

## IMPROVED APPROXIMATIONS OF THE EXPONENTIAL INTEGRAL IN TEMPERING KINETICS

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The exponential integral in non-isothermal kinetic equations for tempering with linear heating can be represented in the following analytical form

$$\int_0^T e^{-E/kT'} dT' = \frac{kT^2/E}{\sqrt{1+4kT/E}} e^{-E/kT},$$

which is one order in  $kT/E \ll 1$  more accurate than two other representations recently proposed in this journal [1, 2]. A few variants of approximated forms for the exponential integral are compared with regard to the error due to the kind of approximation, which appears when activation energies are evaluated from experimental non-isothermal kinetic curves.

In [1] it has been asserted that the integral  $\int_0^T e^{-E/kT'} dT'$  can be represented more accurately by  $\cong \frac{kT^2}{E+2kT} e^{-E/kT}$  (variant *A*) than by variant *B*  $\cong \left(1 - \frac{2kT}{E}\right) \frac{kT^2}{E} e^{-E/kT}$ ; this assertion is indeed true. As a criterion it has been shown that differentiation of the proposed expression *A* with respect to temperature restores the initial differential equation closer than for the case of expression *B*. This serves as a necessary condition only, but not as a sufficient one. No comparison with the exact solution for the above-mentioned integral has been proved, nor with tabulated numerical values of this or near-related integrals [3–8]. (This latter examination, made earlier by Doyle [9], confirmed the high quality of approach *A*.)

Nevertheless, the knowledge and utilization of the exact solution lead to a still better and simple approach, but also point to the care to be taken in further improvement of these approximations; for real needs (which means when the integral is applied for the evaluation of kinetic process parameters), the temperature-dependence can be of more interest than the absolute values of the integral itself.

### The exact solution

Obviously the differential reaction equations can be separated into a part containing only the conversion degree  $\alpha$  (or concentration  $C$  or any related property) for any reaction mechanism  $f(\alpha)$ , for instance  $f(\alpha) = \alpha^m(1 - \alpha)$ , and into another part which contains the kinetic parameters: activation energy  $E$  and frequency factor  $K$ , and the experimental conditions: temperature  $T$  and heating rate  $q$ :

$$\frac{d\alpha}{f(\alpha)} = \frac{K}{q} e^{-E/kT} dT. \quad (1)$$

Simultaneous integration on both sides leads to

$$F(\alpha) \equiv \int_{\alpha_0}^{\alpha(T)} \frac{d\alpha}{f(\alpha)} = \frac{K}{q} \int_0^T e^{-E/kT'} dT' \equiv S(T; E, K/q) \cdot \eta(y). \quad (2)$$

Here we follow a suggestion given by Vand [10] to separate the right integral into two factors. The notation follows [11]. Vand also introduced the term "tempering" for experiments with a constant heating rate, in contrast to isothermal treatment, which he called ageing.

The first term, the tempering function, expresses the main temperature-dependence

$$S(T; E, K/q) \equiv \frac{KkT^2}{qE} \cdot e^{-E/kT}. \quad (3)$$

The second term is then a dimensionless correction factor of the order unity

$$\eta(y) \equiv 1 - R(y) \equiv 1 - \sum_{n=1}^{n'} (-1)^{n+1} (n+1)! y^n; \quad (4)$$

it universally depends only on the small quotient  $y \equiv \frac{kT}{E} \ll 1$ , and for real processes

$y$  is smaller than 0.1. Sometimes it would be convenient to show that  $\eta \simeq 1$  and then  $(1 - R)$  is written instead of  $\eta$ ; it holds that  $y < R \leq \eta \leq 1$ . The values on  $\eta$  as a function of  $y$  are demonstrated in Fig. 1. The representation by the product  $S \cdot \eta$  in Eq. (2) is the exact solution of Eq. (1), to which every other approximation should be compared.  $S \cdot \eta$  equals  $\frac{KE}{qk} \cdot p\left(\frac{E}{kT}\right)$ , where  $p(x)$  is the form

for the description of the integral in (2), proposed and tabulated by Doyle [5]. The precision, and problems of convergency and semiconvergency of the series for  $R(y)$  in Eq. (4) are well described in [4, 7, 8]. To obtain the highest precision, the upper limit is to be taken as  $n' = \left(\frac{1}{y} - 2\right)$ ; however, for small  $y$  the series converges quickly and the numerical value of  $n$  or  $R$  within an accuracy of some, for instance six digits, is reached earlier, with only very few terms of the sum.

It may be mentioned that, by applying the same necessary criterion as in [1], one of course gets the accurate identity:

$$\frac{dF}{dT} = \frac{1}{f} \cdot \frac{d\alpha}{dT} = \frac{d(S \cdot \eta)}{dT} = \frac{K}{q} e^{-E/kT} = \frac{SE}{kT^2} \tag{5}$$

(see Appendix).

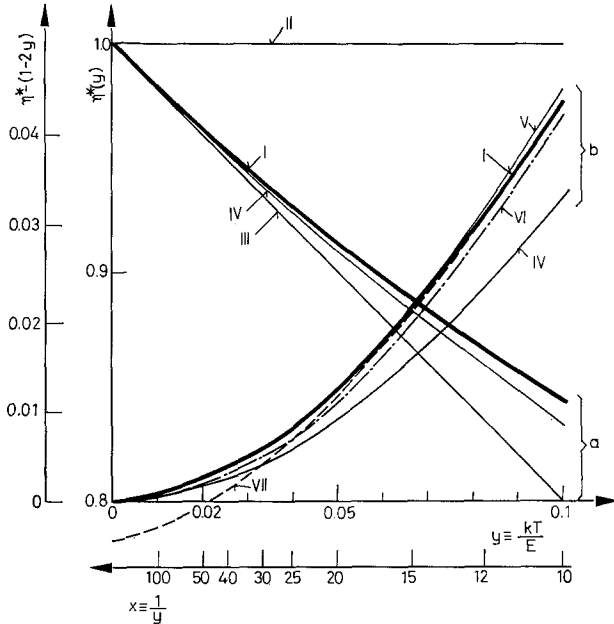


Fig. 1. a:  $\eta$  (curve I) and different approximations  $\eta^*$  as a function of  $y = kT/E$  (left-hand scale), b: the best approximations are shown as differences against variant III:  $\eta^* - (1 - 2y)$  (enlarged left scale), II:  $\eta^* = 1$ ; III:  $\eta^* = 1 - 2y$ ; IV:  $\eta^* = \frac{1}{1 + 2y}$ ; V:  $\eta^* = \frac{1}{\sqrt{1 + 4y}}$ ; VI and VII: see text

*Effects due to a wrong choice of  $\eta(y)$*

If one compares approximations used by various authors for the integral in the solution (2), one can see that they differ just in the estimation of the dimensionless factor  $\eta$ . Some authors restricted this to the first term in the series  $R(y)$ , or neglected this sum; others found effective approximations by polynomials [2, 12]. Not all related papers revealed a search for an explicit analytical expression, but there is no doubt that the main temperature-dependence of the tempering function is of the form  $S(T) \approx y^2 e^{-1/y}$ , and the same holds for  $p(1/y)/\eta(y) = S$ .

Therefore we will simply test wrong values of  $\eta^*(y)$  and look for the influence of this choice on the behaviour of  $S \cdot \eta^* = F^*(\alpha)$  and correlated values. In Table 1 the analytical forms of some such often-used  $\eta^*(y)$  are given. The corresponding absolute and relative errors can be compared; the second column in Table 1 shows the value

$$\frac{\Delta F}{F} = \frac{S(\eta^* - \eta)}{S \cdot \eta} = \frac{\eta^*}{\eta} - 1. \quad (6)$$

Further, one has to compare the influence on the first derivative as an analogue to Eq. (5)

$$\frac{d(S \cdot \eta^*)}{dT} = \frac{dS}{dT}\eta^* + S \frac{d\eta^*}{dT} = \frac{d(S \cdot \eta)}{dT} [1 + \Delta(\eta^*)]. \quad (7)$$

Here

$$\Delta[\eta^*(y)] \equiv \eta^* - 1 + 2y\eta^* + y^2 \frac{d\eta^*}{dy} \quad (8)$$

describes the deviation due to a wrong choice of  $\eta^*$  (see third column in Table 1).

In [11, 12] a method was proposed which permits the direct determination of the activation energy from experimentally observed reactions; there is no longer a demand for trial and error curve fittings as in the method of Doyle [5]. In this method a graph  $\ln F(\alpha) = \ln(S \cdot \eta)$  vs.  $1/kT$  is to be calculated; this is a straight line and its slope is governed by the activation energy  $E$ . The method has the advantages that it makes use of the whole available information  $\alpha(T)$  on the process, and that only a single heating run and one sample are needed. The same procedure is valid with a slight variation for a single isochronal annealing curve [13]. Accordingly, let us consider the following expression for the slope

$$\frac{d \ln(S \cdot \eta)}{d(1/kT)} = - \frac{kT^2}{S \cdot \eta} \cdot \frac{d(S \cdot \eta)}{dT} = - \frac{E}{\eta} \quad (9)$$

and correspondingly

$$\frac{d \ln(S \cdot \eta^*)}{d(1/kT)} = - E \left[ 1 + 2y + \frac{y^2}{\eta^*} \cdot \frac{d\eta^*}{dy} \right]. \quad (10)$$

As one can see for the slope factor in the fourth column of Table 1 for all the seconded variants of  $\eta^*$ , including the true  $\eta$ , there always appears a first correction term  $+2y$  (which can easily be taken into account) and only the higher correction terms of the order  $y^2$  (only variant II),  $y^3$  (variant III) or  $y^4$  (variants IV, V), differ slightly for the chosen variants of  $\eta^*$ . In the crude variant II, where any dependence of  $\eta$  on  $y$  is neglected, one finds that the temperature-dependence of the integral is mainly contained in  $S$ .

Table 1  
Different approximations for the function  $\eta^*(y)$ , and their behaviours

Variants for $\eta^*(y)$	Error $\frac{\eta^* - 1}{\eta}$	Deviation $\Delta(\eta^*) = \eta^* - 1 + 2y\eta^* + y^2 \frac{d\eta^*}{dy}$	Slope factor $\frac{-d \ln F}{E \cdot d(1/kT)} = y^2 \cdot \frac{d\eta^*}{dy} \cdot \frac{1}{\eta^*}$
I. $1 - R = 1 - \sum_{i=1}^{n'} \frac{(-1)^{i+1} (n+1)! y^n}{1 - 2y + 6y^2 - 24y^3 + \dots}$	0	0	$\frac{1}{1-R} = 1 + 2y - \frac{2y^2}{1-R} + \frac{12y^3}{1-R} - \dots$ $= 1 + 2y - 2y^2 + 8y^3 - 40y^4 + \dots$
II. 1	$\frac{R(y)}{1-R}$	$2y$	$1 + 2y$
III. $1 - 2y$	$-\frac{6y^2}{1-R}$	$-6y^2$	$\frac{2y^2}{1-2y} = -1 + 2y - 2y^2 - 4y^3 - 8y^4 - \dots$
IV. $\frac{1}{1+2y} = [1]$	$-\frac{2y^2}{1-R}$	$-\frac{2y^2}{(1+2y)^2}$	$\frac{2y^2}{(1+2y)^2} = 1 + 2y - 2y^2 + 8y^3 - 24y^4 + \dots$
V. $\frac{1}{\sqrt{1+4y}} = 1 - 2y + 6y^2 - 20y^3 + \dots$	$+\frac{4y^3}{1-R}$	$\frac{4y^3}{(1+4y)^{3/2}} \left(1 - \frac{3y}{2} + 3y^2 \dots\right)$	$\frac{2y^2}{1+4y} = 1 + 2y - 2y^2 + 8y^3 - 32y^4 + \dots$

Besides the approximations in an analytically simple form, mention should be made of two approximations with a more complex polynomial approach:

$$\text{Variant VI [2]} \quad \eta^* = \frac{1}{\left(1 - \frac{16y^3}{84y^2 - 4y + 1}\right)(1 + 2y)}$$

$$\text{Variant VII [14, 15]} \quad \eta^* = \frac{0.995924 + 1.430913y}{1 + 3.330657y + 1.681534y^2}$$

Their behaviour is also illustrated in Fig. 1 and can be compared there.

### Discussion

As was suggested at the beginning of this paper, the knowledge of the exact solution for the integral  $\int_0^T e^{-E/kT'} dT'$ , and the separation of this solution into a product  $S \cdot \eta$  and the series  $\eta(y)$ , help in yielding a better approach than those used before. The first three terms in the sum for  $\eta(y)$  are automatically covered by variant V, and therefore this variant is closer to the true solution than variant IV, where the third term in  $y^2$  is only partially taken into account, or variant III, which considers only the second term.

Variant V also approaches more closely the behaviour of the true factor  $\eta(y)$ , when the initial kinetic equation is to be restored by differentiation (Eqs 7 and 8), or when the slope factor for the determination of the activation energy is examined (Eq. 10). The numerical coincidence of variant V with the true value is better than 0.1% for  $y < 0.083$ , and better than 0.05% for  $y < 0.064$ . With regard to the accuracy of experimental data, the theoretical estimation should now be made more accurate.

Variant VI is a further improvement on IV; the relative error over a wide region  $y = 0.03 - 0.1$  is small, but nevertheless of the order 0.1 - 0.2%, and it distorts the slope of  $\eta$ ; for  $y > 0.06$  this variant rises faster than  $\eta$ .

Variant VII is a very good approximation in both numerical value and slope for high values of the argument  $y$ . It fails for small  $y$ , and gives a greater error than the preferential variant V for  $y < 0.075$ .

Usually it is not the integral or  $S \cdot \eta$  which is necessary immediately. For the determination of activation energy values the derivatives (Eqs 9 and 10) are used. Effectively, a value  $\tilde{E} = E/\eta$  is obtained. Because  $\eta$  varies only very slowly with  $E$ , one can get a first estimation both for  $\tilde{y} = k\bar{T}/E$  and for  $\tilde{\eta}(\tilde{y})$ , and then one finds the real activation energy  $E = \tilde{E} \cdot \tilde{\eta}$  or  $E = \tilde{E} - 2k\bar{T} + \dots$  (Here  $\bar{T}$  means the temperature at maximum process velocity.)

There is another favourable possibility for the term  $2y$  in the slope factor to vanish; this term is due to the factor  $T^2$  in the tempering function  $S$ . If all experimental data  $F(\alpha)$  are converted to  $F(\alpha)/T^2$ , one obtains instead of Eqs (9) and (10)

$$\frac{d \ln (F(x)/T^2)}{d(1/kT)} = -E \left[ 1 + \frac{y^2}{\eta} \cdot \frac{d\eta}{dy} \right] = -E[1 - 2y^2 + 8y^3 - + \dots], \quad (11)$$

so that nearly the true value  $E$  can be obtained in the first step.

Lastly there remains a question of principle: Who needs an approximation to the integral, if its exact solution is well known? The reaction runs as the solution describes it. Any attempt to recalculate such processes or to evaluate characteristic process parameters with the help of approximated solutions retains systematic errors, maybe of low values if a good improvisation is employed, but why not use the correct dependence? Perhaps an approximated solution can be more obvious and easier to handle. Then variants VI and VII are too clumsy, and still again the best variant seems to be

$$\frac{K}{q} \int_0^T e^{-E/kT'} dT' = S \frac{1}{\sqrt{1 + 4kT/E}} \quad (12)$$

or

$$\int_0^y e^{-1/y'} dy' = \frac{y^2}{e^{1/y}} \cdot \frac{1}{\sqrt{1 + 4y}}. \quad (13)$$

### Appendix

For the tempering function  $S/T$ ;  $E$ ,  $K(q)$ , defined by Eq. (3), the following derivatives are valid:

$$\frac{dS}{dT} = \frac{S}{kT^2} (E + 2kT) = \frac{SE}{kT^2} (1 + 2y) \quad (A1)$$

$$\frac{d(S \cdot \eta)}{dT} = \frac{SE}{kT^2} \quad (A2)$$

$$\frac{d^2(S \cdot \eta)}{dT^2} = \frac{SE^2}{k^2T^4} \quad (A3)$$

Only the proof for (A2) will be given here;  $\eta(y)$  as defined in (4):

$$\begin{aligned} \frac{d(S \cdot \eta)}{dT} &= \frac{dS}{dT} \cdot \eta + S \frac{d\eta}{dT} = \\ &= \frac{SE}{kT^2} \cdot \left[ (1 + 2y) \cdot (1 - R) - y^2 \cdot \frac{dR}{dy} \right] \\ &= \frac{SE}{kT^2} \cdot \left[ 1 + 2y - \sum_1 (-1)^{n+1} (n + 1)! y^n - \right. \end{aligned}$$

$$- \sum_1 (-1)^{n+1} (n+1)! \cdot n \cdot y^{n+1} - 2 \sum_1 (-1)^{n+1} (n+1)! y^{n+1} \Big].$$

Now in the brackets the term  $2y$  vanishes with the first term in the first sum; the second and the third sums can be added

$$= \frac{SE}{kT^2} \left[ 1 - \sum_2 (-1)^{n+1} (n+1)! y^n - \sum_1 (-1)^{n+1} (n+2)! y^{n+1} \right].$$

If the last sum is reordered with  $n' = n + 1$ , it is obvious that the two sums cancel each other and hence

$$\frac{d(S \cdot \eta)}{dT} = \frac{SE}{kT^2}.$$

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RÉSUMÉ — En cinétique non-isotherme l'intégration de l'exponentielle peut être représentée sous la forme analytique suivante:

$$\int_0^T e^{-E/kT'} dT' = \frac{kT^2/E}{\sqrt{1 + 4kT/E}} e^{-E/kT},$$

Dans le cas où  $kT/E \ll 1$ , cette représentation est plus exacte que les deux autres récemment proposées dans ce périodique [1, 2]. On compare quelques variantes de forme approchée en vue d'évaluer les erreurs dues à la méthode d'approximation, qui se manifestent lors de l'évaluation des énergies d'activation à partir des courbes cinétiques non-isothermes obtenues expérimentalement.



ZUSAMMENFASSUNG — Das in kinetischen Gleichungen für Temperrn mit konstanter Heizrate auftretende Integral kann in der folgenden analytischen Form dargestellt werden

$$\int_0^T e^{-E/kT'} dT' = \frac{kT^2/E}{\sqrt{1 + 4kT/E}} e^{-E/kT},$$

die um eine Größenordnung inbezug auf  $kT/E \ll 1$  genauer ist, als zwei andere Darstellungen, die vor kurzem in dieser Zeitschrift vorgeschlagen wurden [1, 2]. Mehrere Varianten für die genäherte Darstellung des obengenannten Integrales werden verglichen hinsichtlich der durch die Art der Approximation bedingten Fehlerfortpflanzung bei der Bestimmung der Aktivierungsenergie aus experimentellen nichtisothermen kinetischen Kurven.

Резюме — Интеграл, встречающийся в неизотермических кинетических уравнениях может быть аппроксимирован в следующем аналитическом виде

$$\int_0^T e^{-E/kT'} dT' = \frac{kT^2/E}{\sqrt{1 + 4kT/E}} e^{-E/kT},$$

причем эта аппроксимация на один порядок относительно  $kT/E \ll 1$  более точно, чем два приближенных представления, предложенные недавно в этом журнале [1, 2]. Сравниваются несколько вариантов приближенного представления вышеуказанного интеграла и погрешности, вносимые приближениями, при определении энергии активации из экспериментальных неизотермических кинетических кривых.