 |
| 620 | 0.906075 | 480 | 0.977556 | 510 | 0.860381 | 380 | 0.894144 | 420 | 0.952193 |
| 630 | 0.990546 | 490 | 0.999857 | 520 | 0.984293 | 390 | 0.995740 | | |
| $m=0$ | | $m=-1/2$ | | $m=-1$ | | $m=-3/2$ | | $m=-2$ | |
| 400 | 0.032107 | 450 | 0.054209 | 510 | 0.067522 | 570 | 0.039128 | 710 | 0.103760 |
| 410 | 0.068931 | 460 | 0.097758 | 520 | 0.106093 | 590 | 0.079627 | 730 | 0.159954 |
| 420 | 0.139813 | 470 | 0.168989 | 530 | 0.162029 | 610 | 0.151679 | 750 | 0.237011 |
| 430 | 0.264301 | 480 | 0.277648 | 540 | 0.239689 | 630 | 0.268299 | 770 | 0.336568 |
| 440 | 0.454525 | 490 | 0.428099 | 550 | 0.341757 | 650 | 0.434768 | 790 | 0.456324 |
| 450 | 0.687203 | 500 | 0.609378 | 560 | 0.466754 | 670 | 0.634167 | 810 | 0.588328 |
| 460 | 0.885618 | 510 | 0.787805 | 570 | 0.606345 | 690 | 0.820177 | 830 | 0.718990 |
| 470 | 0.980599 | 520 | 0.918669 | 580 | 0.744328 | 710 | 0.941680 | 850 | 0.832227 |
| | | | | 590 | 0.860583 | | | 870 | 0.915537 |
| | | | | 600 | 0.939937 | | | 890 | 0.965667 |

[a] Using previously described method [21].

[b] Computed using $E=200$ kJ mole$^{-1}$

[c] Computed using $E=150$ kJ mole$^{-1}$. All other cases using $E=100$ kJ mole$^{-1}$.

TABLE 2

Values of $X$ and $Y$ of eqn. (12) for different values of $m$

| $m$ | $X$ | $Y$ |
|---|---|---|
| 2 | 0.93139 | 310.184 |
| 3/2 | 0.93943 | 297.632 |
| 1 | 0.94762 | 285 404 |
| 1/2 | 0.95595 | 273.489 |
| 0 | 0.96443 | 261.884 |
| −1/2 | 0.97309 | 250.578 |
| −1 | 0.98187 | 239.611 |
| −3/2 | 0.99086 | 228.919 |
| −2 | 0.99993 | 218 593 |

## RESULTS AND DISCUSSION

The ($\alpha$, $T$) data shown in Table 1 were subjected to analysis by the iterative method described in this work. Table 3 shows the results obtained by means of these computations. These results show that the iterative method produces an intercept that differs from zero by about 0.007 at most. In each case, the value of $n$ is within 0.01 of the "correct" value of $n = 1.00$ used for the computation of the ($\alpha$, $T$) data. Values of the intercept could be found closer to zero by using increments for $n$ smaller than 0.01. Although

TABLE 3

Results computed using the iterative procedure when analyzing ($\alpha$,$T$) data shown in Table 1

| $m$ | Best[a] $n$ | Intercept | −Slope | −Corr. Coeff. | Calcd. $E$ (kJ mole$^{-1}$) |
|---|---|---|---|---|---|
| 2[b] | 1.00 | −0.005711 | 11262.806 | 0.999874 | 197.94 |
| 2[c] | 1.01 | 0.001017 | 8720.059 | 0.996424 | 150.39 |
| 3/2[c] | 0.99 | 0.007135 | 8695.624 | 0.999525 | 151.96 |
| 1 | 1.00 | 0.005144 | 5758.696 | 0.999612 | 99.67 |
| 1/2 | 0.99 | 0 004124 | 5683.246 | 0.999818 | 99.99 |
| 0 | 0.99 | 0.006410 | 5689.732 | 0.999835 | 101 83 |
| −1/2 | 0.99 | 0.001860 | 5552.899 | 0.999904 | 101.01 |
| −1 | 0.99 | 0.003079 | 5529.432 | 0.999927 | 102.31 |
| −3/2 | 1.00 | −0.003063 | 5293.001 | 1.000000 | 99.59 |
| −2 | 1.00 | 0.000242 | 5232.320 | 1.000000 | 100.17 |

[a] $n = 1.00$ used to calculate the ($\alpha$,$T$) data by the Runge–Kutta method.

[b] A value of $E = 200$ kJ mole$^{-1}$ was used to calculate the ($\alpha$,$T$) data.

[c] A value of $E = 150$ kJ mole$^{-1}$ was used to calculate the ($\alpha$,$T$) data.

the results shown in Table 3 have been obtained using data calculated with $n = 1.00$, other values of $n$ produce similar results.

The values of $X$ and $Y$ in eqn. (13) were obtained from linear regression of $-\log I$ and $1/T$ and then treating the slopes and intercepts by linear regression [18,20]. Thus, there are slight errors in these empirically obtained values of $X$ and $Y$. Further, the values of the integrals themselves are not exact [5,17,18,20]. Although the value of $\alpha$ at each value of $T$ is accurately determined by the Runge–Kutta method [21], the solutions are also inexact. Finally, like the method of Reich and Stivala, the iterative method described here makes use of linear regression to determine when the intercept is closest to zero. Thus, the method described here makes use of a considerable amount of numerical analysis and the results of other numerical methods. While each of these procedures could be made slightly more accurate, the increase in computation is hardly worth the effort. This is quite evident from the results shown in Table 3. The total process represents the numerical integration of the temperature integrals, determining $X$ and $Y$ [18,20], calculating the ($\alpha$, $T$) data by a fourth order Runge–Kutta method [21], and the present iterative method of analyzing the ($\alpha$, $T$) data. In fact, the results shown in Table 3 give verification of the consistency of the calculations and that the errors are indeed negligible in each process.

An interesting feature of the iterative computation is that the slope varies considerably even for small differences in intercept as $n$ is varied by units of 0.01. For example, in Table 3 in the case where $m = 0$, the trial value of $n = 0.99$ produces an intercept of 0.006410 while the trial value of $n = 1.00$ yields an intercept of $-0.006942$. Both of these values are close to zero and the actual value of $n$ indicated by the data is between 0.99 and 1.00. However, the corresponding slopes are 5689.732 and 5461.433 when $n = 0.99$ and $n = 1.00$, respectively. The values of $E$ calculated from these slopes are 101.832 and 97.60 kJ mole$^{-1}$, respectively. Thus, an error of about 2% results in the calculated value of $E$ in either case. An intercept closer to zero can be obtained but it requires that increments in $n$ be smaller than 0.01. It is readily apparent from this example that an error in $E$ of perhaps ±2% could result simply because of the difference in the slopes produced by an iteration step for $n$ of 0.01. Obviously, the actual difference from zero that can be tolerated in the intercept will depend on the values of $E$ and $n$. However, from this example, it is clear that determining $E$ to a greater accuracy than ±2% could require iterations smaller than 0.01 in $n$. While it is not difficult to program the computation with an iteration of say 0.001, it is meaningless from a phenomenological point of view to try to interpret a value of $n$ known to three decimal places instead of two. Furthermore, it is highly unlikely that experimental data would ever justify such a procedure [22]. Finally, the example discussed here shows that a sophisticated data analysis technique does not remove all the errors in calculating $E$. Reducing the increment in $n$ to values smaller than 0.01 can increase the accuracy of the computation, but it cannot remove experimental errors in the data which render additional numerical analysis useless. It appears that data analysis methods are now available that are far more precise in calculating kinetic parameters than the experimental data are in providing input data.

For the case where $m = 0$, the temperature integral is of the Arrhenius type and the results are directly comparable with those obtained by the method of Reich and Stivala [16]. We have previously given ($\alpha$, $T$) data for such a case computed with $E = 100$ kJ mole$^{-1}$, $A/\beta = 3 \times 10^{10}$ min$^{-1}$, and $n = 0$, 1/3, 1/2, 2/3, 1, 4/3, 5/3, and 2 [21]. These ($\alpha$, $T$) data have been analyzed by the present method and the method of Reich and Stivala. Table 4 shows a comparison of the results obtained by the two iterative methods. It is readily apparent that two methods give virtually identical results for this case of Arrhenius behavior. The activation energies are, in fact, identical within the errors involved in the variation in slope produced by an iteration of 0.01 in $n$.

The value of the present method of analysis of TG data lies in the fact that the values of the temperature integral have been accurately determined by numerical integration, and the constants in eqn. (12) have been de-

TABLE 4

A comparison of results obtained using the present method and the method of Reich and Stivala

| $n$ | | Intercept | −Slope | −Corr. Coeff. | $E$ (kJ mole$^{-1}$) |
|---|---|---|---|---|---|
| Actual | Calcd. | | | | |
| *Present method* | | | | | |
| 0 | 0.01 | −0.005761 | 5491.03 | 0.999831 | 98.15 |
| 1/3 | 0.33 | −0 000024 | 5582.23 | 0.999966 | 99.83 |
| 1/2 | 0.50 | −0.002764 | 5537.69 | 0.999936 | 99.01 |
| 2/3 | 0.66 | 0.003598 | 5641.95 | 0.999933 | 100.95 |
| 1 | 0.99 | 0 006410 | 5689.72 | 0.999835 | 101.83 |
| 4/3 | 1.33 | −0.002511 | 5540.69 | 0.999979 | 99.07 |
| 5/3 | 1 66 | −0.002237 | 5540.56 | 0.999998 | 99.07 |
| 2 | 1.99 | −0.001545 | 5551.36 | 0.999999 | 99.27 |
| *Reich and Stivala method* | | | | | |
| 0 | 0.02 | −0.000074 | 12055.26 | 0.999636 | 100.23 |
| 1/3 | 0.34 | 0.004982 | 12129.45 | 0.999755 | 100.85 |
| 1/2 | 0.50 | 0.010463 | 12211.07 | 0.999984 | 101.53 |
| 2/3 | 0.67 | 0.005684 | 12137.11 | 0.999822 | 100.91 |
| 1 | 1.00 | 0.007294 | 12155.54 | 0.999986 | 101.06 |
| 4/3 | 1.34 | −0.003485 | 11981.94 | 0.999825 | 99.62 |
| 5/3 | 1.67 | −0.003742 | 11946.07 | 0.999993 | 99.32 |
| 2 | 2.00 | 0.005388 | 12112.45 | 0.999986 | 100.71 |

termined for various *m* values [18,20]. Thus, the accuracy of the expression representing the temperature integral is assured. Second, the constants in equations similar to eqn. (12) have been tabulated for cases having temperature dependent frequency factors [18,20] making the same iterative method applicable to these cases as well when the appropriate *m* value is known for the reaction. Finally, the constants in eqn. (12) have been evaluated for a large range of *E* and *T* values. Therefore, the present method is accurate for all temperatures and activation energies. It is also general in the sense that it can be used for cases involving both temperature dependent and temperature independent frequency factors.

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