

## **THERMOGRAVIMETRY. EMPIRICAL APPROXIMATION FOR THE "TEMPERATURE INTEGRALS"\***

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The temperature integrals  $p_m(x) = \int_x^\infty e^{-x} u^{-2-m} du$  with  $m = 0, 1/2$  and  $1$  are approximated using empirical formulae of the type  $Ax^{-B}e^{-Cx}$ . For estimation of the precision of these approximations, the relative errors were calculated for integral values of  $x$ . It was established that for  $x < 19$  the maximum relative error is 0.26%, while for  $19 \leq x \leq 50$  it is less than 0.1%. The suggested approximations allow a sensible improvement of the integral methods intended to determine the kinetic parameters of the process concerned.

The temperature integrals are often used in thermogravimetry [1], microcalorimetry [2], thermal absorption [3], thermoluminescence [4], thermally stimulated conductivity (T.S.C.) [5], thermal oxidation [6], etc.

The present paper shows that these functions can be approximated with excellent accuracy within the intervals (5, 17) and (17, 50) by using expressions of the type  $Ax^{-B}e^{-Cx}$ .

### **Kinetics**

The thermogravimetric study takes into account the following equation:

$$dc / dt = ZT^m e^{-E/RT} (1-c)^n \quad (1)$$

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where  $t$  is the time,  $c$  the conversion,  $T$  the absolute temperature (K),  $E$  the activation energy ( $\text{cal}\cdot\text{mol}^{-1}$ ),  $R$  the universal gas constant ( $1.987 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$ ) ( $\text{K}^{-1}$ ),  $n$  the order of reaction, and  $Z$  and  $m$  are constants.

The parameter  $m$  shows the temperature-dependence of the frequency factor  $ZT^m$ . The empirical form of the Arrhenius equation implies that  $m = 0$ , while the active collision theory admits  $m = 1/2$  and the Eyring active complex theory admits  $m = 1$ .

The present paper takes into consideration all these alternatives, i.e.  $m = 0$ ,  $m = 1/2$  and  $m = 1$ .

Under non-isothermal conditions, when the heating rate  $\beta = dT/dt$  is constant, Eq. (1) can readily be integrated, giving

$$\frac{1 - (1 - c)^{1-n}}{1 - n} = \frac{Z}{\beta} \left( \frac{E}{R} \right)^{m+1} p_m(x) \quad (2)$$

where

$$x = E/RT; p_m(x) = \int_0^\infty e^{-u} u^{-2-m} du, \text{ with } m = 0, 1/2 \text{ and } 1.$$

The  $p_m(x)$  integrals will be called "the temperature integrals". The numerical values of these functions have been calculated by Vallet [7] (we have not been able to acquire his paper), Biergen and Czanderna [8], and Saint-Georges and Garnaud [9]. Since the table given for these functions in [8, 9] were incomplete, we decided to complete them new values.

With a view to calculating the  $p_0(x)$  and  $p_1(x)$  functions, we used the following relationships:

$$p_0(x) = e^{-x} x^{-1} + Ei(-x)$$

$$p_1(x) = \frac{1}{2} [e^{-x} x^{-2} - p_0(x)]$$

The values of the exponential integrals  $Ei(-x)$  were taken from [10]. For the function  $p_{1/2}(x)$  only the values tabulated by Saint-Georges and Garnaud [9] were taken into account.

### The approximations for the temperature integrals

The function  $p_0(x)$  is frequently used in thermogravimetry. It was called "the temperature integral" by MacCallum and Tanner [11]. In most cases, the functions proposed to approximate this integral have the form

$$p_o(x) \approx e^{-x} R(x),$$

where  $R(x)$  is a rational function of  $x$ . In order to exemplify this, we may mention the following approximations:

Doyle [12]: 
$$p_o(x) \approx x^{-2} e^{-x} \tag{3}$$

Coats and Redfern [13]: 
$$p_o(x) \approx (x - 2) x^{-3} e^{-x} \tag{4}$$

Doyle [14]: 
$$p_o(x) \approx (x + 1) x^{-1} e^{-x} \tag{5}$$

Turner and Schnitzer [14]: 
$$p_o(x) \approx (x + 2)^{-1} x^{-1} e^{-x} \tag{6}$$

Zsakó [16]: 
$$p_o(x) \approx (x - d)^{-1} (x + 2)^{-1} e^{-x} \tag{7}$$

where:

$$d = \frac{16}{x^2 - 4x + 84}$$

Hastings [17]: 
$$p_o(x) \approx x^{-2} \frac{0.995924x + 1.340913}{x^2 + 3.330657x + 1.681534} e^{-x} \tag{8}$$

Luke [18]: 
$$p_o(x) \approx x^{-1} \frac{x + 4}{x^2 + 6x + 4} e^{-x} \tag{9}$$

$$p_o(x) \approx x^{-1} \frac{x^2 + 10x + 18}{x^3 + 12x^2 + 36x + 24} e^{-x} \tag{10}$$

$$p_o(x) \approx x^{-1} \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} e^{-x} \tag{11}$$

The accuracy of these expressions has been estimated both via a direct comparison with the tabulated values of the temperature integrals [14, 16-21] and in the context of a critical analysis of integral methods for determining the kinetic parameters [22-24].

Approximation (3) allows the linearization of (2) with the aim of determining the kinetic parameters  $n$ ,  $Z$  and  $E$ . However, the poor accuracy of

this equation reduces the possibility of its practical utilization. Unfortunately, the other approximations, i.e. Eqs (4)-(11), even though more accurate, do not allow the linearization of Eq. (2).

The following new approximation for the temperature integrals is proposed in the present paper:

$$p_m(x) \approx Ax^{-B}e^{-Cx} \quad (12)$$

This approximation was suggested by an analysis of the table giving the values of  $\log p_o(x)$  and its first difference:

$$\Delta_{0.1}(x) = \log p_o(x + 0.1) - \log p_o(x)$$

with  $x = 5, 6, 7, \dots, 50$ .

By plotting the difference  $\Delta_{0.1}(x)$  vs.  $1/x$ , it was found that the obtained points are situated exactly on two segments that intersect at  $x = 17$ . For each of these segments we can write

$$\Delta_{0.1}(x) = m_i + \frac{n_i}{x} \quad \text{with } i = 1, 2$$

Approximating the difference by a differential and integrating it, we finally found expression (12).

The suggested function contains three parameters, whose values are determined by the method of least squares. In addition, since the function  $p_o(x)$  diminishes rapidly, it is preferable to minimize the sum of the relative error squares, instead of the sum of the squares of the errors. These calculations were carried out by means of a FELIX C 32 computer and the obtained values are listed in Table 1.

Table 1 also presents the variation domain of  $x$ . The parameters  $A$ ,  $B$  and  $C$  corresponding to the other two temperature integrals  $p_{1/2}(x)$  and  $p_1(x)$ , were similarly obtained for each of the considered intervals (see Table 1).

The approximate values of these three integrals can be obtained by replacing the numerical values of  $A$ ,  $B$  and  $C$  in relation (12).

In order to appreciate the precision of the suggested approximations, we have tabulated the three functions for all values of the integer  $x$  (i.e.  $x \in [5-50]$  for  $p_o(x)$  and  $p_1(x)$ , and  $[9-50]$  for  $p_{1/2}(x)$ ).

**Table 1** The values of the parameters A, B, C and C' (see Eqs (12) and (13)) for  $m = 0, 1/2$  and 1

| $m$       | $x$<br>interval | A       | B       | C       | C'     |
|-----------|-----------------|---------|---------|---------|--------|
| $m = 0$   | [5, 17]         | 0.50704 | 1.72760 | 1.01179 | 0.2211 |
|           | [17, 50]        | 0.67102 | 1.88582 | 1.00174 | 0.2190 |
| $m = 1/2$ | [9, 17]         | 0.47977 | 2.23161 | 1.00925 | 0.2206 |
|           | [17, 50]        | 0.61749 | 2.36330 | 1.00203 | 0.2190 |
| $m = 1$   | [5, 17]         | 0.38827 | 2.62868 | 1.01552 | 0.2220 |
|           | [17, 50]        | 0.56639 | 2.83930 | 1.00236 | 0.2191 |

The relative errors were determined according to the equation:

$$\text{Rel. error} = \frac{P_m(x) - A_m(x)}{P_m(x)} \cdot 100\%$$

where  $P_m(x)$  are exact values of the  $p_m(x)$  integrals, while  $A_m(x)$  are the corresponding values calculated with the approximate (12).

Analysis of the obtained data indicates that for  $x < 19$  the maximum relative error is 0.26%, and that for  $19 \leq x \leq 50$  the relative error is less than 0.1%.

Consequently, by using approximation (12), the TG and DTG curves can be simulated precisely, even for high numerical values of  $Z$  and  $E$  [25] (rapid process).

### Integral methods

Taking approximation (12) into account, the following relationships can be written for each of the two intervals,  $x \leq 17$  and  $x > 17$ , by taking logarithms of Eq. (2):

$$\log \frac{1 - (1 - c)^{1-n}}{T^B (1 - n)} = \log \frac{Z}{\beta} A \left( \frac{E}{R} \right)^{m+1-B} - C' \frac{E}{T} \quad (n \neq 1)$$

$$\log \left[ -\frac{\log(1 - c)}{T^B} \right] = -0.3622 + \log \frac{Z}{\beta} A \left( \frac{E}{R} \right)^{m+1-B} - C' \frac{E}{T} \quad (n = 1) \quad (13)$$

where  $C' = \frac{C \log e}{R}$ .

On the basis of these relationships for each of the two intervals ( $x \leq 17$ ), the plot of  $\log \frac{1 - (1 - c)^{1-n}}{(1 - n) T^B}$  vs.  $1/T$  will be a line segment with slope  $-C'E$ . Obviously, the parameters  $A$ ,  $B$  and  $C$  used in the calculations have the values corresponding to the respective interval (Table 1).

Usually, in the thermally decomposition of polymers,  $x > 17$ . This fact allows the replacement of the appropriate values of  $A$ ,  $B$  and  $C$  in Eq. (13). In this case, the corresponding plot will be reduced to a single line segment. If we consider that during the final part of the thermal degradation process,  $x < 17$ , the plot obtained with the values of  $A$ ,  $B$  and  $C$  corresponding to the interval  $x > 17$  will present a very slight curvature, which will not influence the determination of the kinetic values of the parameters  $n$ ,  $E$  and  $Z$ .

In order to determine the activation energy relating to thermograms recorded at different heating rates, we shall consider that in relation (13) the heating rate changes and  $c$  remains constant. Hence, we can write

$$\log \frac{T^B}{\beta} = \text{const.} + C' \frac{E}{T} \quad (14)$$

In this case, taking into consideration the reasons presented above, the activation energy will be obtained from the slope of the linear plot  $\log \frac{T^B}{\beta}$  vs.  $1/T$ .

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**Zusammenfassung** – Für  $m = 0, 1/2$  und 1 werden Temperaturintegrale der Form  $p_m(x) = \int_x^{\infty} e^{-x} u^{-2-m} du$  mit empirischen Formeln des Types  $Ax^{-B} e^{-Cx}$  näherungsweise berechnet.

Zur Bestimmung der Genauigkeit dieser Näherung wurde für Integralwerte von  $x$  der relative Fehler berechnet. Der maximale relative Fehler liegt für  $x < 19$  bei 0.26% und ist im Intervall  $19 \leq x \leq 50$  kleiner als 0.1%.

Die vorgeschlagenen Näherungen erlauben eine wesentliche Verbesserung von Integriermethoden zur Bestimmung kinetischer Parameter diesbezüglicher Prozesse.