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Thermochimica Acta 300 (1997) 83–92

thermochimica
acta

The 'Temperature Integral' – Its use and abuse

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Received 10 September 1996; accepted 26 November 1996

Abstract

This paper first reviews the history of the temperature dependence of reaction rate in reaction kinetics. The various equations which are in use today for expressing this dependence were delineated by van't Hoff almost one hundred years ago. Since an exponential form best describes this dependence for most thermal analysis reactions and, due to the fact that the simple Arrhenius equation (with a temperature-independent preexponential factor) has traditionally been used for this purpose, the mathematically intractable temperature integral often has become a necessary evil in the analysis of thermal analysis kinetics. Methods which avoid the temperature integral in kinetics analysis are discussed. The merits of various evaluations and approximations for the temperature integral are described and assessed in this paper. © 1997 Elsevier Science B.V.

Keywords: Analysis of nonisothermal kinetics; Arrhenius equation; Energy of activation; Preexponential factor; Rate dependence on temperature; The temperature integral

1. Introduction

The temperature integral has played a somewhat enigmatic role in the development of thermal analysis reaction kinetics. That is, it has appeared to be a necessary evil to be dealt with whenever the Arrhenius equation was integrated over time as a function of temperature. Many of the problems connected with its application have resulted from the inability to accurately approximate the temperature integral by a simple closed-form expression which is suitable for use in graphical form to determine the 'Arrhenius Parameters,' i.e. the energy of activation, E, and the preexponential factor, A_0, in Eq. (1) below.

This integral is obtained in thermal analysis when the Arrhenius equation [1],

$$k(T) = A_0\exp(-E/RT), \tag{1}$$

where T is the absolute temperature, $k(T)$ is the 'rate constant,' and R, the 'gas constant,' is the one used to express the temperature dependence of the reaction rate.

When Eq. (1) is integrated over a time dependent temperature range, one obtains the 'temperature integral,' $p(E/RT) = p(x)$, which is defined here as:

$$p(x) = [(-\exp x)/x] - \int_x^\infty (\exp\ -x)\mathrm{d}x/x^2 \tag{2}$$

If a reaction starts at a temperature where its rate is immeasurably slow, the lower limit of the integral in

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PII S0040-6031(97)00046-4

temperature may be taken as zero and Eq. (2) is calculated between x and infinity.

However, before discussing the temperature integral, we review briefly the history of how the Arrhenius equation came into being and its 'theoretical' and its 'practical' implications with respect to condensed phase kinetics. Equations with various forms of 'exponential and other temperature dependences' were developed by Arrhenius, van't Hoff and others over a hundred years ago and are discussed below. Some were, at first, purely empirical proposals, but various rationales and theories for an exponential relationship between the rate and temperature have been developed. These have been based on collision probabilities, energetics, thermodynamics, and/or statistical mechanics. Since these theoretical developments are rigorously applied mainly to homogeneous gas or liquid phase single step processes, they need not be belabored in this discussion which applies to the kinetics of complex condensed phase systems of thermal analysis.

It is surprising to find that almost all the equations used today to express the dependence of the rate on temperature were first proposed by scientists of the 19th century. An interesting discussion of many of the early equations was given in 1899 in van't Hoff's 'Lectures on Theoretical and Physical Chemistry' [2].

Van't Hoff suggested various forms that the temperature dependence of the rate constant, k, might assume. These, along with several others, are listed in Table 1. The first column gives the differential form and the second column, the integral form of the rate constant, k.

In Table 1, A, B, C, a and b are empirical constants. These equations give us a good starting point for the discussion of the problems in developing parameters for the temperature dependence of the rate. Therefore, we discuss them each in turn.

Eq. (a), $\mathrm{d}(\ln k)/\mathrm{d}T = \mathrm{C}$: This equation was first used by Berthelot in 1862 [3] and Hood in 1885 [4] and has been used at times for many years for condensed phase kinetics, especially for 'first order kinetics' where A_0 and C are calculated from ln ln α vs. ln T plots. (α is the extent of reaction.) Vallet [9] published many such plots and justified their use from the near linearity between T and $1/T$ over the usual reaction range and from the easy integration of this equation. He showed that this expression is equivalent to a two-term Taylor's expansion of the Arrhenius Eq. (1) about a reference temperature [10]. Van Kreveland et al. [11] used this reference temperature technique as did Horowitz and Metzger [12] (see Flynn and Wall [13]), and, most recently, Eq. (a) has been applied to many other forms of $f(\alpha)$ by Dollimore [14]. Its practical use is belied by the necessity of transforming its parameters into the common Arrhenius parameters so as to compare them with those obtained from the vast bulk of kinetics analyses. Also, the validity of this transformation depends upon the subjective selection of the correct form of $f(\alpha)$.

Eq. (b), $\mathrm{d}(\ln k)/\mathrm{d}T = \mathrm{B}/T$: This simple dependence of the rate constant on a power of the temperature was suggested by Harecourt and Esson in 1895 [5]. It has never become popular so it need not be discussed further. However, expressing the rate in terms of a power series of the temperature was first suggested by Urech in 1883 [15], and more recently by others [16,17].

Eq. (c), $\mathrm{d}(\ln k)/\mathrm{d}t = \mathrm{A}/T^2$: If $\mathrm{A} = E/R$, then this equation becomes the standard 'Arrhenius Equation' (1) above, developed by Arrhenius in 1889 [1]. It is

Table 1
Equations for the temperature dependence of the rate of reaction

	$\mathrm{d}(\ln k)/\mathrm{d}T =$	$k =$	Reference
(a)	C	$A_0\exp(CT)$	Berthelot [3]; Hood [4]
(b)	$\mathrm{B/T}$	A_0T^{B}	Harecourt and Esson [5]
(c)	A/T^2	$A_0\exp(-\mathrm{A}/T)$	Arrhenius [1]
(d)	$(\mathrm{A}+\mathrm{B}T)/T^2$	$A_0T^{\mathrm{B}}\exp(-\mathrm{A}/T)$	Kooij [6]
(e)	$(\mathrm{A}+\mathrm{C}T^2)/T^2$	$A_0\exp(\mathrm{C}T)\exp(-\mathrm{A}/T)$	van't Hoff [2]
(f)	$(\mathrm{B}T+\mathrm{C}T^2)/T^2$	$A_0T^{\mathrm{B}}\exp(\mathrm{C}T)$	(added for completeness)
(g)	$(\mathrm{A}+\mathrm{B}T+\mathrm{C}T^2)/T^2$	$A_0T^{\mathrm{B}}\exp(\mathrm{C}T)\exp(-\mathrm{A}/T)$	van't Hoff [2]
(h)	$\mathrm{a}/(T+\mathrm{b})^2$	$A_0\exp[-\mathrm{a}/(T+\mathrm{b})]$	VFT [7] or WLF [8]

ironic that it has become the 'equation of choice' for chemical kineticists as it is the one whose integration at constant heating rate leads to intractable solutions (the temperature integral). Much of this paper is devoted to the discussion of these resultant problems. The temperature-independent prexponential factor, A_0, used in this equation has no theoretical justification! The unfortunate selection of this form by classical scientists working with isothermal systems where it is the most suitable for calculations has led to its application to nonisothermal kinetics data where it is most unsuitable.

Eq. (d), $\mathrm{d}(\ln k)/\mathrm{d}T = (\mathrm{A} + \mathrm{B}T)/T^2$: This equation is the most interesting one of the above set. It appears to have been first used by Kooij (Kooy) in 1893 [6]. If B is set equal to 2, then the equation is easily integrated at constant heating rate in a closed form. Such a T^2 term may be introduced into the preexponential term of Equation (c) by employing a heating rate proportional to $1/T$ [18,19,13,20–22]. This technique allows one to retain the traditional definition of the Arrhenius parameters, E/R and $\ln A_0$, as given in Eq. (c) so that these parameters can be directly compared with those ordinarily obtained from constant heating rate and isothermal experiments.

Eq. (d) with a T^2 term ($\mathrm{B} = 2$) also can be posited to be the correct form of the temperature dependence at constant heating rate. In the kinetically complex condensed phase systems encountered in thermal analysis studies, some temperature dependence of the preexponential factor, $\ln A_0$, is undoubtedly often present, although its exact form probably will vary from case to case [23]. There is, of course, considerable theoretical justification for a temperature dependence of the preexponential factor. Simple collision theory of gases suggests a one-half power dependence for bimolecular gas phase reactions. In transition state theory, the power of the temperature is one or greater depending upon the number of reacting species involved in the geometry of the activated complex [24]. In this case, for a gas phase bimolecular reaction complex, the rate constant contains a T^2 in the preexponential term [24]!

Equations obtained from 'modified' temperature integrals containing temperature-dependent preexponential terms have been used occasionally to calculate kinetics parameters for constant heating rate methods [25–29]. However, in all these cases, redefining the Arrhenius equation with a temperature-dependent preexponential factor makes the new calculated parameters, E/R and $\ln A_0$, strictly not comparable with those obtained in practically all other isothermal and nonisothermal calculations in literature where the 'classic' Eq. (c), with a temperature independent A_0, is used in the calculations. Therefore, if the thermal analysis community were to adopt one of these equations with a temperature-dependent preexponential term as the basic equation for temperature dependence of the rate, it would be an incredibly tedious and, in many cases, an impossible task to go back and try to recalculate all activation energies and preexponential factors found in the literature so that valid quantitative comparisons could be made with the new E/R and $\ln A_0$ values and those obtained from the diverse experimental kinetics results of the last century. (Although a preexponential temperature dependence only slightly affects the shape of a 'theoretical' rate curve at constant heating rate [13,25], it does noticeably affect the values of its calculated kinetics parameters.)

There are, of course, several other ways by which the temperature integral may be avoided completely. These are discussed in the next section.

Eqs. (e), (f) and (g), $\mathrm{d}(\ln k/\mathrm{d}T = (\mathrm{A} + \mathrm{C}T^2)/T^2$, $(\mathrm{B}T + \mathrm{C}T^2)/T^2$, $(\mathrm{A} + \mathrm{B}T + \mathrm{C}T^2)/\mathrm{T}^2$: These equations, with their additional parameters, most certainly would result in better fits to experimental data but they have little, if any, theoretical justifications. They have rarely, if ever, appeared in scientific literature and this is probably just as well. There are enough complications already. Of course, in cases of more complex kinetics systems, such as consecutive, competitive, independent, chain, etc, reactions, more complex formulations, which are summations and/or products of Arrhenius equations with differing parameters, are necessary to describe the temperature dependence of the reaction kinetics (unless they can be reduced to a single Arrhenius expression by applying the concept of the 'rate controlling step' [30]).

Eq. (h), $\mathrm{d}(\ln k)/\mathrm{d}T = \mathrm{a}/(T + \mathrm{b})^2$: This is the form of the Vogel–Fulcher–Tammann (VFT) Equation [7] and the Williams–Landel–Ferry (WLF) Equation [8]. This equation is successfully applied to kinetics data for viscoelastic processes occurring in the glass transition temperature region.

2. Avoidance of the temperature integral

Besides keeping to isothermal investigations and using nonlinear heating rates, another way to avoid involvement with the temperature integral in the analysis of constant heating rate kinetics is to perform the analysis directly upon the differential form of the rate equation. Such methods have been available for many years [13] and Friedman's isoconversional technique [31] has been generalized recently [32,33]. Many of the past disadvantages of these 'differential' techniques are no longer as relevant now that data handling and computation are done by computer [33].

Both the temperature integral and a knowledge of the form of the conversion function, $f(\alpha)$ are unnecessary for the determination of Arrhenius parameters at low degree of conversion for 'nonautocatalytic' reactions [34]. If the rate of conversion, $\mathrm{d}\alpha/\mathrm{d}t$, at constant heating rate, β, is a product of functions of conversion only and of temperature only, $f(\alpha)$ and $k(T)$, respectively, then,

$$(\beta)\mathrm{d}\alpha/\mathrm{d}T = f(\alpha)k(T). \tag{3}$$

The substitution of the Arrhenius Eq. (1) into Eq. (3) followed by differentiation with respect to α gives

$$[\mathrm{d}/\mathrm{d}\alpha][\mathrm{d}\alpha/\mathrm{d}T] = E/RT^2 + [f'(\alpha)/f(\alpha)][\mathrm{d}\alpha/\mathrm{d}T] \tag{4}$$

One obtains, for $\alpha \ll 1$, from application of the mean value theorem [34],

$$E/R = [\bar{T}^2/\bar{\alpha}][\Delta(\alpha)/\Delta T] - 2T[\alpha \ll 1], \tag{5}$$

where T and α are values averaged over the intervals ΔT and $\Delta(\alpha)$. Eq. (5) holds for all values of α for zero order reactions, and deviations from it are inverse to the sign of the reaction order. In practice, when $0 < \alpha < 0.05$, the value of E/R is accurately determined for most nonautocatalytic cases whether they follow a reaction order or not.

Flynn [10] in 1969 developed a technique in which 'instantaneous' E/R values, from a single specimen and therefore unbiased by thermal history, are obtained from thermal analysis experiments in which the temperature is either jumped between plateaus or cycled harmonically. In either case, E/R is calculated from temperatures and the rates at each temperature from

$$E/R = \ln[(\mathrm{rate})_1/(\mathrm{rate})_2]/[1/T_2 - 1/T_1] \tag{6}$$

where the values of the rates are extrapolated to the midpoints of the jumps or obtained from the upper and lower envelopes in the cyclic case. This method has been refined and fully automated by Dickens [35]. Rouquerol [36] in 1973, applied a similar jump technique between constant rates to his controlled rate thermal analysis (CRTA) method.

Modulated DSC instruments offer a yet untapped potential for the determination of these instantaneous kinetics parameters. Flynn, in 1976 [37–39], pointed out that "Relaxation phenomena may be studied either by measuring the time constant for a single (temperature) jump directly, or by measuring the phase lag or amplitude change for system which is oscillating between two limiting values...." Study of the relaxation of these oscillating modes comprise many of the present applications of MDSC. However, as indicated in Eq. (6), the envelope for the rate for large amplitude, low frequency oscillations in the temperature can be used to calculate E/R. Thus it should not be too difficult to determine E/R applying Eq. (6) to rate data obtained from the envelope of the nonreversible signal of an MDSC for a nonreversible chemical reaction. Flynn, in 1985, performed such an experiment by manually jumping the temperature back and forth between plateaus to calculate E/R in a DSC study of the oxygen-catalyzed cure of drying oils [40,41]. However, for this diffusion-limited reaction, a period of over 10 min was needed to reach a steady cure rate after each temperature jump!

3. An analysis of solutions to the temperature integral

If the rate of a reaction can be described by the equation

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(T) \tag{7}$$

then upon separation and rearrangement, one obtains at constant heating rate, β, upon integration,

$$\int_0^\alpha \mathrm{d}\alpha/f(\alpha) = g(\alpha) = \int_{T_0}^{T} k(T)\mathrm{d}T/\beta = P(T). \tag{8}$$

If $k(T)$ is defined by the Arrhenius Eq. (1) and the lower limit of integration is assumed to be 0, that is, no reaction has occurred at the initial temperature, $T = T_0$, then, upon substituting $x = E/RT$, we obtain [42]

$$P(z) = [A_0E/\beta R] \int_{x}^{\infty} [\exp(-x)/x^2]\mathrm{d}x \qquad (9)$$

which upon the variable change $x = zy$ becomes

$$P(z) = [A_0E/\beta Rz] \int_{1}^{\infty} [\exp(-zy)]y^{-2}\mathrm{d}y \qquad (10)$$

$$P(z) = [A_0E/\beta Rz]E_2(z) \qquad (11)$$

$E_2(z)$ is a well-known integral [43]. In fact, it is probably the best one to use for calculating the temperature integral as its solutions are quickly converging and easily adaptable to computer routines. It is given accurately for values of x greater than two by the continued fraction,

$$\begin{aligned} E_2(x)/x = (\mathrm{e}^{-x})/x[1/x + 2/1 + 1/x + 3/1 \\ + 2/x + 4/1 + 3/x + 3/x + 5/1 \\ + 4/x + 6/\cdots] \quad (x > 2) \qquad (12) \end{aligned}$$

Truncating the number of terms in the above continued fraction reduces it to the one, two, three and four degree 'rational approximations' [44] for the exponential integral given in Table 2. These are by far the best closed form approximations for the temperature integral.

For values of z less than 2, the following series expansion for E_2 converges rapidly.

$$\begin{aligned} E_2(x)/x = (1/x)[x \ln x + 1 \\ + (1 - 0.5772156649)x - X^2/2! \\ + x^3/2(3!) - x^4/3(4!) \\ + x^5/4(5!) - \cdots] \quad (x < 2) \qquad (17) \end{aligned}$$

where 0.5772156649 is Euler's constant.

Table 2
One, two, three and four degree rational approximations for the exponential integral (see Ref. [44]) [a]:

Degree	$p(x)$	
1	$\frac{\exp(-x)}{x} \cdot \frac{1}{(x+2)}$	(13)
2	$\frac{\exp(-x)}{x} \cdot \frac{(x+4)}{(x^2+6x+6)}$	(14)
3	$\frac{\exp(-x)}{x} \cdot \frac{(x^2+10x+18)}{(x^3+12x^2+36x+24)}$	(15)
4	$\frac{\exp(-x)}{x} \cdot \frac{(x^3+18x^2+86x+96)}{x^4+20x^3+120x^2+240x+120}$	(16)

[a] Reference [44] has an error in the first power of x term of the numerator of the 4th degree approximation equation. That is, it should read 86x, rather than 88x.

From Eqs. (2) and (9), we see that $p(x) = [\exp(-x)/x] - [\beta/A_0xT]P(x)$. Therefore Eq. (17) may be used in conjunction with Eq. (12) to calculate values of whatever degree of accuracy we wish for the temperature integral, $p(x)$, over the whole range of E/RT.

There must be at least several hundred papers in the literature on the temperature integral and its evaluation by series solution and various approximations. These solutions of the temperature integral are classified into three categories – viz. A. Series Solutions; B. Complex Approximations; C. Simple Approximations. Only a few of these have scientific relevancy today. Some others are of historical interest. These are discussed below. (For a more detailed discussion of many of the solutions of the temperature integral, the reader is referred to *Section 4.4 B. Some Useful Rate Equations and Their Integrals* in Charles D. Doyle's massive and excellent review article published in 1966 [45], and *9.2 Integration of the Rate Constant under Nonisothermal Conditions*: Use of Function $p(x)$ (pp. 218–222) in Jaroslav Šesták's book, (Ref. [46]).

3.1. Series Solutions

The tables of values for the temperature integral and many of the Complex and Simple Approximations, which are discussed later, are based upon series solutions and truncations of them. Beside the series solutions to the temperature integral given in Eqs. (12) and (17), there are three that have been used frequently over the years:

3.1.1. Schlömilch Expansion [47]

$$\begin{aligned} p(y) = [(\exp - y)/y(y + 2)][1 - 1/(y + 2) \\ + 2/(y + 2)(y + 3) + 4/(y + 2) \\ \cdots (y + 4) + 14/(y + 2) \cdots (y + 5) \\ + \cdots](y = -x > 15). \qquad (18) \end{aligned}$$

This series has been used occasionally to calculate $p(x)$ tables.

3.1.2. Expansion in Series of Bernouli Numbers [48]

$$p(x) = [(\exp x)/x][-0.0000035 + 0.998710/x + 1.98487646/x^2 + 4.9482092/x^3 + 11.7850792/x^4 + \cdots] \quad (x \leq -2) \tag{19}$$

This series is useful for values of x as small as 2 and has been used frequently to calculate tables for $p(x)$.

3.1.3. The Asymptotic Expansion (obtained by multiple integration by parts)

$$p(x) = [(\exp x)/x^2][1 + 2!/x + 3!/x^2 + 4!/X^3 + \cdots](-x \geq 10, \text{diverges for number of terms} > |x|) \tag{20}$$

This series diverges and is useful only for large values of x; so it is of interest mainly for historical reasons as two and three-term approximations of it were used in some of the classical kinetics methods, most notably that of Coats and Redfern [48]. These methods are now obsolete and probably should not be used in kinetics analyses. They are discussed in the section on Simple Approximations.

As far as tables of $p(x)$ are concerned, only one need be mentioned. It is the 'Tables Numeriques Permettant L' integration des Constantes de Vittesse par Rapport a la Temperature' by Pierre Vallet which was published in French, English and Spanish in 1961 [26]. These tables give $p(x)$ values for 0.1 increments of x from 1.0 to 50.0 and at 1.0 increments from 50.0 to 200.0. The values in the table are correct to eight significant figures. Many other tables for $p(x)$ appear in the literature but none of them are so complete or accurate.

3.2. Complex Approximations

These are too complex to be used to calculate E/R graphically but are easily calculatable using a pocket calculator (for those who are without computational facilities). They may be defined as algebraic ratios containing $x(= E/RT)$ as a quadratic or higher degree. These approximations are to be found throughout thermal analysis literature (and are still appearing). However, the frequency of their use should be dwindling as they are no longer relevant compared to the more exact series described in Section A above. They are now mainly of historical significance. (N.B.: The quality of various approximations for the temperature integral at a particular argument, $x = E/RT$, is assessed in terms of *deviations* or *percentage deviations* from the *correct value*. The terms 'error' and 'percentage error' are not used since they imply that the Arrhenius Equation, Eq. (1), has some sort of theoretical or special physical significance.)

Table 3
Percentage deviation in $[x\,p(x)/(\exp - x)]$ for Complex Approximations of $p(x)$

x	$\frac{(x+4)}{(x^2+6x+6)}$	$\frac{(x^2+10x+18)}{x^3+12x^2+36x+24)}$	$\frac{(x^3+18x^2+86x+96)}{(x^4+20x^3+120x^2+240x+120)}$
1	4.717	−1.584	−0.609
2	1.661	−0.368	−0.095
4	−0.403	−0.051	−0.008
7	−0.097	−0.007	0.000
10	−0.048	−0.002	
15	−0.010	0.000	
20	−0.004		
25	−0.002		
30	−0.001		
35	0.000		

The percentage deviation for the second, third and fourth degree 'rational approximation' equations are given in Table 3. They are more accurate than any of the others of similar complexity (for values of $x = E/RT$ greater than 2). The accuracy of many other of these complex approximations have been reviewed by Doyle [45], Šesták [46], Zsako [49], and many others.

3.3. Simple Approximations

These simple approximate equations for the temperature integral were used extensively during the early days of thermal analysis kinetics and still appear in the literature. Some of these are quite inaccurate but are still preferred by some investigators who are apparently not perturbed by the fact that, when they use two or more of these 'approximate' methods for the same experimental data, they are publishing incorrect and often conflicting values for E/R and $\ln A_0$.

The percentage deviation in $J(x) = [x\,p(x)/(\exp - x)]$ for several simple approximations of

Table 4
Percentage deviation in $[xp(x)/(\exp-x)]$ for Simple Approximations of $p(x)$ $[xp(x)/(\exp-x)]=J(x)$

x	(j) 1	(k) $1-(2/x)$	(1) $1-(1.7/x)$	(m) $\frac{1}{(x+2)}$	(n) $\frac{1}{(x+1.8768)}$	(o) Doyle I	(p) Doyle II
1				−17.42	−13.88		
2.	80.3	−100.0	−73.0	−9.86	−6.99		
4	43.2	−28.4	−17.7	−4.55	−2.55		
7	25.9	−9.68	−4.71	−2.12	−0.76		
10	18.5	−5.18	−1.62	−1.23	−0.20		−95.22
15	12.62	−2.40	−0.14	−0.62	−0.10	−43.41	−17.26
20	9.79	−1.38	+0.27	−0.38	−0.18	−24.42	−1.45
25	7.72	−0.90	0.40	−0.26	−0.20	−10.22	+4.24
30	6.47	−0.63	0.40	−0.19	−0.20	−1.30	+2.17
35	5.57	−0.47	0.44	−0.14	−0.20	+2.91	−5.05
40	4.68	−0.39	0.43	−0.11	−0.19	+3.19	−15.16
45	4.35	−0.28	0.41	−0.09	−0.18	+2.37	−26.43
50	3.93	−0.23	0.39	−0.07	−0.17	−4.64	
60	3.28	−0.16	0.36	−0.05	−0.15	−18.53	
80	2.47	−0.09	0.29	−0.03	−0.12	−48.79	
100	1.98	−0.07	0.25	−0.02	−0.10		
200	1.00	−0.06	0.22	−0.01	−0.06		

$p(x)$ are given in Table 4. These approximations merit further discussion because of either their historical interest or their continued usage.

(j) (*in Table 4*): One-Term approximation of the Asymptotic Expansion [50], $J(x)=1$: Effectively 'ignoring the integration over T' results in a simple equation which can fit the temperature dependence of the rate probably as well as those involving the temperature integral. However, as was discussed with Eq. (d) above, it is not practical to set up a new equation for the temperature dependence of the rate at this time if any continuity with the kinetics works of the last century is desired. Its large deviations from the correct value for $p(x)$ between $1<x<200$ are apparent in Table 4.

(k) *Two-Term Approximation of the Asymptotic Expansion [48]*, $J(x)=1-(2/x)$: This approximation was used extensively in the early days of thermal analysis kinetics, most notably by Coats and Redfern [48]. However it is one of the least accurate approximations, particularly at low values of x. For example, the percentage deviation in $J(x)=[xp(x)/(\exp-x)]$ increases to more than 0.5% below $x=35$ and greater than 5.0% below $x=11$. As seen in (l) below, these deviations can be reduced by adjustment of the factor 2 to 1.7. Therefore it should always be used in this latter form.

(l) *Adjusted Two-Term approximation of the Asymptotic Expansion [51]*, $J(x)=1-(1.7/x)$: This minor adjustment in the constant of the 'Coats–Redfern Equation' approximation improves the percentage deviation in $J(X)$ so that it is less than 5.0% at $x>7$, and less than 0.5% for all values of x greater than 13.

(m) *Two-Term Approximation of the Continued Fraction ('Rational') Expansion [42,44]*, $J(x)=1/(x+2)$: This approximation was first suggested by Doyle [45] in 1966 and later developed by Gorbachev [52] in 1978. It is very much superior to Eq. (k), the 'Coats–Redfern' approximation, for all values of x. The percentage deviation in $J(x)$ is less than 5.0% for all x values, 4 or greater and less than 0.5% for x greater than 17.

(n) *Two-Term Approximation of the Continued Fraction Expansion (Reduced by Application of Tschebychev Approximation) [53]*, $J(x)=1/(x+1.8768)$: This minor adjustment in the 'Doyle–Gorbachev' approximation, suggested by Jones [53] in 1965, improves the percentage deviation in $J(x)$ so that it is less than 5.0% for all values of x greater than 2.5 and less than 0.5% for x greater than 8. It is obvious that it should always be used in place of Eq. (m), the standard 'Doyle–Gorbachev' approximation.

Since the Doyle–Gorbachev approximation is superior to the Coats–Redfern approximation for all values of x, Eq. (n) should be the natural choice when a simple approximation for $p(x)$ is desired.

(o) An Empirical Interpolation Equation by Doyle (I) [54], $\log_{10} p(x) = -2.315 - 0.4567x$: This empirical relationship is based on the fact that $\log_{10} p(x)$ is virtually linear with x over a short range. For this equation, the useful range (under 5% correction) is $28 < x < 50$.

(p) Another Empirical Interpolation Equation suggested by Doyle (II) [54], $\log_{10} p(x) = -2.000 - 0.4667x$: For this equation, the useful range (under 5% correction) is $18 < x < 35$.

Equations like (o) and (p) are noteworthy because Eq. (o) is the basis for the Ozawa [55]–Flynn [56] Isoconversional Method. Obviously, Eq. (o) which is universally used in this method is not sacrosanct. Eq. (p) or any similar empirical equation of this logarithmic form could be used to fit a particular range of values of x. However Eq. (o) has always been the equation of choice for this method and, as all the 'correction procedures' are based on it, it will probably continue to be the equation of choice for this method.

When one observes the large percentage deviations in Eq. (o) from the correct value of x, even in the range of its applicability, it would appear that the Ozawa–Flynn isoconversional method for calculating E/R is, indeed, an imprecise technique. However, fortunately, E/R is determined from $x = E/RT$, which is the slope of $\ln p(x)$ vs. x curve (whose deviation will be zero at one x value and increase in either direction from it). The error involved in this calculation was recognized in 1966 and an iterative method using a mean temperature to correct for this error was suggested by Flynn [56] and elaborated upon in 1983 [57]. A useful algorithm for making this correction has been developed [58].

It is possible to make similar iterative corrections for the adjusted Coats–Redfern Eq. (l) and the adjusted Doyle–Gorbachev Eq. (n) although the corrections are smaller than those needed in the Doyle Interpolation equations. However the great problem with the Coats–Redfern and the Doyle–Gorbachev Eqs. (k), (l), (m), and (n) is not so much their deviations from the correct $p(x)$, but that it is difficult to separate the effects of these deviations on the kinetics parameters from those resulting from the use of incorrect form for $f(\alpha)$. The disastrous results obtained from assuming first or *n*th order for cases for which they are not applicable were pointed out many years ago [13,59]. When the Coats–Redfern or Doyle–Gorbachev equations are used, a wide range of model conversion functions, $f(\alpha)$, should be tested or, better yet, the correct form of $f(\alpha)$ established from isothermal experiments.

4. Conclusions

This is an opportune time to reappraise the accuracy and utility of the equations used to evaluate the temperature integral in thermal analysis kinetics. The sophistication of thermal analysis kinetics methods has advanced considerably in the past several decades and the use of computers has permitted the development of methods for the rapid testing of the fit of experimental data to wide selections of complex kinetics models.

It is distressing to see publications, even at the present time, in which the authors give three or four values for E/R and $\ln A_0$, calculated by applying different approximate formulas for the temperature integral to the same sets of experimental data, and appear either satisfied with or apparently unconscious of the inconsistencies as they give no explanation for the differing values. That is, whether the differences are due to the approximate nature of the equations used for the temperature integral or due to incorrect assumptions as to the form of the conversion function $f(\alpha)$ or even of $k(T)$ itself. If such papers do not even make an effort to explain these contradictions, they should be rejected out of hand by editors and reviewers of journal articles [16].

In any event, as scientists, we should strive to calculate kinetics parameters as precisely as we are able to. Therefore there is no excuse for using poor approximations for the temperature integral when we are able to determine values for it which are as precise as we wish to make them.

Since there is great variation in the literature in the values for E/R and $\ln A_0$, calculated for a 'single reaction,' it has been suggested that an error below 10% in $p(x)$ may be sufficient for many calculations [46]. This author does not agree. If one wishes to apply the above parameters for a useful scientific purpose, viz. to help distinguish between and define reaction mechanisms, more accurate values for them are required. The great variations found in E/R and ln A_0 in the literature are not usually the result of poor measurement of the experimental data but due to not properly controlling and duplicating the procedural factors of the experiment (sample subdivision and geometry, purge gas rate and composition, etc.) and/or due to using incorrect formulas for the $f(\alpha)$ function assumed in the calculations [23,42]. The use of correct values for the temperature integral allows one to better define these experimental and analytical defects. As a result, one may amend the experimental procedures and kinetics formulations to correct for them.

Indeed, in this age of vast computational capabilities, there is no valid reason not to use precise values for the temperature integral when calculating kinetics parameters.

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