

**REPLY TO REMARKS ON
“A NEW EQUATION FOR MODELING
NONISOTHERMAL REACTIONS”**

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(Received April 19, 1988)

There are numerous ways to solve the temperature integral. Integral methods are perhaps one of the most accurate and popularly used methods to solve the temperature integral [1–3]. In a recent paper, Agrawal [4] showed how the integral methods such as Coats–Redfern, Gorbachev and Li equations were related and proposed a better equation based on these equations. The topic of Agrawal’s paper was limited to these integral approximations as they were obtained by integrating the temperature integral by parts. It was not the purpose to review and examine the accuracy of all temperature integral approximations available in the voluminous literature; as this would be a formidable mission. Besides, the accuracy of various integrals were seldom available in the form of a plot of percent error of the temperature integral as a function of the E/RT ratio to make the task attemptable. Further it is futile to make such an attempt as the exact solution can be obtained by numerical techniques. Zsakó [5] in his criticism of my work makes incorrect remarks and quotes some of my statements out of context.

Zsakó simply quotes his own publications to claim that the physical significance of the Arrhenius equation is obscure. No proofs or justifications are available in his quoted papers [6, 7]. As discussed by Agrawal [8] (replying to another of Zsakó’s [9] questions), many authors merely question the physical significance of the Arrhenius equation, but use it anyways. If Arrhenius equation is so objectionable and incorrect, then why isn’t there a better equation available to replace it? The misconception on the use of Arrhenius equation has been referred to in detail by Agrawal [8, 10]. It is sufficient to mention here that Arrhenius equation is perhaps the most used equation and it serves its purpose in correlating the kinetic data *satisfactorily*. The lack of an alternate method to correlate the temperature dependence of the rate constant clearly implies that the Arrhenius equation is universally accepted.

I do not see the reasoning behind Zsakó’s objections to methods to approximate

the function $1/T$ in order to make the temperature integral analytically integrable (i.e. integral methods). In fact the integral methods are the most popular in determining the kinetic parameter from nonisothermal data [1]. From the paper of Agrawal [4] it can be seen how integral methods are related to the asymptotic expansion methods. The integral methods approximate the temperature integral by the generalized form

$$\int \exp(-E/RT) dT = \frac{RT^2}{E} \left[\frac{1 - 2RT/E}{1 - m(RT/E)^2} \right] \exp(-E/RT)$$

where $m=0$ for Coats–Redfern equation, $m=4$ for Gorbachev equation, $m=5$ for Agrawal equation and $m=6$ for the Li equation. For low values of E/RT ratio the ideal value of m varies from 4.6 to 5. The Coats–Redfern equation was obtained from the approximation of asymptotic expansion, where as the Gorbachev equation was obtained from the Schlömlich expansion. As mentioned by Agrawal [4], the Gorbachev equation can also be obtained by integrating the temperature integral by parts. By integrating the temperature integral twice by parts, Li arrived at his equation. The purpose of Agrawal's paper was to show the striking similarity of these equations and to show how a better approximation can be obtained. It was not my objective to obtain "the most accurate" solution as one can easily obtain exact solutions by numerical techniques. Zsakó has therefore taken my statement "is more accurate than previously known approximations" out of context.

Numerical techniques and power series expansion methods (e.g. Eq. (10) in Zsakó's [5] paper) are not capable of extracting the kinetic parameters from the experimental data as E is not known a priori. One must be cautioned against assuming a value of E in order to fit the data. The results of Flynn and Wall [1] indicates that this leads to non-unique solutions. Other problems which could arise from assuming a value of E to fit the data are discussed in Agrawal [10]. Therefore integral approximations are needed to obtain kinetic parameters from experimental data. The kinetic parameters can be obtained from integral approximations from the equation

$$\ln[(\ln \alpha)/T^2] = \ln \left\{ \frac{AR}{\beta E} \left[\frac{1 - 2RT/E}{1 - m(RT/E)^2} \right] \right\} - E/RT$$

Activation energy can be obtained from the slope of a plot of $\ln[(\ln \alpha)/T^2]$ versus $1/T$ and the pre-exponential factor can be obtained from the intercept. Coats–Redfern and Gorbachev equations are perhaps the most popular equations used to obtain kinetic parameter from experimental data. Recent studies [2, 3] confirm my assumption. As the ultimate purpose was to obtain an equation capable of extracting accurate kinetic parameters from experimental data, I had assumed it

was appropriate to limit my study to these equations. The statement of Zsakó that I ignored other available approximations is therefore incorrect; and perhaps misleading.

Zsakó is not totally correct when he says that the Eqs (5), (6) and (10) (equations numbers from his paper [5]) are of "third degree". It is left to the individuals to judge the complexity of Eqs (5), (6) and (10). Although Eq. (6) yields excellent results, Zsakó is incorrect when he claims Eq. (6) to be much better than Eq. (5) for all values of E/RT . From the figure in Zsakó's paper [5], it appears that for E/RT ratio between 6 and 8, Eq. (5) is superior to both Eqs (6) and (10). Therefore Zsakó [5] is incorrect in making a generalized statement that, "the formula proposed by Agrawal . . . is shown to be less accurate than several approximations proposed earlier and being of the same complexity".

Finally, the statement of Zsakó [5], "the problem of the temperature integral $p(x)$ can be considered as being solved satisfyingly" is debatable. Recent publications [11–13] clearly indicates that there is still interest in new and accurate approximations for $p(x)$.

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