Review and Evaluation of the Approximations to the Temperature Integral

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The kinetics of processes involving solids may be determined from experiments under non-isothermal conditions. On analyzing data by integral methods, it is necessary to calculate the temperature integral, which does not have an analytical solution. Instead of performing the numerical integration, most of the researchers prefer to circumvent the problem by using approximate expressions, not always adequate. The widespread use of inaccurate approximations does not contribute to a coherent growth of scientific knowledge. In the present article, a critical review of the known approximations is carried out and a clear ranking is established. Moreover, the deviations of the calculated activation energies relatively to the numerical solution are discussed, and some recommendations are proposed. Namely, it is shown that a "novel" expression, previously presented in another form in the well known "Handbook of Mathematical Functions", approximates very accurately the temperature integral and allows to obtain correct values of the activation energy. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2905–2915, 2007

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Introduction

Thermal analysis is a convenient technique for studying the kinetics of processes involving solids, such as decompositions, gas–solid reactions, dehydrations, or desorption of gases. Experiments are often carried out under non-isothermal conditions. In this method, the solid samples are submitted to a gradual temperature increase, usually corresponding to a linear variation with time. Using this technique based on a single experiment it is possible, in principle, to determine the associated kinetic parameters (activation energy and pre-exponential constant of the Arrhenius law), as well as the kinetic function, related to the process mechanism.[1] On the other hand, several authors have reported the need to consider a set of kinetic data obtained at different heating rates in order to reach meaningful kinetic conclusions.[2,3]

In any case, when we analyze experimental data by integral methods, it is necessary to calculate an integral without analytic solution, the so called "temperature integral" or "Arrhenius integral." Therefore, for convenience, several approximations to that integral have been published, mainly during the 70's and the 80's of the last century. Nowadays, in my opinion, the importance of such expressions is much lower, since the calculations are usually carried out with computers, and the methods and tools needed for numerical integration can be easily introduced in appropriate algorithms or computer programs.[4] An example of this approach is described by Órfão and Martins.[5] A similar point of view was expressed a decade ago by Flynn,[6] who wrote that in this age of vast computational capabilities, there is no valid reason not to use precise values for the temperature integral when calculating kinetic parameters. This is especially im-

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portant, since the presentation of different kinetic results based on the same data by different authors may result, at least in part, from the undue use of approximations with a low degree of accuracy.[7,8]

Nevertheless, several researchers still use the traditional approach, which possibly may justify the publication of new approximate expressions for the calculation of the temperature integral. However, it would be expected that these new formulas would be of higher quality than those published before. Recently, several new approximations appeared in the literature.[9–12] In these papers, the new solutions are compared with the results obtained with some previous expressions, but those comparisons are invariably very limited. For instance, they do not include some of the most interesting formulas, such as those proposed by Senum and Yang,[13] which have been considered very good or excellent approximations of the temperature integral,[2,14] and by Urbanovici and Segal.[15] Obviously, these are generally more complex than those published recently, but as the calculations may be carried out using spreadsheets, the associated calculation "difficulties" seem identical.

As mentioned earlier, I strongly support the use of kinetic analysis methods that directly involve the numerical determinations of the temperature integral, i.e. without considering approximate formulas for those calculations, mainly because, as scientists, we should strive to calculate kinetic parameters as precisely as we are able to.[6] On the other hand, it is impossible to ignore the importance that those approximations generally still have to people working in the field of kinetics by thermal analysis techniques. Additionally, there are few authoritative comparative and critical reviews of the strengths and weaknesses of the various classical expressions that have now served generations of thermal analysts.[3]

Therefore, taking into account the importance of the temperature integral approximations for a large number of practical researchers and, in association, to people involved in the proposal of new expressions or in the process of evaluation and recommendation for publication of papers on that subject, twenty-two known expressions are considered in this work, including the most popular and the most recent, in order to evaluate and compare the respective accuracies. The analysis of the corresponding relative deviations of the determined activation energies is also carried out, allowing to establish quantified recommendations related to the correct (i.e. associated to a very low error) use of each one of those formulas. In addition, three "novel" expressions based on information withdrawn from the "Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables"[16] are also presented and included in the analyses. It is shown that these last expressions have a high degree of accuracy relatively to the numerical solutions, and particularly one of them is much better than all the other approximations considered.

Theoretical Background

Considering the decomposition reactions of solids as an example, it is usually assumed that the respective rate is a function of temperature and amount of solid. If only a single reaction is involved, the equation that describes the progress of the decomposition is

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where t is the reaction time, T the absolute temperature, and α the degree of transformation defined as $\alpha = \frac{W_0 - W}{W_0 - W_\infty}$, where W is the solid weight and the subscripts 0 and ∞ correspond to the initial and residual amounts, respectively. The kinetic function $f(\alpha)$ is related to the reaction mechanism. The more common kinetic functions are listed elsewhere.[5] Equations similar to Eq. 1 may be considered for other processes involving solid materials, such as gas–solid reactions and desorption of gases. For instance, if we consider $\alpha = 1 - \theta$, where θ represents the fraction of sites occupied with adsorbed species on the solid surface, Eq. 1 describes temperature programmed desorption (TPD) processes. Moreover, Eq. 1 is able to describe differential scanning calorimetry (DSC) experiments; in this case, the variable α is the ratio between the area under the DSC curve at a given time and the total area under that curve.

The rate constant is normally expressed by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where E is the activation energy, A the pre-exponential constant, and R the universal gas constant. Therefore, Eq. 1 may be written as

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$

When the reaction is carried out under a linear temperature program ($T = T_0 + bt$, where b is the heating rate and T_0 the starting temperature), Eq. 3 becomes

$$\frac{d\alpha}{dT} = \frac{A}{b}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{4}$$

For the interpretation of experimental data (α vs. T) by the integral method, it is necessary to integrate the differential equation. Then, after separation of variables and integration, Eq. 4 leads to

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{b}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \tag{5}$$

The value of the integral between 0 and T_0 of the function $\exp\left(-\frac{E}{RT}\right)$ is usually considered negligible (relatively to the integral between 0 and T), which is an acceptable simplification if the reactivity is not too high (i.e. if the temperatures involved in the process are significantly higher than the starting temperature).[17] Therefore, we can write:

$$g(\alpha) = \frac{A}{b}\int_0^T \exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

The integral in the right-hand side of Eq. 6 has no analytic solution and several approximations have been considered in the literature. It is possible to change the variable by defining $x = E/RT$, and consequently

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R}\int_u^\infty \frac{\exp(-x)}{x^2} dx = \frac{E}{R} p(u) \tag{7}$$

In this article, I will consider exclusively approximations to the integral $p(u)$ of the type

$$p(u) = \frac{\exp(-u)}{u^2} Q(u) \tag{8}$$

The expressions of $Q(u)$ are frequently rational functions of u (i.e., ratios between polynomial functions) derived from different series expansions or obtained using appropriate fitting procedures relatively to the values calculated by numerical integration in a certain range of u. Other types of approximations are based on expressions with formulas[18–20]

$$p(u) = C_1 \exp\left(-C_2 u^{C_3}\right) \tag{9}$$

or[2,21–24]

$$p(u) = C_1 \frac{\exp(-C_2 u)}{u^{C_3}} \tag{10}$$

where C_1, C_2, and C_3 are constants. In general, such approximations have low accuracy, especially those corresponding to Eq. 9,[25,26] or are only reasonably accurate inside limited intervals of the variable u, normally not associated to low values. For instance, it was verified by the author of this article that the Tang et al.[24] method allows to obtain correct kinetic parameters for curves associated to u values between 20 and 30, but the parameters calculated for simulated curves corresponding to u around 10 do not satisfy the demanding criteria used in this work. This situation becomes worse for lower values of u. The other approximations based on Eqs. 9 and 10 lead to similar or, frequently, even worse results.

After substitution of Eqs. 7 and 8 into Eqs. 6 we get:

$$g(\alpha) = \frac{AR}{bE} T^2 Q\left(\frac{E}{RT}\right) \exp\left(-\frac{E}{RT}\right) \tag{11}$$

The integral method of kinetic analysis may be carried out using an iterative technique, starting with $Q(E/RT) = 1$ for the first estimate of the activation energy, on the basis of Eq. 11, normally considering its linear form:

$$\ln \frac{g(\alpha)}{T^2 Q\left(\frac{E}{RT}\right)} = \ln \frac{AR}{bE} - \frac{E}{RT} \tag{12}$$

It is important to mention the iterative procedure here, since some authors apparently ignore this possibility. On the contrary, it is quite usual to calculate the activation energy from the slope of the line $\ln \frac{g(\alpha)}{T^2}$ versus $\frac{1}{T}$; then, the pre-exponential constant A is evaluated from the intercept, $\ln\left[\frac{AR}{bE} Q\left(\frac{E}{RT}\right)\right]$, of course assuming that the function $Q\left(\frac{E}{RT}\right)$ is constant in the temperature range considered (for instance, see Liu et al.[25]). This unnecessary and incorrect method may lead to completely erroneous values of the kinetic parameters, particularly activation energies.

Another relevant comment is related to highly reactive processes. In these cases, the temperatures to be considered in the analysis are near the starting temperature T_0, which is a situation that may occur when the activation energy is low and/or the pre-exponential constant is high, although the kinetic function also plays an important role. Therefore, Eq. 6 is incorrect, and it is necessary to write

$$g(\alpha) = \frac{A}{b}\left[\int_0^T \exp\left(-\frac{E}{RT}\right) dT - \int_0^{T_0} \exp\left(-\frac{E}{RT}\right) dT\right] \tag{13}$$

Taking into account Eqs. 7 and 8, we get

$$g(\alpha) = \frac{AR}{bE}\left[T^2 Q\left(\frac{E}{RT}\right) \exp\left(-\frac{E}{RT}\right) - T_0^2 Q\left(\frac{E}{RT_0}\right) \exp\left(-\frac{E}{RT_0}\right)\right] \tag{14}$$

After rearrangement, a generalization of Eq. 11 is obtained:

$$g(\alpha) = \frac{AR}{bE} T^2 Q\left(\frac{E}{RT}\right) \times \left\{1 - \left(\frac{T_0}{T}\right)^2 \frac{Q\left(\frac{E}{RT_0}\right)}{Q\left(\frac{E}{RT}\right)} \exp\left[-\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\} \exp\left(-\frac{E}{RT}\right) \tag{15}$$

The respective linear form is:

$$\ln \frac{g(\alpha)}{\mathrm{T}^2 Q\left(\frac{E}{RT}\right)\left\{1 - \left(\frac{T_0}{T}\right)^2 \frac{Q\left(\frac{E}{RT_0}\right)}{Q\left(\frac{E}{RT}\right)} \exp\left[-\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\}} = \ln \frac{AR}{bE} - \frac{E}{RT} \tag{16}$$

The kinetic parameters are obtained by the iterative technique already mentioned, where the first estimate of the activation energy E is calculated, as before, from the slope of the line $\ln \frac{g(\alpha)}{T^2}$ versus $1/T$.

At least in part, some previous publications[2,6,15,27] dealt with the evaluation of a limited number of approximate formulas of the types considered above, namely those defined by Eq. 8 but, as far as I know, a complete picture is not available. On the other hand, the recently published expressions[9–12] are compared with others in the corresponding papers but some of them, which are usually considered very accurate, are omitted from the comparisons. Similar situations occurred in the past. This accumulation of individual reports, partially unrelated to each other, does not contribute to the growth of a coherent body of scientific knowledge.[8] In

Table 1. Expressions of $Q(u)$ Considered in This Work

Authors	$Q(u)$	N	n	Year
Doyle[18]	1	0	0	1961
Coats and Redfern[28]	$\frac{u-2}{u}$	1	1	1964
Gorbachev[29]/Lee and Beck[30]	$\frac{u}{u+2}$	1	1	1975/1984
Balarin[31]	$\sqrt{\frac{u}{u+4}}$	1	–	1977
van Tets[32]	$\frac{u+1}{u+3}$	2	1	1976
Wanjun et al.[9]	$\frac{u}{1.00198882u+1.87391198}$	2	1	2003
Cai et al.[10]	$\frac{u+0.66691}{u+2.64943}$	2	1	2006
Li I[33]	$\frac{u^2-2u}{u^2-6}$	2	2	1985
Agrawal and Sivasubramanian[34]	$\frac{u^2-2u}{u^2-5}$	2	2	1987
Quanyin and Su[35]	$\frac{u^2-2u}{u^2-4.6}$	2	2	1995
Cai and He[11]	$\frac{0.99962u+0.60642}{u+2.56879}$	3	1	2006
Senum and Yang I[13]	$\frac{u^2+4u}{u^2+6u+6}$	3	2	1977
Urbanovici and Segal I[15]	$\frac{u^2+2u-2}{u^2+4u}$	3	2	1990
Urbanovici and Segal II[15]	$\frac{u^2+3.5u}{u^2+5.5u+5}$	3	2	1990
Urbanovici and Segal III[15]	$\frac{u^2+5.347u+1.376}{u^2+7.347u+10.069}$	4	2	1990
Chen and Liu[12]	$\frac{u^2+\frac{16}{3}u+\frac{4}{3}}{u^2+\frac{22}{3}u+10}$	4	2	2006
This work I	$\frac{0.995924u^2+1.430913u}{u^2+3.330657u+1.681534}$	4	2	–
This work II	$\frac{0.99997u^2+3.03962u}{u^2+5.03637u+4.19160}$	4	2	–
Li II[33]	$\frac{u^3-5u}{u^3+2u^2-6u-12}$	4	3	1985
Li III[33]	$\frac{u^3-\frac{16}{3}u}{u^3+2u^2-6u-12}$	4	3	1985
Urbanovici and Segal IV[15]	$2+\frac{2}{u}-\sqrt{1+\frac{8}{u}+\frac{4}{u^2}}$	4	–	1990
Senum and Yang II[13]	$\frac{u^3+10u^2+18u}{u^3+12u^2+36u+24}$	5	3	1977
Zsakó[36]	$\frac{u^4-4u^3+84u^2}{u^4-2u^3+76u^2+152u-32}$	6	4	1975
Senum and Yang III[13]	$\frac{u^4+18u^3+86u^2+96u}{u^4+20u^3+120u^2+240u+120}$	7	4	1977
This work III	$\frac{0.9999936u^4+7.5739391u^3+12.4648922u^2+3.6907232u}{u^4+9.5733223u^3+25.6329561u^2+21.0996531u+3.9584969}$	8	4	–

the present work, I intend to evaluate a much more extensive set of expressions of the type defined by Eq. 8 and establish a clear ranking, in order to contribute for the promotion of the use of the best available formulas by those researchers that prefer the traditional approach. Additionally, the interested kineticists may become aware of the limitations of the methods they use.

Evaluation of Approximate Formulas

A set of known expressions of $Q(u)$ that have been used for the calculation of the integral $p(u)$ according to Eq. 8 are given in Table 1. All the formulas frequently used in practice are included in the table; moreover, the approximations of the temperature integral recently published are also presented and included in the analysis. In addition, it is important to mention that more complex expressions could be added (for instance, Senum and Yang's approximations of order higher than four[13,14]), but taking into consideration that some of the presented expressions, as we will see, already have the desired level of accuracy even for the more demanding practical situations, it was decided not to extend and, probably, complicate the analysis. The expressions are presented in Table 1 in ascending order of complexity, here tentatively measured by N (number of coefficients different from 1 or number of regression parameters involved, depending on the method used to obtain each $Q(u)$ expression) and, when applicable, n (degree of the numerator and denominator polynomials).

As was recognized by several authors,[27,32,37] the function $p(u)$ can be related easily to the exponential integral function, which is well known; the respective values are tabulated in several sources (for instance, in the "Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables"[16]). Actually, after integration by parts of the integral $p(u)$ (see Eq. 7), we get:

$$p(u) = \int_{u}^{\infty} \frac{\exp(-x)}{x^2}dx = \frac{\exp(-u)}{u} - \int_{u}^{\infty} \frac{\exp(-x)}{x}dx = \frac{\exp(-u)}{u} - E_1(u) \quad (17)$$

where $E_1(u)$ is the first-order exponential integral function. Three expressions of a new function $Y(u)$, corresponding to different approximations of $E_1(u)$, are presented in the mentioned handbook.[16] The relationship between the two functions has the following form:

$$u\exp(u)E_1(u) = Y(u) \quad (18)$$

Combining Eqs. 17 and 18, we conclude that

$$p(u) = \frac{\exp(-u)}{u}(1 - Y(u)) \quad (19)$$

and, considering Eq. 8,

$$Q(u) = u(1 - Y(u)) \quad (20)$$

The three expressions of the rational function $Y(u)$, associated to different recommended application ranges and accuracies, as obtained from the "Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables",[16] are:

$$Y(u) = \frac{u^2 + 2.334733u + 0.250621}{u^2 + 3.330657u + 1.681534} \quad (21)$$

$$Y(u) = \frac{u^2 + 4.03640u + 1.15198}{u^2 + 5.03637u + 4.19160} \quad (22)$$

$$Y(u) = \frac{u^4 + 8.5733287u^3 + 18.0590170u^2 + 8.6347609u + 0.2677737}{u^4 + 9.5733223u^3 + 25.6329561u^2 + 21.0996531u + 3.9584969} \quad (23)$$

The derived "novel" $Q(u)$ formulas were included in Table 1 and named as "This work I", "This work II" and "This work III", respectively.

The values of $p(u)$, calculated according to Eq. 8 between $u = 1$ and $u = 250$ for all expressions of $Q(u)$ in Table 1, were compared with the corresponding values determined by numerical integration using the Simpson rule. The differences were quantified defining the absolute value (modulus) of the relative deviations (in percentage) as

$$|\delta_r|(\%) = 100\left|\frac{p(u)^{\text{formula}}}{p(u)^{\text{integration}}} - 1\right| \quad (24)$$

To have an immediate perception of the accuracy of each approximation, the ranges of u associated to relative deviations lower than some selected values, mainly chosen according to the literature, are presented in Table 2. Probably, some of the mentioned values do not guarantee a sufficient level of accuracy for the kinetic parameters determination in the context of non-isothermal thermal analysis; this is certainly the case for $|\delta_r| < 1\%$. On the other hand, the condition $|\delta_r| < 0.02\%$ seems, in principle, too demanding for the same purpose. This type of problem will be treated in the next section of the article. Meanwhile, the information presented in Table 2 gives a good idea about the errors associated to each formula, particularly its evolution relatively to the variable u.

Observation of Table 2 suggests the following comments:

1) A large variety of expressions, with different accuracy levels, is available. Probably, the publication of novel approximations is no longer necessary.

2) There is no apparent correlation between the accuracy of the approximations and the respective publication date. For instance, the expressions of Zsakó[36] and Senum and Yang[13] were published in the 70's and are among the most accurate.

3) The expression derived by Coats and Redfern,[28] which is by far the most used by practical scientists, corresponds to the worst approximation of the temperature integral.

4) The simplification $Q(u) = 1$ usually leads to gross errors. As previously mentioned, this approach is actually used by several authors to calculate activation energies (see Eq. 12 and related commentaries).

5) The expression developed by Balarin[31] is the best among the simpler ones ($N = 1$). It is even better than most of the approximations corresponding to $N = 2$.

Table 2. Intervals of u that Guarantee Relative Deviations of $p(u)$ Lower than the Indicated Values

Authors	Range of (u)				
	$\lvert\delta_r\rvert < 1\%$	$\lvert\delta_r\rvert < 0.5\%$	$\lvert\delta_r\rvert < 0.1\%$	$\lvert\delta_r\rvert < 0.05\%$	$\lvert\delta_r\rvert < 0.02\%$
Doyle[18]	≥199	–*	–*	–*	–*
Coats and Redfern[28]	≥24	≥34	≥77	≥109	≥173
Gorbachev[29]/Lee and Beck[30]	≥11.5	≥18	≥42	≥61	≥98
Balarin[31]	≥4.5	≥6.5	≥13	≥17	≥25
van Tets[32]	≥6	≥8.5	≥15.5	≥21	≥29
Wanjun et al.[9]	≥7	≥9	14–112	16–66	18–22 and 32–50
Cai et al.[10]	≥3.5	≥4	≥6	≥6.5	6.5–7 and ≥18
Li I[33]	≥10	≥12.5	≥22	≥28	≥38
Agrawal and Sivasubramanian[34]	≥5.5	≥6	7.5 to 8 and ≥25	≥39	≥65
Quanyin and Su[35]	≥4	4 to 4.5 and ≥12	≥34	≥49	≥80
Cai and He[11]	≥3	≥4	≥5.5	≥6	7–185
Senum and Yang I[13]	≥3	≥4	≥7	≥9	≥12
Urbanovici and Segal I[15]	≥5	≥6	≥10	≥12.5	≥16
Urbanovici and Segal II[15]	≥2	≥2.5	≥4.5	≥5	≥6
Urbanovici and Segal III[15]	≥2	≥2.5	≥4	≥4.5	≥5.5
Chen and Liu[12]	≥2	≥2.5	≥3.5	≥4	≥5
This work I	≥1	≥1	1–21	1–17	1–4 and 9.5–13
This work II	≥1.5	≥2.5	≥3.5	≥4.5	≥5.5
Li II[33]	≥6	≥6.5	7.5 to 8.5 and ≥25	7.5 to 8 and ≥39	≥65
Li III[33]	≥4.5	5 to 6 and ≥10.5	≥32	≥48	≥78
Urbanovici and Segal IV[15]	≥2	≥2.5	≥5.5	≥7	≥9.5
Senum and Yang II[13]	≥1.5	≥2	≥3.5	≥4.5	≥5.5
Zsakó[36]	≥1.5	≥2	6.5 to 9.5 and ≥35	7.5 to 8.5 and ≥55	≥93
Senum and Yang III[13]	≥1	≥1.5	≥2	≥2.5	≥3.5
This work III	≥1	≥1	≥1	≥1	≥1

*Inside the u range analyzed ($u \in [1, 250]$) the relative deviations are higher than 0.8%.

6) In spite of its simplicity, the recently published expression of Cai et al.[10] is quite better than all the others that involve two parameters different from unity ($N = 2$).

7) The approximation of Cai and He[11] is better than the previous one. Among the expressions corresponding to $N = 3$, only the Urbanovici and Segal II[15] is more accurate.

8) The recently published formula developed by Chen and Liu[12] shows an accuracy similar to the expressions of Urbanovici and Segal III,[15] Senum and Yang II,[13] and that named "This work II", derived in this article, although the last two are slightly better for very low values of u.

9) In spite of the associated relative complexities ($N = 4$, $n = 3$), the approximations named Li II[33] and Li III[33] are worse than most expressions that involve two or three parameters different from one, and even the Balarin's[31] formula. Additionally, the associated $Q(u)$ expressions, as well as the function corresponding to the simpler approach Li I,[33] present a point of discontinuity at $u = \sqrt{6}$. Therefore, convergence problems in the application of the iterative procedure already mentioned (Eqs. 12 and 16) may arise when low values of u are involved. A similar situation may occur with the expressions of Agrawal and Sivasubramanian[34] (discontinuity at $u = \sqrt{5}$) and Quanyin and Su[35] (discontinuity at $u = \sqrt{4.6}$). The Zsakó[36] function also has a discontinuity at $u = 0.192$, but at this very low value there should not be any divergence problems under practical or even interesting theoretical situations. The impossibility of arriving to a solution when using the mentioned approximations was proved on the basis of a simulated thermogravimetric curve corresponding to $f(\alpha) = \alpha^{2/3}$, $E = 24.344$ kJ mol^{-1}, $A = 1.702$ min^{-1}, $T_0 = 293$ K, and $b = 5$ K min^{-1}, for which the u values associated to the points considered in the analysis vary between 3.1 and 3.8.

10) The Urbanovici and Segal IV[15] formula presents an accuracy lower than the expressions of the same authors Urbanovici and Segal II[15] and Urbanovici and Segal III,[15] which are simpler.

11) Comparatively to other approximations of similar complexity, the expression derived by Zsakó[36] and, in particular, the formula "This work I" have a very good accuracy relatively to the numerical solution for u values near 1, but the accuracy is somewhat reduced when that variable increases.

12) The Senum and Yang III[13] formula presents a high level of accuracy practically for the whole range of u.

13) The expression named "This work III", which is the most complex among those considered here, shows excellent levels of approximation to the temperature integral. Actually, the absolute values of the relative deviations are always lower than $5 \times 10^{-4}\%$ inside the analyzed interval ($u \in [1,250]$). Therefore, more complex formulas were not considered in this manuscript.

Accuracy of Calculated Activation Energies

To complete this work, it seems important to analyze the errors involved in the determination of activation energies when the different approximations are used (compared with the values calculated on the basis of the numerical solution of the temperature integral, taken as the exact or correct solution). For that purpose, the methodology developed by Ortega et al.[38] is followed.

According to Eq. 12, activation energies are calculated from the slope of the line $\ln\frac{g(\alpha)}{T^2 Q\left(\frac{E}{RT}\right)}$ versus $\frac{1}{T}$. Therefore, we may write:

$$\frac{E}{R} = -\frac{d\left[\ln \frac{g(\alpha)}{T^2 Q\left(\frac{E}{RT}\right)}\right]}{d\left(\frac{1}{T}\right)} = -\frac{d \ln g(\alpha)}{d\left(\frac{1}{T}\right)} - 2T + \frac{d \ln Q\left(\frac{E}{RT}\right)}{d\left(\frac{1}{T}\right)} \tag{25}$$

This equation shows that the errors of calculated activation energies associated to the utilization of unsuitable approximations $Q(u) = Q\left(\frac{E}{RT}\right)$ are only contained in the term $\frac{d \ln Q\left(\frac{E}{RT}\right)}{d\left(\frac{1}{T}\right)}$. Considering that E_a and E are, respectively, the solution obtained through an approximate expression $Q_a(u)$ and the exact (i.e. numerically calculated) one, and taking into account that $u = \frac{E}{RT}$, it is possible to determine the relative deviation (in percentage) of the calculated activation energies as

$$\varepsilon_r(\%) = 100\left(\frac{E_a}{E} - 1\right) = 100\left[\frac{d \ln Q_a(u)}{du} - \frac{d \ln Q(u)}{du}\right] \tag{26}$$

where $Q(u)$ would correspond hypothetically to the numerical integration of the temperature integral. Finally, representing the derivative of $Q(u)$ by $Q'(u)$, and recognizing that $\frac{d \ln Q(u)}{du} = \frac{Q'(u)}{Q(u)}$, Eq. 26 can be written in the form:

$$\varepsilon_r(\%) = 100\left[\frac{Q'_a(u)}{Q_a(u)} - \frac{Q'(u)}{Q(u)}\right] \tag{27}$$

The deduced analytic expressions of $\frac{Q'(u)}{Q(u)}$ for the approximations considered in this manuscript are shown in Table 3.

It is important to notice that Ortega et al.[38] analyzed by this method only the gross approximation $Q(u) = 1$ (which they improperly called "Coats and Redfern approximation") considering the fourth order expression of Senum and Yang[13] (Senum and Yang III in this work) as reference (i.e. representative of the numerical solution). Here, the method is extended to all the selected expressions. On the other hand, analyzing a large number of simulated α versus T curves corresponding to u values in the range of 3–30 (data not shown), with a special interest in the results obtained for the curves associated to low values of that variable, it was verified that the approximation "This work III" led to activation energies with an accuracy at least equal to 99.99%, relatively to the numerical solution as obtained by the integration method described by Órfão and Martins.[5] In addition, the accuracies obtained for simulated curves in the upper zone of that interval were typically in the order of 99.999%. Moreover, the deviations were equal or lower than those associated with the Senum and Yang III[13] expression. Therefore, the approximation "This work III" was taken as reference, i.e. was used to calculate the values of $\frac{Q'(u)}{Q(u)}$ in Eq. 27.

Recently, Cai and Liu[39] showed that Eqs. 26 and 27 are not correct. Actually, as E_a (approximate solution) is different from E (true solution) and, consequently, $u_a = \frac{E_a}{RT}$ is also different from $u = \frac{E}{RT}$, a similar reasoning to that used to derive Eqs. 26 and 27 leads to the corrected equation:

$$E_a - E = E_a \frac{d \ln Q_a(u_a)}{du_a} - E\frac{d \ln Q(u)}{du} = E_a \frac{Q'_a(u_a)}{Q_a(u_a)} - E\frac{Q'(u)}{Q(u)} \tag{28}$$

where $u_a = \frac{E_a}{E} u = (\varepsilon_r + 1)u$. Dividing both members of Eq. 28 by E, we get:

$$\varepsilon_r = (\varepsilon_r + 1)\frac{Q'_a(u_a)}{Q_a(u_a)} - \frac{Q'(u)}{Q(u)} \tag{29}$$

This equation can be solved numerically to obtain the relative deviation of the activation energy for each u and each approximate formula. Comparing the values determined by Eq. 29, presented in the paper of Cai and Liu,[39] with those calculated by the simplified Eq. 27, we may conclude that they are identical for the cases where E_a does not significantly differ from E, i.e. when $|\varepsilon_r|$ is relatively small. Effectively, in these circumstances, it may be easily proved that Eq. 29 reduces to Eq. 27, since $|\varepsilon_r| \ll 1$ and $u_a \cong u$. As the approximate expressions associated to very low values of $|\varepsilon_r|$ are those important in the scope of this work, it was decided to consider the simplified Eq. 27 to carry out the calculations.

The relative deviations of activation energies for selected values of u, calculated by Eq. 27 using the analytical expressions of $\frac{Q'(u)}{Q(u)}$ corresponding to the various formulas studied, are shown in Table 4.

As previously discussed, if the process under study (reaction, desorption) occurs at temperatures near the starting temperature, it is necessary to consider Eq. 16 for the evaluation of the kinetic parameters. In this case:

$$\frac{E}{R} = -\frac{d \ln g(\alpha)}{d\left(\frac{1}{T}\right)} - 2T + \frac{d \ln Q\left(\frac{E}{RT}\right)}{d\left(\frac{1}{T}\right)} + \frac{d \ln\left\{1 - \left(\frac{T_0}{T}\right)^2 \frac{Q\left(\frac{E}{RT_0}\right)}{Q\left(\frac{E}{RT}\right)} \exp\left[-\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\}}{d\left(\frac{1}{T}\right)} \tag{30}$$

The two last terms in the right-hand side of Eq. 30 depend on the approximation used. Therefore, introducing the variable $u = \frac{E}{RT}$, with $u_0 = \frac{E}{RT_0}$, and defining $Q(u), Q'(u)$, $Q_a(u), Q'_a(u)$ as before, we get:

$$\varepsilon_r(\%) = 100\left\langle \frac{Q'_a(u)}{Q_a(u)} + \frac{d \ln\left\{1 - \left(\frac{u}{u_0}\right)^2 \frac{Q_a(u_0)}{Q_a(u)} \exp[-(u_0 - u)]\right\}}{du} - \frac{Q'(u)}{Q(u)} - \frac{d \ln\left\{1 - \left(\frac{u}{u_0}\right)^2 \frac{Q(u_0)}{Q(u)} \exp[-(u_0 - u)]\right\}}{du} \right\rangle \tag{31}$$

After derivation and rearrangement, this expression becomes:

$$\varepsilon_r(\%) = 100\left[\frac{\left(\frac{u_0}{u}\right)^2 \frac{Q'_a(u)}{Q_a(u_0)} \exp(u_0 - u) - \left(\frac{2}{u} + 1\right)}{\left(\frac{u_0}{u}\right)^2 \frac{Q_a(u)}{Q_a(u_0)} \exp(u_0 - u) - 1} - \frac{\left(\frac{u_0}{u}\right)^2 \frac{Q'(u)}{Q(u_0)} \exp(u_0 - u) - \left(\frac{2}{u} + 1\right)}{\left(\frac{u_0}{u}\right)^2 \frac{Q(u)}{Q(u_0)} \exp(u_0 - u) - 1}\right] \tag{32}$$

Table 3. Expressions of $\frac{Q'(u)}{Q(u)}$

Authors	$\frac{Q'(u)}{Q(u)}$
Doyle[18]	0
Coats and Redfern[28]	$\dfrac{2}{u(u-2)}$
Gorbachev[29]/Lee and Beck[30]	$\dfrac{2}{u(u+2)}$
Balarin[31]	$\dfrac{2}{u(u+4)}$
van Tets[32]	$\dfrac{2}{(u+1)(u+3)}$
Wanjun et al.[9]	$\dfrac{1.87391198}{u(1.00198882u+1.87391198)}$
Cai et al.[10]	$\dfrac{1.98252}{(u+0.66691)(u+2.64943)}$
Li I[33]	$\dfrac{2u^2-12u+12}{(u^2-2u)(u^2-6)}$
Agrawal and Sivasubramanian[34]	$\dfrac{2u^2-10u+10}{(u^2-2u)(u^2-5)}$
Quanyin and Su[35]	$\dfrac{2u^2-9.2u+9.2}{(u^2-2u)(u^2-4.6)}$
Cai and He[11]	$\dfrac{1.96139}{(0.99962u+0.60642)(u+2.56879)}$
Senum and Yang I[13]	$\dfrac{2u^2+12u+24}{(u^2+4u)(u^2+6u+6)}$
Urbanovici and Segal I[15]	$\dfrac{2u^2+4u+8}{(u^2+2u-2)(u^2+4u)}$
Urbanovici and Segal II[15]	$\dfrac{2u^2+10u+17.5}{(u^2+3.5u)(u^2+5.5u+5)}$
Urbanovici and Segal III[15]	$\dfrac{2u^2+17.386u+43.730}{(u^2+5.347u+1.376)(u^2+7.347u+10.069)}$
Chen and Liu[12]	$\dfrac{2u^2+\frac{52}{3}u+\frac{392}{9}}{\left(u^2+\frac{16}{3}u+\frac{4}{3}\right)\left(u^2+\frac{22}{3}u+10\right)}$
This work I	$\dfrac{1.886168u^2+3.349360u+2.406129}{(0.995924u^2+1.430913u)(u^2+3.330657u+1.681534)}$
This work II	$\dfrac{1.99660u^2+8.38295u+12.74087}{(0.99997u^2+3.03962u)(u^2+5.03637u+4.19160)}$
Li II[33]	$\dfrac{2u^4-2u^3-26u^2+60}{(u^3-5u)(u^3+2u^2-6u-12)}$
Li III[33]	$\dfrac{2u^4-\frac{4}{3}u^3-\frac{76}{3}u^2+64}{\left(u^3-\frac{16}{3}u\right)(u^3+2u^2-6u-12)}$
Urbanovici and Segal IV[15]	$\dfrac{-\dfrac{2}{u^2}+\dfrac{\dfrac{4}{u^2}\left(1+\dfrac{1}{u}\right)}{\sqrt{1+\dfrac{8}{u}+\dfrac{4}{u^2}}}}{2+\dfrac{2}{u}-\sqrt{1+\dfrac{8}{u}+\dfrac{4}{u^2}}}$
Senum and Yang II[13]	$\dfrac{2u^4+36u^3+216u^2+480u+432}{(u^3+10u^2+18u)(u^3+12u^2+36u+24)}$
Zsakó[36]	$\dfrac{2u^6-16u^5+320u^4-1344u^3+13152u^2-5376u}{(u^4-4u^3+84u^2)(u^4-2u^3+76u^2+152u-32)}$
Senum and Yang III[13]	$\dfrac{2u^6+68u^5+872u^4+5280u^3+15600u^2+20640u+11520}{(u^4+18u^3+86u^2+96u)(u^4+20u^3+120u^2+240u+120)}$
This work III	$\dfrac{1.9993219u^6+26.3357997u^5+127.0384026u^4+264.7838961u^3+258.3449989u^2+98.6844743u+14.6097164}{(0.9999936u^4+7.5739391u^3+12.4648922u^2+3.6907232u)(u^4+9.5733223u^3+25.6329561u^2+21.0996531u+3.9584969)}$

Table 4. Relative Deviations (in Percentage) of Activation Energies Associated to Selected *u* Values

Authors	$\varepsilon_r(\%)$							
	$u = 2.5$	$u = 5$	$u = 7.5$	$u = 10$	$u = 15$	$u = 20$	$u = 30$	$u = 50$
Doyle[18]	–*	-4.8	-2.4	-1.5	-0.71	-0.42	-0.20	-7.4×10^{-2}
Coats and Redfern [28]	–*	–*	$+2.4$	$+1.0$	$+0.31$	$+0.13$	$+4.1 \times 10^{-2}$	$+9.1 \times 10^{-3}$
Gorbachev[29]/Lee and Beck[30]	$+3.6$	$+0.95$	$+0.39$	$+0.20$	$+7.2 \times 10^{-2}$	$+3.4 \times 10^{-2}$	$+1.1 \times 10^{-2}$	$+2.7 \times 10^{-3}$
Balarin[31]	-1.8	-0.32	-0.10	-4.1×10^{-2}	-1.1×10^{-2}	-4.1×10^{-3}	-9.7×10^{-4}	-1.4×10^{-4}
van Tets[32]	-3.8	-0.60	-0.18	-7.1×10^{-2}	-1.8×10^{-2}	-6.7×10^{-3}	-1.5×10^{-3}	-2.3×10^{-4}
Wanjun et al.[9]	$+3.0$	$+0.68$	$+0.24$	$+0.11$	$+2.6 \times 10^{-2}$	$+6.8 \times 10^{-3}$	-1.4×10^{-3}	-2.1×10^{-3}
Cai et al.[10]	-2.0	-0.19	-2.7×10^{-2}	-4.7×10^{-4}	$+4.2 \times 10^{-3}$	$+2.7 \times 10^{-3}$	$+9.5 \times 10^{-4}$	$+1.0 \times 10^{-4}$
Li I[33]	–*	-4.1	-0.75	-0.25	-5.2×10^{-2}	-1.8×10^{-2}	-3.7×10^{-3}	-5.1×10^{-4}
Agrawal and Sivasubramanian[34]	–*	-1.4	-0.17	-2.2×10^{-2}	$+9.8 \times 10^{-3}$	$+8.2 \times 10^{-3}$	$+3.8 \times 10^{-3}$	$+1.1 \times 10^{-3}$
Quanyin and Su[35]	–*	-0.45	$+5.5 \times 10^{-2}$	$+6.6 \times 10^{-2}$	$+3.5 \times 10^{-2}$	$+1.8 \times 10^{-2}$	$+6.8 \times 10^{-3}$	$+1.7 \times 10^{-3}$
Cai and He[11]	-1.7	-0.14	-1.5×10^{-2}	$+2.1 \times 10^{-3}$	$+2.8 \times 10^{-3}$	$+1.1 \times 10^{-3}$	-2.1×10^{-4}	-4.6×10^{-4}
Senum and Yang I[13]	$+0.87$	$+0.12$	$+3.0 \times 10^{-2}$	$+1.0 \times 10^{-2}$	$+2.1 \times 10^{-3}$	$+6.3 \times 10^{-4}$	$+1.1 \times 10^{-4}$	–†
Urbanovici and Segal I[15]	–*	$+0.49$	$+0.10$	$+3.1 \times 10^{-2}$	$+5.6 \times 10^{-3}$	$+1.6 \times 10^{-3}$	$+2.5 \times 10^{-4}$	–†
Urbanovici and Segal II[15]	$+0.51$	$+4.5 \times 10^{-2}$	$+5.7 \times 10^{-3}$	$+1.4 \times 10^{-4}$	-6.9×10^{-4}	-4.2×10^{-4}	-1.4×10^{-4}	–†
Urbanovici and Segal III[15]	-0.46	-2.6×10^{-2}	-3.1×10^{-3}	-4.3×10^{-4}	–†	–†	–†	–†
Chen and Liu[12]	-0.41	-1.9×10^{-2}	-8.8×10^{-4}	$+4.5 \times 10^{-4}$	$+2.6 \times 10^{-4}$	$+1.0 \times 10^{-4}$	–†	–†
This work I	$+9.3 \times 10^{-3}$	$+1.0 \times 10^{-2}$	-4.2×10^{-3}	-9.5×10^{-3}	-1.1×10^{-2}	-8.8×10^{-3}	-5.7×10^{-3}	-2.7×10^{-3}
This work II	$+0.32$	$+2.1 \times 10^{-2}$	$+2.1 \times 10^{-3}$	$+1.5 \times 10^{-4}$	–†	–†	–†	–†
Li II[33]	–*	-1.7	-0.19	-2.7×10^{-2}	$+9.3 \times 10^{-3}$	$+8.1 \times 10^{-3}$	$+3.8 \times 10^{-3}$	$+1.1 \times 10^{-3}$
Li III[33]	–*	-0.83	-2.4×10^{-3}	$+4.7 \times 10^{-2}$	$+3.0 \times 10^{-2}$	$+1.7 \times 10^{-2}$	$+6.3 \times 10^{-3}$	$+1.6 \times 10^{-3}$
Urbanovici and Segal IV[15]	$+0.39$	$+5.2 \times 10^{-2}$	$+1.3 \times 10^{-2}$	$+4.7 \times 10^{-3}$	$+9.5 \times 10^{-4}$	$+2.9 \times 10^{-4}$	$+5.2 \times 10^{-5}$	–†
Senum and Yang II[13]	$+0.23$	$+1.7 \times 10^{-2}$	$+2.8 \times 10^{-3}$	$+6.8 \times 10^{-4}$	$+7.3 \times 10^{-5}$	–†	–†	–†
Zsakó[36]	$+5.1 \times 10^{-2}$	-4.7×10^{-2}	-7.1×10^{-2}	-4.0×10^{-2}	-2.1×10^{-3}	$+6.2 \times 10^{-3}$	$+5.2 \times 10^{-3}$	$+1.9 \times 10^{-3}$
Senum and Yang III[13]	$+6.5 \times 10^{-2}$	$+2.8 \times 10^{-3}$	$+3.2 \times 10^{-4}$	$+5.6 \times 10^{-5}$	–†	–†	–†	–†
This work III	–‡	–‡	–‡	–‡	–‡	–‡	–‡	–‡

*$|\varepsilon_r| > 5\%$.

†$|\varepsilon_r| < 5 \times 10^{-5}$ %.

‡The expression "This work III" was taken as reference.

If $u \ll u_0$, the exponential terms both in the numerator and denominator of the fractions are much higher than, respectively, $\left(\frac{2}{u}+1\right)$ and 1; then, Eq. 32 tends towards Eq. 27. When u is close to u_0 (and, evidently, lower), the moduli of relative deviations calculated according to Eq. 32 are generally lower than those presented in Table 4, but in all circumstances, they are of the same order of magnitude. Therefore, in order to maintain the extension of this article within acceptable limits, it was decided not to include additional tables (corresponding to relative deviations calculated for selected u_0 values), since the analysis of Table 4 suffices to outline the main general conclusions about the accuracies of the activation energies as calculated on the basis of the different approximations.

Before coming to the main conclusions resulting from the analysis of Table 4, two preliminary remarks are necessary. The first is related to the fact that an approximation able to substitute the numerical solution is searched; reasoning in this way, it is possible to follow the recommendation of Flynn[6] to calculate kinetic parameters as accurately as we can. On the other hand, it must be stressed that, in practice, real kinetic analyses are carried out relatively to experimental curves that correspond to a more or less extended range of u values, while in Table 4 a relative deviation is associated to each u. This means that a rigorous criterion is necessary and, therefore, errors for individual values of the variable u higher than about 0.05%, in the interval under consideration, are unacceptable. Taking into account these comments and the results shown in Table 4, the following conclusions about activation energy determinations can be listed:

1) A large number of practical situations correspond to values of u in the interval 20 to 50. For $u \geq 20$, almost all approximations allow the determination of activation energies identical to those obtained by numerical integration. The exceptions are the gross simplification $Q(u) = 1$ and the Coats and Redfern[28] expression, which curiously are the most used among the available methods. This conclusion is in agreement with a few authors, such as Galwey,[40] but explicitly or implicitly contradicts most of the researchers in the area (for instance, see Liu et al.[25] and Ortega et al.[38]).

2) Some phenomena are associated to low activation energies (low values of u). For instance, this situation is relatively frequent in dehydration processes[17] and in the desorption of gases from solid surfaces.[14] Moreover, similar situations may also occur when lumped models are used to determine the decomposition kinetics of complex materials, such as coal[41] or lignocellulosic materials[42,43]; some of the pseudo-components defined in that way can decompose by reactions with low activation energies. The importance of this type of processes, among others, justifies the preferential utilization of very accurate approximations. Therefore, considering processes that correspond to values of u between 15 and 20, also quite frequent, the formulas of Gorbachev/Lee and Beck[29,30] and Li I[33] may not be used, in addition to the previous mentioned approximations.

3) When u approaches 10, also the approximations of van Tets,[32] Wanjun et al.[9] and Quanyin and Su[35] fail to be adequate.

4) For processes that correspond to values of u close to 5 but higher, the approximations of Balarin,[31] Agrawal and Sivasubramanian,[34] Urbanovici and Segal I,[15] Li II,[33] and Li III[33] become inapplicable. In addition, the approaches of Cai et al.,[10] Cai and He,[11] and Senum and Yang I[13] are probably near the limit of applicability.

5) When the u values to be considered in the kinetic analysis are very low (for instance, in the neighborhood of 2.5), only the formulas of Zsakó[36] and Senum and Yang III,[13] and the expressions presented in this manuscript "This work I" and "This work III" originate negligible deviations relatively to the activation energies determined by the numerical integration of the temperature integral.

6) As mentioned earlier, the accuracy level of the expression "This work III" is extraordinarily high, even for values of u close to 1; then this approximation is strongly recommended.

Almost all these conclusions, deduced from data in Table 4, were validated carrying out the kinetic analysis of a large set of simulated thermogravimetric curves, corresponding to a broad range of values of activation energies, pre-exponential constants and kinetic functions, using all expressions considered in this investigation.

Conclusions

The main purpose of this article is to contribute to bring some order to the theme of approximate functions utilization, in the scope of non-isothermal kinetic analysis. This includes the evaluation of the published approximations of the temperature integral, the comparison of activation energies as calculated using approximate formulas or, correctly, by numerical integration and the correction of inappropriate calculation procedures. The partial conclusions resulting from this study were already mentioned in the previous sections. Summarizing, the most important results and comments, are:

1) Nowadays, there are no special limitations to the use of numerical methods in the kinetic analysis of experimental data obtained under non-isothermal conditions. Then, whenever is possible, methods that involve the numerical integration of the temperature integral are preferable.

2) A large number of expressions that intend to approximate the values of the temperature integral are available in the literature. Probably, there is no need for new expressions, and research in this area should be considered obsolete.

3) When approximate expressions are used in kinetic analyses, based on linear regressions (see Eqs. 12 and 16), an iterative procedure must be applied, as explained in the text. The hypotheses frequently seen that $Q(u) = 1$ or constant inside the analyzed interval may lead to gross errors in activation energy determinations.

4) It was shown that the most popular approximations, namely $Q(u) = 1$ and the Coats and Redfern[28] $Q(u) = \frac{u-2}{u}$, should never be used, independently of the range of the variable u under consideration.

5) Not surprisingly, the approximations that guarantee calculated activation energies with a high level of accuracy relatively to the numerical solution for a wide range of u ($u \in [2.5, 250]$) are those named Zsakó,[36] Senum and Yang III[13] and the expressions developed in this manuscript "This work I" and "This work III". Particularly, this last expression is able to fit excellently the temperature integral until $u = 1$ and, therefore, allows to obtain values of the kinetic parameters practically coincident with the numerical integration approach. In conclusion, the approximation "This work III" is recommended for use by those not comfortable with

programming and/or numerical methods of integration, because it is based on a classical and credible reference[16] and because it has a general applicability (accuracy independent of the *u* range under consideration). In spite of the complexity of the associated mathematical expression, it is important to point out that calculations may (must) be carried out with the assistance of spreadsheets, thus involving difficulties similar to any other approximation.

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