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AN APPROXIMATE SOLUTION OF THE ADIABATIC EXPLOSION PROBLEM

LOUIS C. SMITH
University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544 (U.S.A.)
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ABSTRACT

The accuracy of a simple, well-known approximation to the solution of the adiabatic explosion problem is examined, and it is shown that, with a minor modification, the approximation can be converted to a form accurate to 1% or better for a wide range of the input parameters. The final result lies well within the capabilities of even the simpler scientific calculators. The effects of depletion of the reactant and a temperature-dependent heat capacity, not included in the development, are briefly evaluated.

INTRODUCTION

The differential equation describing the time–temperature history of an isolated system in which a substance is undergoing an *m*th-order exothermal decomposition with an Arrhenius temperature dependence is

$$c\frac{d\theta}{d\tau} = Q(1-\lambda)^m Z e^{-E/R\theta} \tag{1}$$

where c, Q, Z, and E are the heat capacity, heat of reaction, pre-exponential factor, and activation energy, respectively, R is the gas constant, θ is the absolute temperature, τ is the time, and λ is the fraction of the substance decomposed (constant factors involving concentration units have been absorbed into Z). In the most general case, c, and possibly Q, will depend on temperature, while λ can be expressed as a function of temperature through the equation

$$\lambda = \int_{T_0}^{T} \frac{c}{Q}\, d\theta \tag{2}$$

On rearranging and integrating (1) we obtain

$$t = \int_{T_0}^{T} \frac{c e^{E/R\theta}}{QZ(1-\lambda)^m}\, d\theta \tag{3}$$

as the equation defining $T(t)$ given the initial condition $\theta = T_0$ at $t = 0$.

An exact, explicit form for the right-hand side of eqn (3) has not been obtained, but a number of approximate solutions, of varying degrees of accuracy and complexity, have been proposed[1]. For the special case c and Q constant and $m=0$, a convenient and useful approximation is

$$t \simeq \frac{cR}{ZQE}\left(T_0^2\, e^{E/RT_0} - T^2\, e^{E/RT}\right) \tag{4}$$

If only the explosion time (not the time–temperature history) is desired, then $T \gg T_0$ and eqn (4) reduces further to the familiar result

$$t = \frac{cRT_0^2\, e^{E/RT_0}}{ZQE} \tag{5}$$

In this paper we examine the accuracy of eqns (4) and (5) and show how, with a minor modification, they can be converted to forms of more than adequate accuracy for a wide range of the parameters E, T_0, and T.

THEORY

For c and Q constant and $m=0$ eqn (3) becomes

$$t = \frac{c}{QZ}\int_{T_0}^{T} e^{\alpha/\theta}\, d\theta \tag{6}$$

where $\alpha \equiv E/R$. A common way of obtaining eqn (4) from eqn (6) is to make the substitution $x=\alpha/\theta$. We then have

$$\int_{T_0}^{T} e^{\alpha/\theta}\, d\theta = \alpha \int_{x(T)}^{x(T_0)} \frac{e^x}{x^2}\, dx \tag{7}$$

In the integrand, the exponential is the dominant term, and hence we can write

$$\alpha \int_{x(T)}^{x(T_0)} \frac{e^x}{x^2}\, dx \simeq \frac{\alpha}{x^2}\int_{x(T)}^{x(T_0)} e^x\, dx \simeq \alpha \left[\frac{e^x}{x^2}\right]_{x(T)}^{x(T_0)} = \frac{1}{\alpha}\left(T_0^2\, e^{\alpha/T_0} - T^2\, e^{\alpha/T}\right) \equiv$$

$$\equiv F_1(\alpha, T_0, T) \tag{8}$$

The result given in eqn (8) can be derived in a more illuminating way by integrating the series expansion of the exponential. Since the series converges uniformly on any closed interval not containing 0, it can be integrated term by term to obtain the result

$$\int_{T_0}^{T} e^{\alpha/\theta}\, d\theta = \int_{T_0}^{T} \sum_{n=0}^{\infty} \frac{(\alpha/\theta)^n}{n!}\, d\theta = T - T_0 + \alpha \ln\frac{T}{T_0} + \sum_{n=1}^{\infty} \frac{\alpha^{n+1}}{n(n+1)!\, T_0^n} -$$

$$- \sum_{n=1}^{\infty} \frac{\alpha^{n+1}}{n(n+1)!\, T^n} \equiv F_2(\alpha, T_0, T) \tag{9}$$

The individual terms in the infinite series can be written

$$\frac{\alpha^{n+1}}{n(n+1)!\,T_0^n} = \frac{\alpha}{T_0}\,\frac{\alpha}{2T_0}\cdots\frac{\alpha}{nT_0}\,\frac{\alpha}{n(n+1)} \tag{10}$$

For values of α and T_0 of practical interest, $\alpha/T_0 > 1$. Thus the terms of the series increase with n until $\alpha/nT_0 \simeq 1$, after which they decrease monotonically. More precisely, if $a_{n'}$ is the largest term in the sum, then $a_{n'+1}/a_{n'} < 1$ and $a_{n'-1}/a_{n'} < 1$ jointly imply

$$|\alpha/T_0 - (n' + 2.5 + 2/n')| < 0.5 \tag{11}$$

Setting $n' = \alpha T_0 - 2.7$ will suffice for our purposes. For example, for $\alpha = 23000$ and $T_0 = 500$ K, $n' \cong 43$. This suggests that, with little error, we can write

$$\sum_{n=1}^{\infty} \frac{\alpha^{n+1}}{n(n+1)!\,T_0^n} \cong \sum_{n=1}^{\infty} \frac{\alpha^{n+1}}{(n+2)!\,T_0^n} = \frac{T_0^2}{\alpha}\left(\sum_{n=0}^{\infty} \frac{\alpha^n}{n!\,T_0^n} - 1 - \frac{\alpha}{T_0} - \frac{\alpha^2}{2T_0^2}\right) =$$

$$= \frac{T_0^2}{\alpha}\left[e^{\alpha/T_0} - 1 - \frac{\alpha}{T_0} - \frac{\alpha^2}{2T_0^2}\right] \tag{12}$$

Introducing this result, and the corresponding result for the series in T, in eqn (9) we obtain

$$\int_{T_0}^{T} e^{\alpha/\theta}\,d\theta \cong 2(T - T_0) + \frac{1}{\alpha}(T^2 - T_0^2) + \alpha \ln\frac{T}{T_0} + \frac{T_0^2}{\alpha}e^{\alpha/T_0} - \frac{T^2}{\alpha}e^{\alpha/T} \tag{13}$$

It is now in order to insert some typical values for α, T_0, and T in eqn (13) and examine the magnitudes of the various terms on the right-hand side of this equation. Thus, for $\alpha = 23000$, $T_0 = 500$ K, and $T = 510$ K, we have $2(T - T_0) = 20$, $(T^2 - T_0^2)/\alpha = 0.4$, $\alpha \ln T/T_0 = 455$, $(T_0^2/\alpha)e^{\alpha/T_0} = 1.032 \times 10^{21}$, and $(T^2/\alpha)e^{\alpha/T} = 4.36 \times 10^{20}$. It is thus clear that all but the last two terms can be discarded with negligible error, and we again have the result given in eqn (8). However, we are now in a position to estimate the error involved in using this approximation, for by far its largest contribution came from replacing $n(n+1)!$ by $(n+2)!$ to obtain the result given in eqn (12). Since the principal contributions to the sum come from terms near the maximum, it can be seen from the discussion in the preceding paragraph that the error is given approximately by $n'/(n'+2)$ where $n' = \alpha/T_0 - 2.7$; or, alternatively, the error from this source can largely be eliminated by using the more accurate equation*

$$\int_{T_0}^{T} e^{\alpha/\theta}\,d\theta \cong \frac{n'+2}{\alpha n'}\left(T_0^2 e^{\alpha/T_0} - T^2 e^{\alpha/T}\right) \equiv F_3(\alpha, T_0, T) \tag{14}$$

*The correction obviously undercorrects terms for which $n < n'$ and overcorrects terms for which $n > n'$, being most accurate for the largest terms in the sum. Little is gained by using a different value of n' for the term in T.

When T is sufficiently large in comparison with T_0, the last term in eqn (13) can also be omitted, and eqn (14) then becomes

$$\int_{T_0}^{T} e^{\alpha/\theta} \, d\theta \cong \frac{n'+2}{\alpha n'} T_0^2 \, e^{\alpha/T_0} \equiv F_4(\alpha, T_0) \tag{15}$$

In Table 1 the results given by eqns (8) and (14) are compared, in terms of percentage errors, with the results obtained by a numerical evaluation of the right-hand side of eqn (9) for selected values of α, T_0, and T covering the range of practical interest. The $T = 3000$ values also represent the percentage errors in explosion times as calculated from F_4 and the equivalent part of F_1. The errors in F_3 are negligible, while those in F_1 range as high as 18%.

TABLE 1
PERCENTAGE ERRORS OF F_1 AND F_3 FOR VARIOUS VALUES OF α, T_0, AND $T = T_0 + \Delta T$
(1) = $100\,(F_1 - F_2)/F_2$; (2) = $100\,(F_3 - F_2)/F_2$.

		T_0					
α	ΔT	400		600		800	
		(1)	(2)	(1)	(2)	(1)	(2)
10 000	1	−8.0	0.2	−12.0	0.6	−16.0	1.1
	10	−8.1	0.2	−12.1	0.5	−16.1	1.0
	100	−8.4	−0.1	−12.6	−0.1	−16.8	0.7
	T = 3000	−8.4	−0.2	−13.0	−0.5	−18.1	−1.4
20 000	1	−4.0	0.1	−6.0	0.1	−8.0	0.2
	10	−4.0	0.0	−6.0	0.1	−8.0	0.2
	100	−4.1	0.0	−6.2	−0.1	−8.3	−0.1
	T = 3000	−4.1	0.0	−6.2	−0.1	−8.4	−0.2
30 000	1	−2.7	0.0	−4.0	0.1	−5.3	0.1
	10	−2.7	0.0	−4.0	0.0	−5.4	0.1
	100	−2.7	0.0	−4.1	0.0	−5.5	0.0
	T = 3000	−2.7	0.0	−4.1	0.0	−5.5	−0.1

The question naturally arises as to whether some of the other approximations we have made introduce larger errors than those we have corrected. We have, for example, ignored depletion of the reactant, taking $m = 0$. If $m = 1$, with c and Q constant, eqn (3) becomes

$$t = \frac{c}{QZ} \int_{T_0}^{T} \frac{e^{\alpha/\theta}}{1-\lambda} \, d\theta \simeq \frac{c}{QZ} \int_{T_0}^{T} (1+\lambda) e^{\alpha/\theta} \, d\theta \tag{16}$$

Letting $t_1 = \frac{c}{QZ}\int_{T_0}^{T} e^{\alpha/\theta}\,d\theta$ and $t_\lambda = \frac{c}{QZ}\int_{T_0}^{T} \lambda e^{\alpha/\theta}\,d\theta$ we obtain, after some manipulation, with $\lambda = \frac{c}{Q}(\theta - T_0)$,

$$t = t_1 + t_\lambda = t_1 + \frac{c}{2Q}\left[\frac{c}{QZ}(T^2 e^{\alpha/T} - T_0^2 e^{\alpha/T_0}) + (\alpha - 2T_0)t_1\right] \tag{17}$$

from which the effect of depletion of reactant can be evaluated. For small α and large T_0 the effect can be large, with $t_\lambda \simeq 0.2t_1$. For the more usual values of α, however, the error caused by ignoring depletion is much smaller, typically a percent or so in t. Unfortunately, the depletion error and the error associated with the use of F_1 are in the same direction, so there is still merit in the use of F_3 rather than F_1.

For a temperature-dependent heat capacity, with $m=0$ and $c=a+bT$, eqn (3) becomes

$$t = \frac{1}{QZ}\int_{T_0}^{T}(a+b\theta)e^{\alpha/\theta}\,d\theta =$$

$$= \left(\frac{a}{QZ} + \frac{b\alpha}{2QZ}\right)\int_{T_0}^{T} e^{\alpha/\theta}\,d\theta + \frac{b}{2QZ}(T^2 e^{\alpha/T} - T_0^2 e^{\alpha/T_0}) \tag{18}$$

As an example we have evaluated, for RDX, eqns (6), (17), and (18) with $\int e^{\alpha/\theta}d\theta = F_2$ and with $\int e^{\alpha/\theta}d\theta = F_3$. The parameters used are[2]:

$T_0 = 460$ K
$\alpha = 2.3716 \times 10^4$ K
$Z = 2.02 \times 10^{18}$ sec^{-1}
$Q = 500$ cal g^{-1}
$c = 0.035 + 7.2 \times 10^{-4}\,T$ (K) cal g^{-1}–K^{-1}

TABLE 2
CALCULATED VALUES OF t (sec)

T	$F_2 \times 10^{-22}$	cF_2/QZ	cF_3/QZ	(17)[a]	(18)[a]
461	2.3261	8.43	8.44	8.44	8.44
462	4.4067	15.98	15.99	15.99	16.01
464	7.9351	28.77	28.79	28.81	28.88
466	10.766	39.04	39.06	39.12	39.26
470	14.873	53.93	53.95	54.09	54.36
475	18.055	65.46	65.49	65.74	66.22
480	19.935	72.28	72.30	72.64	73.26
500	22.404	81.23	81.24	81.75	82.63
550	22.835	82.79	82.80	83.38	84.36
700	22.842	82.82	82.82	83.40	84.38
1000	22.842	82.82	82.82	83.40	84.38

[a] With $\int_{T_0}^{T} e^{\alpha/\theta}\,d\theta = F_2$.

The value of c at 460 K (0.3662) was used in eqns (6), (17), and cF_3/QZ. The results for various values of T are given in Table 2. The explosion time obtained from F_2 or F_3 is 82.8 sec. With depletion this increases to 83.4 sec. With a temperature-dependent heat capacity (no depletion) the explosion time becomes 84.4 sec. Note that, because of the excellent agreement between columns 3 and 4 in Table 2, we can use F_3 in place of F_2 in either eqn (17) or (18). The error resulting from the use of a constant heat capacity could, of course, be reduced by using a value corresponding to a temperature somewhat higher than T_0. Further refinements are hardly justified, however, because of the uncertainities in the various thermochemical and kinetics constants.

CONCLUSION

We have derived a relatively simple and accurate approximation to the solution of the adiabatic explosion problem. If desired, a temperature-dependent heat capacity or depletion of the reactant by a first-order reaction can be included without unduly complicating the calculation.

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REFERENCES

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