THERMOGRAVIMETRY. EMPIRICAL APPROXIMATION FOR THE "TEMPERATURE INTEGRALS"*

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The temperature integrals \( p_m(x) = \int_x^\infty e^{-x u} u^{-2-m} du \) 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:

\[
\frac{dc}{dt} = ZT^m e^{-E/RT} (1-c)^n
\]  

(1)

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where $t$ is the time, $c$ the conversion, $T$ the absolute temperature (K), $E$ the activation energy (cal.mol$^{-1}$), $R$ the universal gas constant (1.987 cal. mol$^{-1}$deg$^{-1}$) (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

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

where

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

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:

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

$$p_1(x) = e^{-x} x^{-1} + Ei(-x)$$

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

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