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Thermogravimetry.
Analysis of the parameters of the DTG maximum

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Abstract

The general relationships $f'(\alpha_{\max}) \times F(\alpha_{\max}) = -Q(x_{\max})$ and $(\mathrm{d}\alpha/\mathrm{d}x_{\max}) = f(\alpha_{\max})/f'(\alpha_{\max})$ have been established, for a non-iosthermal thermogravimetric rate equation, where $f(\alpha)$ is the conversion function, $F(\alpha)$ is the conversion integral and $Q(x) = x^2 e^x p(x)$.

For an nth order reaction, the dependence $x_{\max} = x_{\max}\ (n, AE/\beta R)$ is analysed by solving of a transcendental equation, using an iterative method.

The temperature integral, $p(x)$, was inverted using a minimax approximation, with a relative percentage error of 2.13×10^{-4} in the interval $x \in [5, 92]$.

Keywords: DTG maximum; Inversion of temperature integral; *n*th order reaction; Thermogravimetry

1. Introduction

Theoretical studies have shown that the parameters of the DTG maximum can be used in some applications. For example, in the case of an nth order reaction, it is possible to find the kinetic parameters n, E and A by using the experimental values of $\alpha_{\max}$, $T_{\max}$ and $(\mathrm{d}\alpha/\mathrm{d}T)_{\max}$ [1]. Also, a differential method based on the expression of these parameters can be used to determine the kinetic parameters mentioned and to prove the supposed kinetic model [2].

The present paper has two parts. In the first part, two general relationships valid at the DTG maximum have been established. The second part is dedicated to a procedure for determination of the temperature at the DTG maximum, in the case where the kinetic parameters are known. This analysis enabled some new numerical methods of inversion of the temperature integral $p(x)$ to be elaborated.

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2. General

It is known that the kinetics of thermal destruction may be described by the following differential equation with separable variables [3]:

$$\frac{d\alpha}{dt} = A e^{-(E/RT)} f(\alpha) \tag{1}$$

where the notations have the usual meaning.

If the heating rate, $\beta = (dT/dt)$, is constant, the solution of Eq. (1) is:

$$F(\alpha) = \int_0^\alpha \frac{dc}{f(c)} = \frac{AE}{\beta R} p(x) \tag{2}$$

where: $x = E/RT$ and $p(x) = \int_x^\infty (e^{-u}/u^2) du$.

3. First general relationship

At the DTG maximum, because $(d^2\alpha/dt^2) = 0$, Eq. (1) leads to Eq. (3) [3].

$$\frac{\beta E}{RT_{\max}^2} + A e^{-x_{\max}} f'(\alpha_{\max}) = 0 \quad \text{if} \quad f(\alpha) \not\equiv 1 \tag{3}$$

where $f'(\alpha)$ is the derivative of $f(\alpha)$ with respect to α.

Eq. (3) can be rewritten as:

$$\frac{AE}{\beta R} f'(\alpha_{\max}) = -x_{\max}^2 e^{x_{\max}} \tag{3'}$$

A first general relationship can now be obtained by eliminating the parameter A between Eqs. (2) and (3). This relationship has the following expression:

$$f'(\alpha_{\max}) F(\alpha_{\max}) = -Q(x_{\max}) \tag{4}$$

where: $Q(x) = x^2 e^x p(x)$.

When $f(\alpha) \equiv 1$, it follows that $\alpha_{\max} = 1$, and thus $(AE/\beta R) p(x_{\max}) = 1$, from which

$$x_{\max}^2 e^{x_{\max}} = \frac{AE}{\beta R} Q(x_{\max}) \tag{5}$$

Writing Eq. (4) for the case of an nth order reaction ($f(\alpha) = (1-\alpha)^n$), the well known relationships (6) [4] can be easily obtained:

$$(1-\alpha)_{\max}^{n-1} = 1 + \frac{1-n}{n} Q(x_{\max}) \quad \text{if} \quad n \neq 1 \tag{6a}$$

$$-\ln(1-\alpha_{\max}) = Q(x_{\max}) \quad \text{if} \quad n = 1 \tag{6b}$$

It is appropriate to introduce a new function, $r(x)$, defined by the relationship:

$$r(x) = 1 - Q(x) \tag{7}$$

As a result, Eq. (6a) changes to Eq. (8) which, for $x_{\max} \to \infty$, changes to the well-known relationship, Eq. (9) [4,5] because $\lim_{x \to \infty} r(x) = 0$:

$$(1-\alpha)_{\max} = n^{1/(1-n)}[1+(n-1)r(x_{\max})]^{1/(n-1)} \tag{8}$$

$$(1-\alpha)_{\max} = n^{1/(1-n)} \tag{9}$$

Taking into account Eq. (9), the bracket on the RHS of Eq. (8) can be interpreted as a correction factor which reflects the finite character of x.

Adopting the approximation [6,7]:

$$r(x) \approx \frac{2}{x+3} \tag{10}$$

Eq. (8) becomes:

$$(1-\alpha)_{\max} \approx n^{1/(1-n)}\left[1+2\frac{n-1}{x_{\max}+3}\right]^{1/(n-1)} \tag{11}$$

Expanding the right hand side of Eq. (11) in a binomial series, gives Eq. (12) for high enough values of $x_{\max}$

$$(1-\alpha)_{\max} \approx n^{1/(1-n)}\left(1+\frac{2}{x_{\max}+3}\right) \tag{12}$$

For example, if $x = 30$, the following approximation, which is nearly identical with that of Gyulai and Greenhow [8], results

$$(1-\alpha)_{\max} \approx 1.061 n^{1/(1-n)} \tag{13}$$

4. A second general relationship

In order to find the reaction rate at the DTG maximum for a certain conversion function $f(\alpha)$, it is necessary to eliminate the parameter A between Eqs. (1) and (3) and Eqs. (1) and (5). The following relationships result:

$$\left(\frac{d\alpha}{dT}\right)_{\max} = -\frac{E}{RT_{\max}^2}\frac{f(\alpha_{\max})}{f'(\alpha_{\max})} \quad \text{if} \quad f(\alpha) \not\equiv 1 \tag{13a}$$

$$\left(\frac{d\alpha}{dT}\right)_{\max} = \frac{E}{RT_{\max}^2}\frac{1}{Q(x_{\max})} \quad \text{if} \quad f(\alpha) \equiv 1 \tag{13b}$$

Considering now that $(dx/dt) = -(E/RT^2)$, Eqs. (13) take the following forms:

$$\left(\frac{d\alpha}{dx}\right)_{\max} = \frac{f(\alpha_{\max})}{f'(\alpha_{\max})} \quad \text{if} \quad f(\alpha) \not\equiv 1 \tag{13'a}$$

$$\left(\frac{d\alpha}{dx}\right)_{\max} = -\frac{1}{Q(x_{\max}^2)} \quad \text{if} \quad f(\alpha) \equiv 1 \tag{13'b}$$

For an nth order reaction Eq. (13′a) changes to Eq. (14) or (14′), the latter being a well known relationship [3]:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)_{\max} = -\frac{1-\alpha_{\max}}{n} \quad \text{with} \quad n \neq 0 \tag{14}$$

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max} = \frac{\beta E}{nRT_{\max}^2}(1-\alpha)_{\max} \tag{14'}$$

Eq. (14′) can be written in an equivalent form, Eq. (15), in order to determine kinetic parameters:

$$E = \mathscr{A} n \tag{15}$$

where $\mathscr{A} = (RT_{\max}^2)/(\beta(1-\alpha)_{\max})(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$. Here, it is necessary to emphasize that the experimental determination of $\mathscr{A}$ implies a knowledge of the absolute rate $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$, which requires a previous calibration of DTG.

If it is supposed that $\mathscr{A}$ and $T_{\max}$ are exactly determined, Eq. (15) leads to the following relationship between the relative errors in E and n.

$$\frac{\Delta n}{n} = \frac{\Delta E}{E} \tag{16}$$

This relationship shows that the relative error in the estimation of a parameter (determined by a particular method or arbitrarily chosen) leads to a similar relative error for an other parameter, determined using Eq. (15).

If the experimental value of $(1-\alpha)_{\max}$ is precisely determined, more accurate approximations of kinetic parameters n and E can be iteratively determined by coupling Eqs. (8) and (15). Usually, the initial approximation of n is found by using Eq. (9), therefore considering $x = \infty$, what means an overestimated value of n [1].

5. Determination of the DTG maximum temperature

This section refers to the determination of the temperature corresponding to the DTG maximum, in the particular case of an nth order reaction for which the kinetic parameters are known.

By elimination of $f'(\alpha_{\max})$ from Eqs. (3′) and (6), the following relationship can be written:

$$x_{\max}^2 e^{x_{\max}} = \frac{AE}{\beta R}[1 + (n-1)r(x_{\max})] \tag{17}$$

where: $r(x) = 1 - Q(x)$.

Eq. (17) is a transcendental equation in $x_{\max}$ which allows the determination of the temperature corresponding to the DTG maximum when the kinetic parameters n, A and E are known. For consideration in Section 6, it is interesting to notice that the solution of Eq. (17), for the particular case of $n = 0$, is expressible in terms of the inversion of the temperature integral, i.e.

$$x_{\max} = p^{-1}\left(\frac{\beta R}{AE}\right) \tag{18}$$

Eq. (17) was solved using the method of iteration [9] (i.e. the method of successive approximations). For this purpose, Eq. (17) was written in the form:

$$x_{k+1} = \ln \frac{AE}{\beta R}[1 + (n-1)r(x_k)] - 2\ln x_k \tag{19}$$

Inserting an initial value, x_0, in the right hand side, the first approximation x_1 is obtained; this is substituted again leading to x_2, etc. The convergence of the procedure occurs since $\lim_{k\to\infty} x_k = x^*$.

In order to apply this procedure it is necessary to calculate accurately the values of $r(x)$ and of the logarithms. By calculation it was found that, for $(AE)/(\beta R) \geq 10^5$ and $x_0 = 10$, the procedure converges for any value of n. Naturally, the convergence rate depends on the numerical parameters involved (n and $(AE)/(\beta R)$) as well as the initial approximation adopted for x_0.

The maximum precision obtainable is dependent only on the performance of the computation machine. However, it will be shown that a reasonable precision for the DTG maximum temperature does not require a high precision in $x_{\max}$. Indeed, taking into account the definition of $x = (E)/(RT)$ it can be shown that

$$\frac{\Delta x}{x} \approx -\frac{\Delta T}{T} \tag{20}$$

Supposing, for example, that $x_{\max} = 30$ and $T = 500$ K, the above relationship shows that an error of $\Delta T = 1$ K corresponds to $\Delta x = 0.06$.

Solving Eq. (17) enables the following to be established:

$$x_{\max} = x_{\max}\left(n, \frac{AE}{\beta R}\right)$$

Tabulation of this dependence was performed for different values of n (0, 0.5, ... 4.0) and $AE/\beta R$ (10^9, 10^{10}... 10^{25}). It was found that $x_{\max}$ for a given value of $AE/\beta R$, changes slowly as n changes (see Table 1).

However, the variation of $x_{\max}$ as a function of log $AE/\beta R$ (n being fixed) is more pronounced (see below).

The plots of $x_{\max}$ as a function of log $AE/\beta R$, for an established value of n, suggest a dependence of the following type:

$$x_{\max} \approx a + \frac{b}{z} + cz \quad \text{where:} \quad z = \log \frac{AE}{\beta R} \tag{21}$$

Table 1
The values of x_{max} for various values of n and $AE/\beta R = 10^5$

n	x_{max}
0.0	27.820
0.5	27.852
1.0	27.883
1.5	27.913
2.0	27.941
2.5	27.969
3.0	27.996
3.5	28.023
4.0	28.048

The coefficients a, b, c from Eq. (21) were determined by using the method of least squares. In this way, the following relations were obtained for $z \in [9, 25]$:

$$n = 0: x_{max} \approx -6.72775 + \frac{16.3425}{z} + 2.23069z$$

$$n = 1: x_{max} \approx -6.72197 + \frac{17.2409}{z} + 2.23050z$$

$$n = 2: x_{max} \approx -6.70052 + \frac{17.9187}{z} + 2.22997z$$

$$n = 3: x_{max} \approx -6.66949 + \frac{18.4414}{z} + 2.22925z$$

$$n = 4: x_{max} \approx -6.63258 + \frac{18.8513}{z} + 2.22843z \tag{22}$$

It was found that the relative percentage errors, $(|\Delta x_{max}|)/(x_{max})$, according to Eqs. (22) for $n \in [0, 4]$ and $z \in [9, 25]$, were smaller than 0.1 (see, for example, Table 2). Taking into account Eq. (20), one can say that the approximations Eq. (22) provide a determination of T_{max} with satisfactory accuracy.

6. On the inversion of the temperature integral

If the kinetic model and the parameters A and E are specified, Eq. (2) allows the thermograms to be simulated. Such an operation may be carried out in two different ways with the conversion α as known and calculating T, or the reverse.

The first method, which requires a knowledge of the inverse of temperature integral, has the following advantages:

Table 2
A comparison of the accurate and approximate (Eq. (22)) values of $x_{\max}$ for $n = 1$ and various values of $z = \log(AE/\beta R)$

z	$x_{\max}$	x_{approx}(Eq. (22))
9	15.271	15.268
11	19.398	19.381
13	23.610	23.601
15	27.883	27.885
17	32.200	32.211
19	36.552	36.565
21	40.931	40.940
23	45.332	45.329
25	49.751	49.730

(1) as long as the problem of inversion is not difficult to solve, the calculation time is significantly reduced;

(2) it is not necessary to find the explicit expression for α from Eq. (2) — this operation can be carried out only for certain kinetic models [10];

(3) by refining the calculations, the experimental data can be analysed by carrying out a regression after α (it is supposed that the conversion data are accurately determined, while the temperature values may be affected by errors);

(4) by simulating the experimental errors with a pseudo-random number generator, it is possible to study how the calculated values of kinetic parameters are affected by the distribution of the sampling points on the TG curve [11], etc.

The problem of inverting the temperature integral was first solved by Elder [12] using an original approximation:

$$\ln p(x) \approx \sum_{j=0}^{j=3} a_j x^j$$

which he called the generalized Doyle equation [13]. In this way, Elder reduced this problem to the inversion of a third degree polynomial. It is possible that the author comments the precision of the procedure in the original paper [14].

An alternative method is to use a new type of generalized Doyle equation [15]:

$$-\ln p(x) \approx Ax^B + C \tag{23}$$

which, as observed, allows a facile determination of the explicit expression for x. In addition, to achieve the highest possible accuracy ($\varepsilon < 2.4 \times 10^{-6}\%$), a Taylor correction can be applied to the value of x_{app} established by Eq. (23):

$$\Delta x = x - x_{\text{app}} \approx Q(x_{\text{app}}) \ln \frac{p(x_{\text{app}})}{p(x)} \tag{24}$$

because: $-(\mathrm{d}\ln p(x))/(\mathrm{d}x)) = 1/(Q(x))$.

One observes that to calculate the correction, Eq. (24), it is necessary to use a routine providing very accurate values for $p(x)$.

The considerations in the previous section enable new methods of inversion of the temperature integral

Adapting the iteration method derived here, the following relationship can be written:

$$x_{k+1} = y + \ln p(x_k) + x_k \quad \text{where:} \quad y = -\ln p(x^*) \tag{25}$$

For $x \geq 5$ and $x_0 = 5$ the procedure converges. The convergence rate depends both on the initial approximation and the value of x. It was found by calculation that for a given initial value of x_0 there exists a value $x(x_0)$ from which the convergence rate increases monotonously with x.

The approximate relationship, Eq. (21), suggests an approximate inversion of the temperature integral is given by equations of the type:

$$x \approx a + \frac{b}{y} + cy \quad \text{where:} \quad y = -\ln p(x) \tag{26}$$

In order to obtain high precision, the interval $x \in [5, 100]$ was divided into two sub-intervals: [5, 16] and [16, 100]. The coefficients a, b, and c corresponding to each sub-interval were found by a least squares method applied for integer x. The following relationships were obtained:

$$\begin{aligned} x &\approx -4.45235 + \frac{14.3643}{y} + 0.912701y \quad \text{if} \quad y \in [8.521, 21.654] \\ x &\approx -7.54281 + \frac{50.8793}{y} + 0.979678y \quad \text{if} \quad y \in [21.657, 109.230] \end{aligned} \tag{27}$$

The maximum values of the relative percentage error were found to be 0.207 (at $x = 5$) for the first interval and 0.237 (at $x = 23$) for the second.

Applying the correction, Eq. (24), very accurate values were obtained. In this case, the maximum values of the relative percentage error corresponding to the two subintervals were: 5.07×10^{-5} (at $x = 5$) and 1.11×10^{-5} (at $x = 16$).

In fact, the approximation, Eq. (27), corresponding to the interval [16, 100] covers a wider range of x values. For example, the relative percentage error at $x = 200$ was found to be 0.49, according to Eq. (27), and 1.17×10^{-5} if Eq. (24) is applied. The last value is very near to that corresponding to the interval [16, 100] and proves the exceptional "efficiency" of the correction, Eq. (24).

These results suggest strongly that the rational expressions of $y = -\ln p(x)$ can be used to approximate with high accuracy the inversion temperature integral $p^{-1}(x)$, on broad intervals of x values. As a consequence, a new approximation characterized by the lowest possible relative errors (the minimax approximation [16, 17]), has been established in the interval $x \in [5, 92]$:

$$x = \frac{6.2953654 \times 10^{-1} + 1.3631926 \times 10^{-1} y + 1.20371 \times 10^{-1} y^2 + 1.7090519 \times 10^{-3} y^3}{1 + 1.3998524 y + 1.7181581 \times 10^{-3} y^2} \tag{28}$$

where $y = -\ln p(x)$.

The maximum relative percentage error of the approximation, Eq. (28), in the interval $x \in [5, 92]$ (or $8.521 \le y \le 101.065$) is 2.13×10^{-4}. Taking into account Eq. (20), and supposing $T = 1000$ K, the error induced by the approximation, Eq. (28), is at most 0.0021 K. Such an error is clearly insignificant for thermogravimetric studies. For $x > 92$, the relative percentage error increases monotonously (being 0.0086 at $x = 150$, for example) but remains much lower than the experimental error.

As expected, the use of correction Eq. (24) for values given by the approximation Eq. (28) leads to extremely low relative errors (lower than 5.4×10^{-11} for $x \in [5, 92]$) and as such is of no practical interest.

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