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THE EFFECTS OF IMPERFECT TEMPERATURE PROGRAMMING ON THE KINETIC EVALUATION OF THERMOANALYTICAL CURVES. PART 1. A SIMPLE MATHEMATICAL EXAMPLE

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ABSTRACT

In thermal analysis, the actual temperature inside the sample usually differs from the prescribed temperature. This fact may influence the evaluation of the kinetic parameters. In this paper the effects of slightly curved actual temperature–time functions are studied. It is shown that an alteration of about 5 K from the prescribed linear temperature program and its neglect in the kinetic evaluation can change the formal reaction order and the apparent activation energy by about 20%.

NOTATION

a	heating rate
A	pre-exponential factor
c and C	constants
E	activation energy (molar)
n	formal reaction order
r	a shape index characterizing the peak asymmetry
R	gas constant
t	time
T	temperature
u and v	parameters of a hyperbolic temperature program
x	reacted mole fraction
$\langle\ \rangle$	indicates averages

Subscripted symbols

C_1 and C_2	constants of eqn. (9)
T_1, T_2 and $\bar{T}$	two arbitrarily chosen temperatures and their arithmetic mean, respectively
T_i, T_f and T_m	the initial and final temperatures of a reaction and their arithmetic mean, respectively
T_{LIN} and T_{HYP}	temperatures of linear and hyperbolic temperature programs, respectively
x_p	reacted mole fraction at the peak maximum

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Functions

$f(x)$	describes the dependence of dx/dt on x
$g(x)$	the integral of $1/f(x)$
g^{-1}	the inverse function of $g(x)$

INTRODUCTION

The mathematical model most frequently used for the kinetic description of thermoanalytical curves is

$$dx/dt = A\ e^{-E/RT} f(x) \tag{1}$$

where x is the reacted mole fraction and $f(x)$ is a continuous function with positive values in the interval $0 < x < 1$. When $f(x)$ is a decreasing function, it is usually approximated by the formula

$$f(x) = (1-x)^n \tag{2}$$

where n is the formal reaction order.

The evaluation of the unknown parameters of eqn. (1) is greatly influenced by the various types of experimental errors. According to experience, it is relatively easy to fight against the effects of random errors by carefully collecting, handling and processing the experimental data. A more serious problem may be caused, however, by the systematic experimental errors. In thermal analysis, a frequent error of this type is the systematic alteration of the actual sample temperature from the values prescribed by the temperature program. We shall examine in this paper how an unwanted

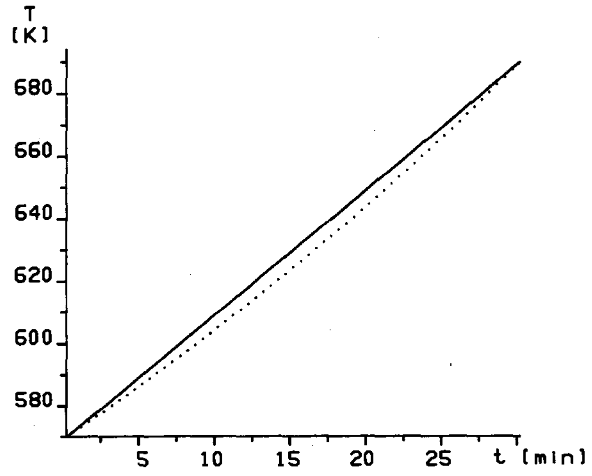

Fig. 1. A hyperbolic temperature program modelling a thermal lag in the domain of a first order reaction with $E = 160$ kJ mole^{-1} and $A = 10^{12}$ s^{-1}.

curvature of the actual $T(t)$ function changes the width and shape of the thermoanalytical curves and the values of the estimated kinetic parameters. The treatment will be restricted to a mathematically simple special case where it is easy to deduce explicitly the effects of the curvature of the actual temperature function in the evaluation of the kinetic parameters. Of course, the examination of a particular case cannot lead to complete and general solutions, but it can be shown in this way, step by step, how a relatively small alteration can lead to significant errors in the kinetic parameters. The general case of the imperfect temperature programming will be discussed later [1].

The considerations to be outlined may be useful in the judgement of the reliability of the published kinetic data and may help in deciding whether the evaluation methods deduced for strictly linear temperature functions are suitable for the evaluation of particular data.

A SIMPLIFIED MODEL TO STUDY THE EFFECTS OF CURVED TEMPERATURE PROGRAMS

Rearrangement and integration of eqn. (1) give

$$g(x) = \int A\, e^{-E/RT}\, dt \qquad (3)$$

where $g(x)$ is the integral of $1/f(x)$. From a mathematical point of view, the simplest $T(t)$ function is the hyperbola, since in this case a differential of t is proportional to $d(1/T)$ and the integration on the right-hand side can be carried out immediately [2]. Thus the simplest way of studying the effects of the curvature of the temperature programs is to assume that the planned

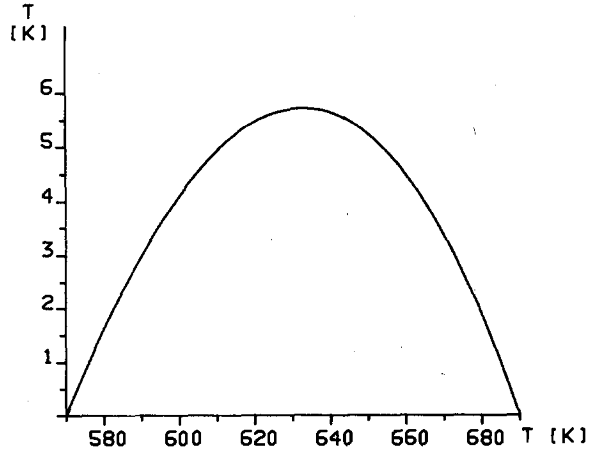

Fig. 2. The difference between the linear and hyperbolic temperature programs shown in Fig. 1.

$T(t)$ is linear and the actual $T(t)$ can be approximated by a hyperbolic function in the range of the reaction being examined. In mathematical form

$$T_{\mathrm{ACT}} \cong T_{\mathrm{HYP}} = \frac{1}{u - vt} \qquad (T_{\mathrm{i}} \leqslant T \leqslant T_{\mathrm{f}}) \tag{4}$$

where T_{ACT} is the actual temperature, T_{HYP} is a hyperbolic $T(t)$, u and v are parameters, and T_{i} and T_{f} are the initial and final points of the temperature interval considered.

Figure 1 shows an example when a hyperbolic $T(t)$ models a thermal lag. The thermal lag itself is shown in Fig. 2. Figure 3 shows an example when a hyperbolic $T(t)$ is lagging at the beginning of the reaction interval and precedes the prescribed linear $T(t)$ at the end of the reaction interval. The domain of these figures corresponds to the reaction interval of a first order reaction with parameters $E = 160$ kJ mole^{-1} and $A = 10^{12}$ s^{-1} at a heating rate of 4 K min^{-1}.

These figures can be regarded as typical examples. Let (t_1, T_1) and (t_2, T_2) stand for the points of interception of a linear and a hyperbolic $T(t)$. (If a hyperbolic $T(t)$ does not intercept the prescribed linear $T(t)$ at two points, it is not suitable to model an erroneous actual temperature function.) It can be shown (see the Appendix) that the difference in a linear and a hyperbolic $T(t)$ between the points of interception is always similar to that in Fig. 2 since it is always a convex function of t with a maximum slightly right of the middle point of interval $[t_1, t_2]$. The magnitude of this maximum is given by

$$\max(T_{\mathrm{LIN}} - T_{\mathrm{HYP}}) \cong (T_2 - T_1)^2/4\bar{T} \tag{5}$$

where T_1, T_2 and $\bar{T}$ are the temperatures of the points of interceptions and their arithmetic mean, respectively (the deduction can be found in the

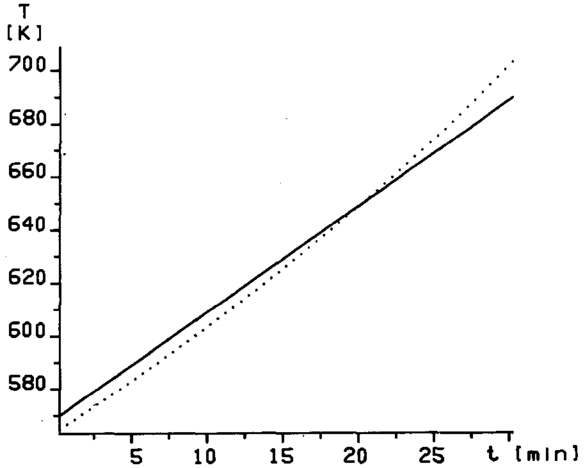

Fig. 3. A hyperbolic temperature program modelling a systematic alteration from a linear temperature program.

Appendix). Equation (5) serves only for illustration. It can help to calculate, for example, that a thermal lag of 5 K corresponds to a domain of $T_2 - T_1 = 90$ K around 400 K and to $T_2 - T_1 = 155$ K around 1200 K. It may be worth noting that a domain of $T_f - T_i = 90$ K corresponds to a first order reaction of $E = 80$ kJ mole^{-1} around 400 K while a domain of $T_f - T_i = 155$ K belongs to $E = 420$ kJ mole^{-1} around 1200 K. [These activation energies were calculated by eqn. (13).]

EVALUATION OF (x, T) DATA

Considering first the simplest case, we shall examine in this section what errors arise in the estimation of the kinetic parameters if $T(t) = T_{\mathrm{HYP}}(t)$ and a set of (x, T) data is evaluated by mathematical formulae deduced for linear $T(t)$ functions. This example models those cases of the kinetic evaluation when the actual temperature of the sample is measured and recorded with an acceptable precision and the only error of the evaluation is the use of inappropriate mathematical equations. (The cases when the prescribed values of T are used instead of the actual ones will be examined in the next section.)

Equation (4) shows that $\mathrm{d}(1/T) = -v\,\mathrm{d}t$ at hyperbolic heating programs and, as pointed out by Zsakó [2], integration of eqn. (3) immediately yields

$$\mathrm{g}(x) = \frac{AR}{vE}\,\mathrm{e}^{-E/RT} \equiv \exp\left(\ln \frac{AR}{vE} - E/RT\right) \tag{6}$$

Denoting the inverse function of $\mathrm{g}(x)$ by g^{-1}, x can be expressed as a function of temperature

$$x = \mathrm{g}^{-1}\left[\exp\left(\ln \frac{AR}{vE} - E/RT\right)\right] \tag{7}$$

At linear temperature programs, the Coats–Redfern approximation [3] can be used. Its general form is

$$\ln \mathrm{g}(x)/T^2 \cong c_1 - c_2/T \tag{8}$$

where c_1 and c_2 are constants. It can be shown [4] that

(i) the relative precision of eqn. (8) is about 10^{-4} at the usual values of E/RT;

(ii) c_2 is approximately equal to E/R within an error of 0.5%;

(iii) c_1 is approximately equal to $\ln AR/aE$ within an error of 3%.

Equation (8) can be transformed into a more suitable form if its left-hand side is written as $\ln \mathrm{g}(x) + 2 \ln (1/T)$ and $\ln (1/T)$ is approximated by a linear function of $1/T$. In this way the well-known approximation is obtained

$$\ln \mathrm{g}(x) \cong C_1 - C_2/T \tag{9}$$

where C_1 and C_2 are constants.

Several methods of deduction can lead to approximations of this type. We prefer the deduction from the more precise eqn. (8) for two reasons:

(i) the errors of eqn. (8) can be directly deduced from reliable Padé approximations and in this way it can be shown [4] that the error of eqn. (9) consists almost entirely of the error of the linearization of the term $2 \ln 1/T$ and, at usual reaction intervals, the relative precision of eqn. (9) is in the order of 10^{-3};

(ii) the connection between the constant C_2 and the parameter E can be given by a mathematically simple formula. If $2 \ln (1/T)$ is developed into a Taylor series around the middle point of the temperature interval, T_m, then the following approximation can be obtained

$$C_2 \cong E/R + 2T_m = (E + 2RT_m)/R \tag{10}$$

In a similar way it can be shown that C_1 is approximately equal to $\ln(AR/aE + 2 \ln T_m$.

From eqn. (9) x can be expressed in the form

$$x \cong g^{-1}[\exp(C_1 - C_2/T)] \tag{11}$$

Note that from a mathematical point of view, the right-hand sides of eqns. (7) and (11) are identical, the only difference between them is the physical interpretation of the constants. Thus data (x, T) of a hyperbolic $T(t)$ can be described by equations deduced for linear $T(t)$, but in this case the obtained values of E and $\log A$ will differ systematically from the true values. The difference between the true and the obtained value of E, as can be read from eqn. (10), is about $-2RT_m$. [If eqn. (11) is used instead of eqn. (7), the coefficients of $1/T$ are interpreted as $(E + 2RT_m)/R$ instead of E/R.] In the case of Figs. 1 and 3 the error of E would be about -10 kJ mole^{-1} which corresponds to -6% at $E = 160$ kJ mole^{-1}. Since the mean temperature of the reaction is correlated with E, an error of $-2RT_m$ usually represents a relative error of roughly the same magnitude. For example, if we assume that $20 \leqslant E/RT \leqslant 50$, then $-2RT_m$ represents a relative error between -10 and -4%.

Finally a few remarks will follow about the geometric interpretation of eqns. (7) and (11). If data x are plotted vs. $1/T$, C_1 and C_2 can be interpreted as scale factors defining the position and width of the curve. Regarding the width of the curves on the plots x vs. $1/T$, it is entirely defined by the value of C_2. Let us choose, for example, two arbitrary values of x, say x_1 and x_2, and denote the corresponding temperatures by T_1 and T_2. Now we can write

$$1/T_1 - 1/T_2 \cong [\ln g(x_2) - \ln g(x_1)] R/(E + 2RT_m) \tag{12}$$

if $T(t) = T_{LIN}$ and

$$1/T_1 - 1/T_2 = [\ln g(x_2) - \ln g(x_1)] R/E \tag{13}$$

if $T(t) = T_{HYP}$. A comparison of these equations shows that the x vs. $1/T$ curves are sharper at $T(t) = T_{LIN}$ than at $T(t) = T_{HYP}$. It will be shown later

[1] that any concave curvature of the temperature program widens the curves on the x vs. $1/T$ diagrams and in this way diminishes the apparent activation energy.

ESTIMATION OF THE KINETIC PARAMETERS WITHOUT KNOWLEDGE OF THE ACTUAL TEMPERATURE

In the previous section, the actual temperature of the sample was supposed to be available. In the present section, we shall deal with those cases when the prescribed temperature values are used instead of the actual ones. In other words: it will be supposed here that the measured x or $\mathrm{d}x/\mathrm{d}t$ data are evaluated with such temperature data which have been calculated from the equation

$$T = T_0 + at$$

where a is the heating rate and T_0 is the starting point of the prescribed temperature program. From a mathematical point of view, it means that the measured x or $\mathrm{d}x/\mathrm{d}t$ data are related to time instead of temperature and are evaluated by the assumption of such theoretical $x(t)$ or $\mathrm{d}x/\mathrm{d}t(t)$ functions which have been deduced for linear temperature programs.

First, let us study the estimation of E at a given $\mathrm{f}(x)$ function. As has been pointed out, E is strongly connected with the average width of curves $x(1/T)$, and as has been illustrated by eqns. (12) and (13), the curvature of the temperature program actually changes this average width. The use of the prescribed temperature data instead of the real sample temperature changes virtually the width of curves $x(1/T)$. The resultant error is obviously the sum of these actual and virtual changes.

In the following, we shall briefly examine how the average width of curves $x(1/T)$ are changed by the use of erroneous temperature values in the calculations. The average width can be formed by choosing several points (x_1, T_1) and (x_2, T_2) and calculating either the arithmetic mean or some weighed average of differences $1/T_1 - 1/T_2$. (If weight factors are used, they have to be deduced by statistical considerations.) Denoting the averages by angle brackets, eqn. (12) immediately yields

$$\langle 1/T_1 - 1/T_2 \rangle = \langle \ln \mathrm{g}(x_2) - \ln \mathrm{g}(x_1) \rangle R/(E + 2RT_\mathrm{m}) \qquad (14)$$

Using the Taylor series, for the relative error of $\langle 1/T_1 - 1/T_2 \rangle$

$$\frac{\delta\langle 1/T_1 - 1/T_2 \rangle}{\langle 1/T_1 - 1/T_2 \rangle} \approx \frac{\delta\langle T_2 - T_1 \rangle}{\langle T_2 - T_1 \rangle} = \frac{\langle \delta T_2 \rangle - \langle \delta T_1 \rangle}{\langle T_2 - T_1 \rangle} \qquad (15)$$

Here $\langle \delta T_1 \rangle$ and $\langle \delta T_2 \rangle$ are the average errors of T_1 and T_2, respectively. In the case of thermal lags, e.g., in Fig. 1, $\langle \delta T_1 \rangle$ and $\langle \delta T_2 \rangle$ have the same sign, thus they partially compensate each other. In other cases, however, eqn. (15) may give a considerable value. Regarding Fig. 3, for example, $\langle \delta T_1 \rangle$ is about

-1 and -2 K while $\langle \delta T_2 \rangle$ is around $+2$ and $+3$ K, depending on the way of averaging. These values lead to a relative error of E in the magnitude of -5 and -10%. Now let us study those cases when function $f(x)$ contains an unknown, adjustable parameter. Continuing with the example treated in the previous section, it will be supposed that the temperature of the sample is a hyperbolic function of t while the prescribed temperature is linear. Putting a hyperbolic $T(t)$ into eqn. (7) and $T = T_0 + at$ into eqn. (11), it is seen that, contrary to the case of functions $x(T)$, the $x(t)$ functions have different forms at hyperbolic and linear heating programs. Consequently, erroneous $f(x)$ functions may give a better fit than the true ones. If $f(x)$ contains an unknown parameter, then the evaluation by the prescribed temperature values may result in an error of this parameter. Since the estimators of the energy of activation depend on $f(x)$ [see, e.g., eqn. (12)], an extra error term may be added to E in this way. In the following parts of this section, the estimation of the formal reaction order, n, will be discussed as an example.

The formal reaction order is strongly correlated to the degree of asymmetry of curves $x(t)$ or $\mathrm{d}x(t)/\mathrm{d}t$ [5–11]. The degree of asymmetry can be characterized in an endless number of ways. We shall use Balarin's characterization [7]: the degree of asymmetry will be characterized by the ratio of the amounts of sample reacted after the peak maximum and before the peak maximum. This ratio will be denoted by r. The mathematical form of this definition can be written in the form $r = (1 - x_\mathrm{p})/x_\mathrm{p}$, where x_p is the reacted mole fraction at the peak maximum. Accurate formulae for the calculation of x_p are available at linear temperature programs [8–10] as well as at hyperbolic temperature programs [9,11]. Using these formulae, we have calculated the values of r at linear and hyperbolic temperature programs.

At a hyperbolic $T(t)$, r is a function of only n while at a linear $T(t)$ it depends slightly on the value of E/RT_p, too, where T_p is the temperature of the peak maximum. In the present calculations a medium value of E/RT_p, 30, was supposed. The values of r are shown in Table 1. The data corresponding to the linear and hyperbolic temperature programs are denoted by r_LIN and r_HYP, respectively. At low values of n, there are no significant differences between the values of r_LIN and r_HYP. This is not surprising, since r_LIN and r_HYP are continuous functions of n and any rising temperature program has to lead to $r = 0$ at $n = 0$. At higher values of n, however, especially above $n = 1$, there are significant differences. Between $n = 1$ and $n = 2$, for example, a value of $r_\mathrm{HYP}(n)$ is roughly equal to a value of $r_\mathrm{LIN}(n - 0.25)$. Thus if a data set (x, t) or $(\mathrm{d}x/\mathrm{d}t, t)$ which belongs to a hyperbolic $T(t)$ is evaluated by the assumption of a linear $T(t)$, then the erroneous interpretation of the degree of asymmetry leads to an error of $\delta n \approx -0.25$ in this range. The errors of n also affect the evaluation of E. As can be shown [10], an error of $\delta n \approx -0.25$ decreases E by about 8%. (Note that this error has the same sign as the error treated in the previous section.) Since n is only a formal reaction order, it may also have values higher than 2.

TABLE 1

Values of a shape index at linear and hyperbolic heating programs

n	r_{LIN}	r_{HYP}
0	0	0
0.25	0.20	0.19
0.50	0.36	0.33
0.75	0.51	0.46
1.00	0.64	0.58
1.25	0.77	0.69
1.50	0.89	0.80
1.75	1.01	0.90
2.00	1.13	1.00
2.25	1.24	1.10
2.50	1.36	1.19
2.75	1.47	1.28
3.00	1.57	1.37

Above $n = 2$, the error of n (and in this way, also the error of E) is considerably higher. At $n = 3$, for example, the error of n would be about -0.5 which would add an error term of -16% to E.

CONCLUSIONS

Three types of errors have been treated. It may be worth noting that these errors may cumulate in the evaluation of the activation energy. The cumulation of the errors depends only slightly on the method of evaluation, since any useful evaluation method should give a good fit for such fundamental properties of the experimental data as the peak asymmetry of curves $dx(t)/dt$ or the average width of curves x vs. $1/T$. The cumulation of the errors can lead to a decrease of E by as much as 20% if the formal reaction order is between 1 and 2 and it can lead to a higher decrease if n is higher than 2. It will be shown in a subsequent paper [1] that the hyperbolic temperature programs have no special features discriminating them from the other slightly curved $T(t)$ functions. Thus other temperature programs having the same magnitude of curvature may also lead to the same magnitude of errors. If a higher precision is required in the kinetic evaluation, then, obviously, a higher precision is required in the measurements, e.g., thermal lags of about 5 K are not permitted inside the samples. More details on this subject will be given in Parts 2 and 3 of this work.

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APPENDIX: PROPERTIES OF THE DIFFERENCE OF A LINEAR AND A HYPERBOLIC $T(t)$ FUNCTION

The place and the magnitude of the maximum of $(T_{\mathrm{LIN}} - T_{\mathrm{HYP}})$ will be deduced here.

Notation

Let (t_1, T_1) and (t_2, T_2) be the points of interception. [Only such $T_{\mathrm{LIN}}(t)$ and $T_{\mathrm{HYP}}(t)$ will be treated here, which intercept each other.] The value of t at $\max(T_{\mathrm{LIN}} - T_{\mathrm{HYP}})$ will be denoted by $t_{\max}$. $\bar{T}$ and ΔT will stand for the arithmetic mean and the difference of T_2 and T_1. To simplify the treatment t_1 will be chosen to be the null point of the time scale. Thus $T_{\mathrm{HYP}}(0) = T_1$ and $T_{\mathrm{HYP}}(t)$ will have the form

$$\frac{1}{T_{\mathrm{HYP}}} = \frac{1}{T_1} - vt \tag{A1}$$

Lemma

T_{HYP} is equal to $\sqrt{T_1 T_2}$ at the maximum of $T_{\mathrm{LIN}} - T_{\mathrm{HYP}}$.

Proof

Let us express v from eqn. $T_{\mathrm{HYP}}(t_2) = T_2$. Rearranging $1/T_2 = 1/T_1 - vt_2$, we get

$$v = (1/T_1 - 1/T_2)/t_2 \equiv (1/T_1 - 1/T_2)/(t_2 - t_1)$$

$$= \frac{T_2 - T_1}{t_2 - t_1} \frac{1}{T_1 T_2} = a/T_1 T_2 \tag{A2}$$

where a is the slope of the linear $T(t)$ drawn through points (t_1, T_1) and (t_2, T_2).

Differentiation of eqn. (A1) gives

$$\mathrm{d}T_{\mathrm{HYP}}/\mathrm{d}t = v\, T_{\mathrm{HYP}}^2 \tag{A3}$$

Equations (A2) and (A3) yield

$$\mathrm{d}(T_{\mathrm{LIN}} - T_{\mathrm{HYP}})/\mathrm{d}t = a - v\, T_{\mathrm{HYP}}^2 = a - a\, T_{\mathrm{HYP}}^2 / T_1 T_2 \tag{A4}$$

At $T_{\mathrm{HYP}} = \sqrt{T_1 T_2}$, the right-hand side vanishes. Since $\mathrm{d}^2(T_{\mathrm{LIN}} - T_{\mathrm{HYP}})/\mathrm{d}t^2 = -\mathrm{d}^2 T_{\mathrm{HYP}}/\mathrm{d}t^2 < 0$, there is a maximum at $T_{\mathrm{HYP}} = \sqrt{T_1 T_2}$.

Lemma

$$\max(T_{\mathrm{LIN}} - T_{\mathrm{HYP}}) = 2(\bar{T} - \sqrt{T_1 T_2}) \tag{A5}$$

Proof

Let us express $t_{\max}$ from the equation $T_{\mathrm{HYP}}(t_{\max}) = \sqrt{T_1 T_2}$

$$t_{\max} = (1/T_1 - 1/\sqrt{T_1 T_2})/v = (T_2 - \sqrt{T_1 T_2})/a \tag{A6}$$

Hence

$$\begin{aligned}\max(T_{\mathrm{LIN}} - T_{\mathrm{HYP}}) &= T_{\mathrm{LIN}}(t_{\max}) - \sqrt{T_1 T_2} = T_1 + T_2 - 2\sqrt{T_1 T_2} \\ &= 2(\bar{T} - \sqrt{T_1 T_2})\end{aligned} \tag{A7}$$

Statement

Equation (5), quoted at the beginning of this paper, is valid.

Proof

$$\begin{aligned}\sqrt{T_1 T_2} &\equiv \sqrt{\left(\bar{T} - \frac{1}{2}\,\Delta T\right)\left(\bar{T} + \frac{1}{2}\,\Delta T\right)} \equiv \sqrt{\bar{T}^2 - \left(\frac{1}{2}\,\Delta T\right)^2} \\ &\cong \bar{T} - (\Delta T)^2/8\bar{T}\end{aligned} \tag{A8}$$

If ΔT is comparable to a reaction interval, then $\bar{T}^2 \gg (\frac{1}{2}\,\Delta T)^2$. Thus the Taylor series used in the last transformation is a good approximation.

Substituting the right-hand side into eqn. (A5), we get

$$\max(T_{\mathrm{LIN}} - T_{\mathrm{HYP}}) \cong (\Delta T)^2/4\bar{T} \tag{A9}$$

Q.e.d.

Statement

$$0.5\, t_2 < t_{\max} < 0.55\, t_2 \tag{A10}$$

Proof

The combination of eqns. (A6) and (A8) gives

$$t_{\max} = \left[T_2 - \bar{T} + (\Delta T)^2/8\bar{T}\right]/a = 0.5\, t_2(1 + \Delta T/4\bar{T}) \tag{A11}$$

If ΔT is comparable to a reaction interval, $\Delta T/4\bar{T}$ is smaller than 0.1.