

On the evaluation of the accuracy of activation energies calculated by integral methods: rebuttal of a putative correction

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Abstract In this short communication, a recent article published in the Journal of Thermal Analysis and Calorimetry, which presents an erroneous conclusion based on incorrect calculations, is critically discussed. Since the observations made in that report are based on part of the content of a publication of my authorship, trying to reject some expressions I presented, obviously it came to my attention. This brief note emphasizes that some of the arguments used and the main conclusion stressed in the manuscript under discussion are wrong and must be dismissed.

Keywords Accuracy · Activation energy · Integral method · Kinetics · Non-isothermal · Temperature integral approximations

Introduction

The kinetic analysis of processes involving solids, such as decompositions, dehydrations, desorption of gases or gas–solid reactions, is often carried out under non-isothermal conditions, varying the temperature linearly with time. This is an important subject for different disciplines (chemical, materials, energy, environmental, forest and agricultural engineering; chemistry; catalysis; pharmacy; physics; etc.). On analyzing the corresponding data by integral methods, it is necessary to calculate the temperature integral, which has no analytical solution. Instead of developing suitable

computer programs able to carry out the numerical integration of the mentioned integral, which nowadays may be done with generally available tools, most of the researchers prefer to circumvent the problem using approximate expressions. The widespread use of inaccurate approximations does not contribute to the growth of a coherent body of scientific knowledge. Moreover, some new approximate expressions still continue to be periodically proposed in the literature. Usually, the corresponding authors claim that the new expressions introduced are the best, but it is noticeable that generally they do not compare them with those that are recognized by some experts as effectively the best known, for instance some expressions derived by Senum and Yang in the 70's [1].

With this background in mind, I carried out recently [2] a comparative and critical review of the strengths and weaknesses of 22 published approximations, evaluating their accuracies in comparison with the numerical solution of the temperature integral. Additionally, three other expressions, based on the information withdrawn from the well known (but frequently forgotten) classic reference Handbook of Mathematical Functions [3], were also included in the analysis. It was verified that one of these expressions approaches extraordinarily well the values of the temperature integral (modulus of relative deviations lower than 0.0005%, even for low values of the exponential argument). The accuracies of the kinetic parameters (namely, the activation energy) calculated by the different approximations were also determined, which allowed to propose some practical recommendations about the ideal range of application of each of them. Finally, several inappropriate calculation procedures, currently used by some authors, were highlighted. I strongly believe that the mentioned publication [2] contributes to bring some order to the subject of approximate expressions utilization, in the

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scope of kinetic laws determination from thermal analysis using non-isothermal data.

In a recent publication, Cai and Liu [4] questioned the validity of the expression I used for the determination of the activation energy accuracies [2]. Accordingly to them, that equation originates relative errors in the activation energy much higher than those calculated with the correct equation (about 2.5 to 33 times higher, as shown in the table of reference [4]).

In this short communication, I will show that the results of Cai and Liu [4] are definitively incorrect, and that the equation used in [2] generally gives very good estimates of the relative errors of activation energies calculated according to the approximate expressions used to describe the values of the temperature integral. Effectively, as it was stressed in my previous article, the results and conclusions obtained in that study were validated carrying out the kinetic analysis of a large set of simulated curves, corresponding to a broad range of activation energies, pre-exponential constants and kinetic functions [2]. Therefore, a different conclusion was not expected.

Theoretical considerations

In this report, to facilitate the exposition and the understanding of my reasoning, I will use the nomenclature of Cai and Liu [4], which has some differences relatively to that I considered in my previous article [2].

The integrated equation that describes the progress of reaction in non-isothermal analysis is:

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \tag{1}$$

In most cases, this equation can be simplified, since the integral between 0 and T_0 is often negligible compared with the integral between 0 and T . Therefore, we can write:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \tag{2}$$

In these equations, α is the degree of transformation, $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$, where $f(\alpha)$ is the kinetic function (related to the mechanism of the process under study), T is the absolute temperature and β the heating rate. A and E are the Arrhenius parameters (pre-exponential constant and activation energy, respectively).

Defining $x = \frac{E}{RT}$ and changing variables, it results the equation

$$g(\alpha) = \frac{A E}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{A E}{\beta R} p(x) \tag{3}$$

which can be written in a more practical form as

$$g(\alpha) = \frac{A R}{\beta E} T^2 \exp\left(-\frac{E}{RT}\right) Q(x) \tag{4}$$

where the function $Q(x)$ is defined by the expression:

$$Q(x) = x^2 \exp(x) p(x) = x^2 \exp(x) \int_x^\infty \frac{\exp(-x)}{x^2} dx \tag{5}$$

The values of $Q(x)$ must be calculated numerically, since the integral $p(x)$ has no analytical solution. Nevertheless, several expressions have been considered in the literature in order to approximate those values. Frequently, these expressions are rational functions of x , derived from different series expansions or obtained using appropriate fitting procedures applied to some values calculated by numerical integration. My previous article [2] deals with the evaluation of this type of approximations.

If an approximate expression h is used in the kinetic analysis by the integral method, instead of the values calculated from Eq. 5, then it will result the determination of an apparent (or approximate) activation energy, E_a , and the associated pre-exponential constant, A_a , which verify the equation:

$$g(\alpha) = \frac{A_a R}{\beta E_a} T^2 \exp\left(-\frac{E_a}{RT}\right) h(x_a) \tag{6}$$

where $x_a = \frac{E_a}{RT}$.

According to Eqs. 4 and 6, correct and approximate values of the activation energy are calculated, respectively, from the slopes of the lines $\ln \frac{g(\alpha)}{T^2 Q(x)}$ and $\ln \frac{g(\alpha)}{T^2 h(x_a)}$ versus $\frac{1}{T}$. It is possible to conclude that:

$$\frac{E}{R} = -\frac{d \ln \left[\frac{g(\alpha)}{T^2 Q(x)} \right]}{d \left(\frac{1}{T} \right)} = -\frac{d \ln g(\alpha)}{d \left(\frac{1}{T} \right)} - 2 T + \frac{d \ln Q(x)}{d \left(\frac{1}{T} \right)} \tag{7}$$

and

$$\frac{E_a}{R} = -\frac{d \ln \left[\frac{g(\alpha)}{T^2 h(x_a)} \right]}{d \left(\frac{1}{T} \right)} = -\frac{d \ln g(\alpha)}{d \left(\frac{1}{T} \right)} - 2 T + \frac{d \ln h(x_a)}{d \left(\frac{1}{T} \right)} \tag{8}$$

The difference between these two values can be easily calculated. Moreover, as $d \left(\frac{1}{T} \right) = \frac{R}{E} dx = \frac{R}{E_a} dx_a$, we may arrive to Eq. 9:

$$\begin{aligned} E_a - E &= E_a \frac{d \ln h(x_a)}{dx_a} - E \frac{d \ln Q(x)}{dx} \\ &= E_a \frac{h'(x_a)}{h(x_a)} - E \frac{Q'(x)}{Q(x)} \end{aligned} \tag{9}$$

where $Q'(x) = \frac{dQ(x)}{dx}$ and $h'(x_a) = \frac{dh(x_a)}{dx_a}$. This expression was presented in [2], using a different nomenclature.

Defining the relative error of the determined approximate activation energies as $\epsilon = \frac{E_a - E}{E}$ and taking into account that $\frac{E_a}{E} = \epsilon + 1$, we get from Eq. 9:

$$\epsilon = (\epsilon + 1) \frac{h'(x_a)}{h(x_a)} - \frac{Q'(x)}{Q(x)} \tag{10}$$

which is also presented in [2].

In the scope of my previous investigation [2], I was searching for conditions and/or approximate expressions corresponding to high accuracy levels. Then, I only considered low values of the relative error ϵ . In these circumstances, $|\epsilon| \ll 1$, and therefore Eq. 11 applies to the calculations:

$$\epsilon = \frac{h'(x)}{h(x)} - \frac{Q'(x)}{Q(x)} \tag{11}$$

since $x_a = \frac{E_a}{E} x = (\epsilon + 1) x$ and $x_a \approx x$ for low values of ϵ .

Discussion of Cai and Liu observations and rebuttal of their conclusion

In their paper [4], Cai and Liu stated that the equation which allows the rigorous calculation of the ϵ values is:

$$(\epsilon + 1) \left(\frac{d \ln h[(\epsilon + 1) x]}{d[(\epsilon + 1) x]} \right) = 1 - \frac{d \ln Q(x)}{dx} \tag{12}$$

Of course, there is a print error in Eq. 12. Actually, as deduced in a previous article of the same authors [5], the correct equation is:

$$(\epsilon + 1) \left(1 - \frac{d \ln h[(\epsilon + 1) x]}{d[(\epsilon + 1) x]} \right) = 1 - \frac{d \ln Q(x)}{dx} \tag{13}$$

Nevertheless, this error is not important in the scope of the present discussion, since Cai and Liu calculated the values of ϵ presented in the table of reference [4] using the correct Eq. 13.

Next, they wrote [4] that I put in reference [2] two simple equations for the estimation of the relative error in the apparent activation energy calculated by integral methods:

$$\epsilon = \frac{d \ln h(x)}{dx} - \frac{d \ln Q(x)}{dx} \tag{14}$$

$$\epsilon = (\epsilon + 1) \frac{d \ln h(x)}{dx} - \frac{d \ln Q(x)}{dx} \tag{15}$$

$$\epsilon = (\epsilon + 1) \frac{d \ln h(x_a)}{dx_a} - \frac{d \ln Q(x)}{dx} \tag{16}$$

Apparently, Cai and Liu [4] did not realize that Eq. 16 (or Eq. 10) is equal to the expression they used for the calculations (Eq. 13). Actually, after applying to the left-hand member of Eq. 13 the distributive property of multiplication and taking into consideration that $x_a = (\epsilon + 1)x$, it is very easy to rearrange it in order to arrive to the form presented in Eq. 16. Therefore, the values of ϵ calculated by Eq. 13 must be equal to those calculated using Eq. 16 (or Eq. 10), contrarily to what is shown in [4]. Additionally, it is wrong to say that the latter equation is a simplified one. This analysis is sufficient to prove that gross errors were done in the calculations that led to the results presented in the table of the Cai and Liu article [4].

Now, let us focus in the simplified Eq. 14 (or the equivalent Eq. 11). To calculate ϵ according to that equation, for a certain approximation, we must know the corresponding analytical expressions of $h(x)$ and $h'(x)$, which for the Coats and Redfern method [6], taken as example by Cai and Liu [4], are:

$$h(x) = 1 - \frac{2}{x} \tag{17}$$

$$h'(x) = \frac{2}{x^2} \tag{18}$$

Then:

$$\frac{h'(x)}{h(x)} = \frac{2}{x(x-2)} \tag{19}$$

On the other hand, the values of $Q(x)$, calculated numerically by Eq. 5, and the respective derivatives with respect to x are also necessary. Instead, for simplicity, I used for the calculations an excellent approximation, derived from [3], that I presented in my previous publication [2], and that was proven to originate relative deviations to the numerical solutions lower than 0.0005% in the interval $x \in [1, 250]$. The corresponding analytical expression is:

$$Q(x) = \frac{0.9999936 x^4 + 7.5739391 x^3 + 12.4648922 x^2 + 3.6907232 x}{x^4 + 9.5733223 x^3 + 25.6329561 x^2 + 21.0996531 x + 3.9584969} \tag{20}$$

Equation 14 is effectively equal to my simplified Eq. 11, but Eq. 15 is wrongly indicated, since the equation I presented (Eq. 10) is equivalent to (the nomenclature is not the same in [2]):

The values of $Q(x)$ calculated from Eq. 20 are compared in Table 1 with those obtained from Eq. 5, i.e., by calculating the integral numerically, showing its excellent level of accuracy.

Table 1 Values of $Q(x)$ calculated numerically or using Eq. 20

x	$Q(x)$ Eq. 5	$Q(x)$ Eq. 20
5	0.739446	0.739446
10	0.843666	0.843666
15	0.887937	0.887937
20	0.912582	0.912582
25	0.928313	0.928314
30	0.939235	0.939236
35	0.947264	0.947264
40	0.953416	0.953416
45	0.958281	0.958281
50	0.962225	0.962225
55	0.965487	0.965487
60	0.968230	0.968230
65	0.970570	0.970569
70	0.972588	0.972587
75	0.974347	0.974346
80	0.975893	0.975892
85	0.977264	0.977263
90	0.978487	0.978486
95	0.979586	0.979584
100	0.980577	0.980575

Table 2 Accuracy of activation energies determined by the Coats and Redfern method (non-simplified vs. simplified equation)

x	ϵ /% Eq. 13	$\frac{h'(x)}{h(x)}$ Coats- Redfern	$\frac{Q'(x)}{Q(x)}$ Eq. 21	ϵ /% Eqs. 11/14
5	7.15007	1.333333×10^{-1}	4.763547×10^{-2}	8.570
10	0.99939	2.500000×10^{-2}	1.469765×10^{-2}	1.030
15	0.30924	1.025641×10^{-2}	7.127633×10^{-3}	0.3129
20	0.13395	5.555556×10^{-3}	4.207877×10^{-3}	0.1348
25	0.069824	3.478261×10^{-3}	2.777403×10^{-3}	0.07009
30	0.040938	2.380952×10^{-3}	1.970526×10^{-3}	0.04104
35	0.026037	1.731602×10^{-3}	1.470737×10^{-3}	0.02609
40	0.017579	1.315789×10^{-3}	1.139729×10^{-3}	0.01761
45	0.012424	1.033592×10^{-3}	9.091842×10^{-4}	0.01244
50	0.0091035	8.333333×10^{-4}	7.421780×10^{-4}	0.009116
55	0.0068692	6.861063×10^{-4}	6.173236×10^{-4}	0.006878
60	0.0053105	5.747126×10^{-4}	5.215349×10^{-4}	0.005318
65	0.0041900	4.884005×10^{-4}	4.464387×10^{-4}	0.004196
70	0.0033640	4.201681×10^{-4}	3.864748×10^{-4}	0.003369
75	0.0027416	3.652968×10^{-4}	3.378330×10^{-4}	0.002746
80	0.0022639	3.205128×10^{-4}	2.978315×10^{-4}	0.002268
85	0.0018910	2.834869×10^{-4}	2.645381×10^{-4}	0.001895
90	0.0015957	2.525253×10^{-4}	2.365322×10^{-4}	0.001599
95	0.0013589	2.263724×10^{-4}	2.127505×10^{-4}	0.001362
100	0.0011667	2.040816×10^{-4}	1.923839×10^{-4}	0.001170

From Eq. 20, we get the corresponding derivative $Q'(x)$, and therefore:

$$\begin{aligned}
 Q'(x)/Q(x) = & 1.9993219 x^6 + 26.3357997 x^5 \\
 & + 127.0384026 x^4 + 264.7838961 x^3 + 258.3449989 x^2 \\
 & + 98.6844743 x + 14.6097164 / (0.9999936 x^4 \\
 & + 7.5739391 x^3 + 12.4648922 x^2 + 3.6907232 x) \\
 & (x^4 + 9.5733223 x^3 + 25.6329561 x^2 \\
 & + 21.0996531 x + 3.9584969) \tag{21}
 \end{aligned}$$

Table 2 presents the values of ϵ for the Coats and Redfern approximation, calculated by Cai and Liu [4, 5] using Eq. 13, and determined according to the simplified Eq. 11 (or the equivalent Eq. 14). It may be concluded, contrarily to what is stated by Cai and Liu [4], that the simplified equation I used before [2] gives results very close to the real ones, except for the case of low values of x , as expected, accordingly to the relatively large values of ϵ obtained. Since in my previous report [2] I was searching for approximate formulas that might give rise to low relative errors in the calculation of activation energies, the use of the simplified equation is perfectly justified.

I do not feel obliged to find the cause of the errors made in the calculations that led to the values shown in [4] and the related conclusion of Cai and Liu, but on the other hand I hope to have demonstrated that my assumptions are more than reasonable and that the calculations and the associated discussion presented in [2] are solid and reliable.

Conclusions

In this short communication, contrarily to what is concluded recently by Cai and Liu [4], it was proven unequivocally that the simplified expression presented in reference [2] for the calculation of the accuracies of activation energies determined by the integral method, based on non-isothermal kinetic data, and using approximate expressions for the temperature integral, leads to values very close to the rigorous solution.

Summarizing, Cai and Liu [4] raised a non-existent problem and arrived at an erroneous and even absurd conclusion, making several errors in the way. In my opinion, this type of publication does not contribute at all to the advance of scientific knowledge. On the contrary, it may contribute to confuse the minds of some non-experienced readers. Therefore, I hope that this particular work of these authors may be ignored from now on.

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