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Thermal-Runaway Approximation for Ignition Times of Branched-Chain Explosions

Gonzalo Del Álamo* and Forman A. Williams†
University of California, San Diego, La Jolla, California 92093-0411

An asymptotic analysis for high activation energy of the branching step is developed for predicting ignition times of branched-chain explosions on the basis of a criterion of thermal runaway in homogeneous, isobaric, adiabatic systems. The chemistry includes an initiation step, a branching step, and a recombination step and leads to a nonlinear second-order ordinary differential equation for the temperature as a function of time under adiabatic conditions. One or both of the branching and recombination steps must be exothermic, whereas the initiation step can be endothermic or exothermic. A two-term expansion is derived in a small parameter representing the ratio of the initiation rate to the branching rate, yielding explicit expressions for the ignition time. At leading order, the ignition time is found to be inversely proportional to the net branching rate, the proportionality constant being the logarithm of the ratio of the branching rate to the initiation rate multiplied by energetic and rate parameters associated with branching and recombination. Resulting ignition times are shown to correspond closely with those calculated by numerical integration of the full equations on the basis of a temperature-inflection criterion, except near crossover, where the branching rate equals the recombination rate. Application of the theory to fuel-rich hydrogen–oxygen systems demonstrates good agreement.

I. Introduction

INTEREST in supersonic-combustion ramjet engines and in detonative-combustion engine concepts for aerospace propulsion, as well as concerns about safe storage, handling, and transportation of gaseous and volatile liquid fuels, motivate studies of autoignition processes. Two different classes of approaches can be identified. One primarily computational is based on numerical integrations, marching forward in time, of conservation equations that include detailed elementary chemistry, exothermic overall, believed to apply at the molecular level for the combustion system addressed.[1,2] Another, largely analytical, is to investigate implications of model chemistry, not tied to specific elementary steps but thought to describe reasonably the overall influences of the elementary chemistry.[3–8] It is of interest to attempt to combine these two approaches by developing simplified analytical models but relating the parameters appearing therein to rate parameters for the elementary combustion chemistry of real fuel-oxidizer mixtures. Some steps in that direction have been taken recently,[9,10] and the present work attempts to further that objective. Besides improving understanding of autoignition processes, such studies can provide formulas for calculating ignition times of combustible mixtures encountered in applications. Attention is focused here on branched-chain thermal explosions, which are characteristic of hydrogen–oxygen systems and which can also apply to other combustibles, such as acetylene-oxygen mixtures.

Branched-chain thermal explosions have been defined as processes in which chain branching and heat release both occur in the same strongly temperature-dependent overall steps.[9] Although parametric expressions for ignition times have been obtained through activation-energy asymptotics,[9] in applying the results to hydrogen–oxygen shock-tube ignition, we found quantitative deficiencies that prompted us to investigate possible alternative simplified formulations. The purpose of this communication is to present an alternative theory and to compare theoretical predictions with computational results.

Because ignition processes evolve in time, there is always some arbitrariness in defining a single ignition time. The most thorough procedure would be to provide the entire time history, but to facilitate understanding and to enable ignition estimates to be made readily it is helpful to define one most relevant characteristic time. This ignition time often is taken to be the inflection point in the temperature-time profile, calculated for a homogeneous, adiabatic, isobaric system. The rationale for this choice in explosion theory is that the inflection point usually marks the onset of heat release to a level at which the chemistry begins to affect the gas dynamics, causing rapid pressure buildup, while the effect of chemistry on the pressure field remains fairly negligible prior to that time. This particular ignition time, also often termed an induction time, is the one to which simple approximations are considered here.

Although calculation of the temperature-inflection ignition time is rather straightforward computationally (given a chemical-kinetic scheme with associated elementary rate parameters and thermochemical data), it is convenient for quick estimates and for improved understanding to have formulas that provide good approximations to the computational results and that are derived by rational systematic methods. One such approximation for branched-chain explosions is the time for radical concentrations to reach partial equilibrium isothermally.[10] Although often reasonable, this approximation can overestimate ignition times by neglecting the rate increase associated with the temperature increase caused by the heat release that occurs during radical buildup. This effect has been taken into account through a thermal-runaway criterion based on activation-energy asymptotics when the dominant heat release occurs in the branching step.[9] A similar criterion is developed here for processes in which important heat release also occurs in a temperature-insensitive recombination step.

II. Model Problem

Consider a homogeneous, adiabatic, isobaric system experiencing the two-step chemical process

$$F + O \to P + X, \qquad X \to P \tag{1}$$

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*Graduate Student, Department of Mechanical and Aerospace Engineering. Student Member AIAA.

†Professor of Engineering Physics and Combustion and Director, Center for Energy Research, Department of Mechanical and Aerospace Engineering. Fellow AIAA.

where F denotes fuel, O oxidizer, P collections of products, and X an active species such that the rates of both steps increase with increasing concentration of X, the mole fraction of which is denoted by X. The rate of the first step divided by the total number of moles of the mixture (assumed constant) is written as $A + BX$, where $A = A_0 \exp(T_i/T_0 - T_i/T)$ and $B = B_0 \exp(T_a/T_0 - T_a/T)$ are reciprocal times, the first measuring the initiation rate and the second the branching rate. Here T denotes temperature, T_0 is the initial temperature, T_a the activation temperature for branching, and T_i the activation temperature for initiation. Both A_0 and B_0 are constants during ignition, although in general they depend on T_0, pressure, and the initial composition of the system. The rate of the second step divided by the total number of moles of the mixture is written as cB_0X, where c is the ratio of the recombination rate to the branching rate at the initial temperature, a constant that also depends on T_0, pressure, and the initial composition. A pressure-dependent crossover temperature is defined by putting $c = 1$; below this temperature, a branched-chain explosion cannot occur because the rate of radical removal exceeds the rate of radical production, and somewhat above this temperature typically $c \ll 1$, because of the strong temperature dependence of the branching rate.

Initiation is usually endothermic, and its heat absorbed per mole of oxidizer consumed divided by the heat capacity per mole of mixture (assumed constant) is denoted here by q_i. Branching and recombination steps are assumed to be exothermic, and their heat released per mole of oxidizer consumed, divided by the heat capacity per mole of mixture are denoted by q_b and q_r, respectively. These definitions enable conservation of energy to be written as

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -q_i A + q_b BX + q_r cB_0X \tag{2}$$

with t denoting time. The equation for conservation of the active species is

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A + BX - cB_0X \tag{3}$$

Initial conditions for Eqs. (2) and (3) at $t = 0$ are $T = T_0$ and $X = X_0$, the latter generally taken to be zero because the initiation serves to generate X, removing the necessity of artificially assuming a positive initial radical concentration to enable chemistry to begin.

The relationship of the model problem to a problem with detailed chemistry depends on the chemical system. For fuel-rich hydrogen–oxygen systems there is a good systematically reduced two-step description,[9,11,12] based on steady-state approximations for O and OH, that has a branching step $3H_2 + O_2 \rightarrow 2H_2O + 2H$, principally at the rate of the elementary reaction $H + O_2 \rightarrow OH + O$, followed by a recombination step, $2H \rightarrow H_2$, at the rate of the elementary step $H + O_2 + M \rightarrow HO_2 + M$. Besides branching and recombination, an initiation step is needed for auotignition in the absence of initial radicals. Based on reaction-rate information in the earlier literature, we previously[10] included two initiation steps, namely, $H_2 + O_2 \rightarrow 2OH$ and $H_2 + O_2 \rightarrow HO_2 + H$, but more recent work[13] shows fairly convincingly that the first of these does not occur, whence initiation is presumed here to proceed only by the second. This results in the model problem addressed here, X representing H, with the branching rate twice that of $H + O_2 \rightarrow OH + O$ and the recombination rate that of $H + O_2 + M \rightarrow HO_2 + M$, provided that the reactant consumption is neglected. With this correspondence, A is proportional to the product of the concentrations of H_2 and O_2, B_0 is proportional to the concentration of O_2, and c is the ratio of the recombination rate to twice the branching rate, so that it is proportional to pressure away from fall-off but independent of the chemical composition except insofar as chaperon efficiencies depend on composition.

It is of interest to compare this model problem with the earlier, simpler model problem.[9] The earlier analysis was more general in the sense that the branching rate was allowed to be proportional to a power of X that could be different from unity. Because that power is generally unity for real branching chemistry, there is little motivation to address this degree of generalization. The previous work did not allow for recombination and thus pertains to the limit $c = 0$ of the present description. In addition, for simplicity, so that it only would be necessary to work with a first-order ordinary differential equation, the earlier study was based on a one-equation model, which in a formal sense implicitly requires initiation to be exothermic with the same heat release as branching ($q_i = -q_b$), a generally unrealistic restriction that nevertheless turns out to be not exceedingly severe because the energetic effect of initiation will be shown here to be unimportant. Equations (2) and (3) imply that, in contrast to the previous model,[9] the present study requires consideration of a second-order ordinary differential equation, that is, it is a two-equation model. The previous work[9] also required the initiation rate to be constant, an approximation that will be shown below to apply correctly at $c = 0$ for sufficiently small initiation rates even though the activation energy for this step typically is the largest.

III. Formulation for Activation-Energy Asymptotics

In the Frank–Kamenetskii approach,[4] to leading order in the small parameter T_0/T_a, the approximations $A = A_0 e^{i\theta}$ and $B = B_0 e^{\theta}$ apply, where $\theta = (T - T_0)T_a/T_0^2$ and $i = T_i/T_a$. The resulting exponential, with reactant consumption neglected, drives the temperature to infinity at a finite time whenever the endothermicity of initiation is unimportant, yielding a thermal runaway that can replace the temperature-inflection criterion for determining an ignition time. These results can be justified by a formal asymptotic expansion in the samll parameter T_0/T_a, which underlies the present development. In this approximation, Eqs. (2) and (3) become

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\alpha_i A_0 e^{i\theta} + \left(\alpha_b e^{\theta} + \alpha_r c\right) B_0 X \tag{4}$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = A_0 e^{i\theta} + (e^{\theta} - c) B_0 X \tag{5}$$

subject to the initial conditions $\theta = 0$ and $X = 0$ at $t = 0$, where the definitions $\alpha_i = q_i(T_a/T_0^2)$, $\alpha_b = q_b(T_a/T_0^2)$, and $\alpha_r = q_r(T_a/T_0^2)$ have been introduced. Use of Eq. (4) to eliminate X from Eq. (5) gives

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\tau^2} = -a\epsilon i e^{i\theta} \frac{\mathrm{d}\theta}{\mathrm{d}\tau} + \epsilon e^{i\theta}\left(\frac{e^{\theta} + bc}{1 + bc}\right) + (e^{\theta} - c)\left(\frac{\mathrm{d}\theta}{\mathrm{d}\tau} + a\epsilon e^{i\theta}\right) + \frac{e^{\theta}}{e^{\theta} + bc}\left(\frac{\mathrm{d}\theta}{\mathrm{d}\tau}\right)\left(\frac{\mathrm{d}\theta}{\mathrm{d}\tau} + a\epsilon e^{i\theta}\right) \tag{6}$$

where the nondimensional time is $\tau = tB_0$, the ratio of the recombination to branching heat release is $b = \alpha_r/\alpha_b$, and the ratio of the heat absorbed in initiation to the heat released in branching and recombination is $a = \alpha_i/(\alpha_b + \alpha_r c)$. A measure of the ratio of the initiation rate to the branching rate

$$\epsilon = A_0(\alpha_b + \alpha_r c)/B_0 \tag{7}$$

is generally small in explosion problems and will be treated as a small parameter in an asymptotic analysis.

IV. Asymptotic Analysis for Small Initiation Rates

Equation (6) is to be solved subject to the initial conditions $\theta = 0$, $\mathrm{d}\theta/\mathrm{d}\tau = -a\epsilon$ at $\tau = 0$, as an asymptotic expansion for small ϵ. It is convenient to define $f(\theta) = \mathrm{d}\theta/\mathrm{d}\tau$ and to write Eq. (6) in a phase plane:

$$f\frac{\mathrm{d}f}{\mathrm{d}\theta} = -a\epsilon i e^{i\theta} f + \epsilon e^{i\theta}\left(\frac{e^{\theta} + bc}{1 + bc}\right) + (f + a\epsilon e^{i\theta})(e^{\theta} - c) + \frac{e^{\theta}}{e^{\theta} + bc} f(f + a\epsilon e^{i\theta}) \tag{8}$$

with $f = -a\epsilon$ at $\theta = 0$. A uniformly valid matched asymptotic expansion of the solution $f(\theta)$ to Eq. (8) is to be sought.[14,15] The nondimensionalized ignition time τ_∞, defined as the value of τ at which θ goes to infinity, can be obtained from this solution as

$$\tau_\infty = \int_0^\infty \left(\frac{\mathrm{d}\theta}{f}\right) \tag{9}$$

It is evident that, in addition to its dependence on the expansion parameter ϵ, τ_∞ might depend on the fixed parameters a, b, c, and i. To ensure that thermal runaway occurs on the timescale τ, attention is restricted here to nonnegative values of b, to values of a and i of order unity or smaller, and to $c < 1$, with $1 - c$ of order unity. The Appendix addresses the question of what happens as c approaches unity. With this ordering, there is an inner zone near $\theta = 0$ in which appropriate variables are $y = \theta/\epsilon$ and $F = f/\epsilon = \mathrm{d}y/\mathrm{d}\tau$, both of order unity, as can be inferred from Eq. (8) in view of the ϵ in the initial condition for f. For $\epsilon \ll 1$, in these variables Eq. (8) becomes

$$\begin{aligned} F\frac{\mathrm{d}F}{\mathrm{d}y} &= -a\epsilon i(1 + i\epsilon y + \cdots)F + \left(1 + \frac{\epsilon y}{1+bc} + i\epsilon y + \cdots\right) \\ &\quad + (F + a + ai\epsilon y + \cdots)(1 - c + \epsilon y + \cdots) \\ &\quad + \frac{\epsilon}{1+bc}F(F + a + ai\epsilon y + \cdots)(1 + bc\epsilon y + \cdots) \end{aligned} \tag{10}$$

With the expansion $F = F_0 + \epsilon F_1 + \ldots$, Eq. (10) gives

$$F_0\frac{\mathrm{d}F_0}{\mathrm{d}y} = 1 + (1 - c)(F_0 + a) \tag{11}$$

with the initial condition $F_0 = -a$ at $y = 0$, and

$$\begin{aligned} &\frac{\mathrm{d}F_1}{\mathrm{d}y} + \frac{F_1[1 + (1 - c)a]}{F_0^2} \\ &\quad = -ai + \frac{y\{1 + i + [F_0 + a + ai(1 - c)](1 + bc)\}}{(1 + bc)F_0} \\ &\quad + \frac{F_0(F_0 + a)}{(1 + bc)F_0} \end{aligned} \tag{12}$$

with the initial condition $F_1 = 0$ at $y = 0$. The solution to Eq. (11), subject to the initial condition, is expressed as

$$\begin{aligned} &[1/(1 - c)]^2\{(1 - c)(F_0 + a) \\ &\quad - [1 + a(1 - c)]\ln[1 + (1 - c)(F_0 + a)]\} = y \end{aligned} \tag{13}$$

Equation (12) is linear and has the solution

$$\begin{aligned} F_1 &= \exp\left[-\int_0^y \frac{1 + (1 - c)a}{F_0^2}\,\mathrm{d}y\right] \\ &\times\left(1 + \int_0^y \exp\left[\int_0^y \frac{1 + (1 - c)a}{F_0^2}\,\mathrm{d}y\right]\right. \\ &\times\left.\left\{\frac{y[1 + i + (F_0 + a)(1 + bc)]}{(1 + bc)F_0} - \frac{ai(1 + bc)F_0 + F_0(F_0 + a)}{(1 + bc)F_0}\right\}\mathrm{d}y\right) \end{aligned} \tag{14}$$

These results show that F_0 approaches $(1 - c)y$ as y approaches infinity, while F_1 becomes proportional to y^2 in this limit, explicitly demonstrating the lack of uniform validity of the inner solution.

For θ and f of order unity, the leading-order outer solution to Eq. (8), f_0, in the expansion $f = f_0 + \epsilon f_1 + \ldots$, is obtained by solving the equation

$$f_0\frac{\mathrm{d}f_0}{\mathrm{d}\theta} = f_0(e^\theta - c) + \frac{e^\theta}{e^\theta + bc}f_0^2 \tag{15}$$

Then

$$f_0 = (e^\theta + bc)\{k + \ln(e^\theta + bc) + (1/b)\ln[(e^\theta + bc)/e^\theta]\} \tag{16}$$

where k is a constant of integration. Matching with the inner solution gives $k = -(1 + 1/b)\ln(1 + bc)$. The composite solution to Eq. (8) at leading order then becomes

$$\begin{aligned} f &= \epsilon F_0 + (e^\theta + bc)\left[\ln\left(\frac{e^\theta + bc}{1 + bc}\right)\right. \\ &\quad \left.+ \frac{1}{b}\ln\left(\frac{1 + bce^{-\theta}}{1 + bc}\right)\right] - (1 - c)\theta \end{aligned} \tag{17}$$

the last term of which is the common part that matched. The nondimensional ignition time is then recovered from Eq. (9) by substituting Eq. (17) into the integrand, with F_0 determined by Eq. (13).

An asymptotic expansion of τ_∞ for small values of ϵ can be obtained from Eq. (17) by breaking the integral in Eq. (9) into two parts:

$$\tau_\infty = \int_0^\delta \left(\frac{\mathrm{d}\theta}{f}\right) + \int_\delta^\infty \left(\frac{\mathrm{d}\theta}{f}\right)$$

with $\epsilon \ll \delta \ll 1$. To leading order, the first of these integrals is

$$\int_0^{\delta/\epsilon}\left(\frac{\mathrm{d}y}{F_0}\right)$$

which is found from Eq. (11) to be $(1 - c)^{-1}\ln[1 + (1 - c)(F_0 + a)]$, with F_0 evaluated at $y = \delta/\epsilon$. Because δ/ϵ is large, Eq. (13) shows that to leading order this result can be written as $(1 - c)^{-1}\ln[1 + a(1 - c) + (1 - c)^2\delta/\epsilon]$, which approaches $(1 - c)^{-1}\ln[(1 - c)^2\delta/\epsilon]$ for large values of δ/ϵ. The second integral to leading order is

$$\int_\delta^\infty\left(\frac{\mathrm{d}\theta}{f_0}\right)$$

with f_0 given by Eq. (16). Because the resulting integrand approaches $[(1 - c)\theta]^{-1}$ as θ approaches zero, there is a divergent contribution of $-(1 - c)^{-1}\ln\delta$ from this integral at its lower limit, which cancels the divergent contribution $(1 - c)^{-1}\ln\delta$ of the previous integral.

Combining these two results for large values of δ/ϵ in the limit of vanishing δ gives a convergent expression for τ_∞, which can be written as

$$\tau_\infty = [1/(1 - c)]\ln(1/\epsilon) + [2/(1 - c)]\ln(1 - c) - K(b, c) \tag{18}$$

up to terms of order ϵ, where

$$\begin{aligned} K(b, c) &\equiv \lim_{\delta\to 0}\left(-\frac{\ln\delta}{1 - c} - \int_\delta^\infty\left\{\frac{1}{e^\theta + bc}\left[\ln\left(\frac{e^\theta + bc}{1 + bc}\right)\right.\right.\right. \\ &\quad \left.\left.\left.+ \frac{1}{b}\ln\left(\frac{1 + bce^{-\theta}}{1 + bc}\right)\right]^{-1}\right\}\mathrm{d}\theta\right) \\ &= \int_0^\infty\left\{\frac{1}{(1 - c)\theta e^\theta} - \frac{1}{e^\theta + bc}\left[\ln\left(\frac{e^\theta + bc}{1 + bc}\right)\right.\right. \\ &\quad \left.\left.+ \frac{1}{b}\ln\left(\frac{1 + bce^{-\theta}}{1 + bc}\right)\right]^{-1}\right\}\mathrm{d}\theta + \frac{\gamma}{1 - c} \end{aligned} \tag{19}$$

The identity

$$\gamma = \lim_{\delta\to 0}\left[\ln(\delta^{-1}) - \int_\delta^\infty(\theta e^\theta)^{-1}\,\mathrm{d}\theta\right]$$

where $\gamma = 0.5772$ is Euler's constant, has been employed here to enable $K(b, c)$ to be written as a convergent integral. Numerical evaluation of this integral results in the curves of $K(b, c)$ shown in Fig. 1 for finite values of b. To leading order, the value of τ_∞ is independent of the values of the parameters a and i, and the result dimensionally gives the runaway ignition time t_∞ as

$$\begin{aligned} t_\infty &= [1/B_0(1 - c)]\ln[B_0/A_0(\alpha_b + \alpha_r c)] \\ &\quad - (1/B_0)\{[2/(1 - c)]\ln[1/(1 - c)] + K(b, c)\} \end{aligned} \tag{20}$$

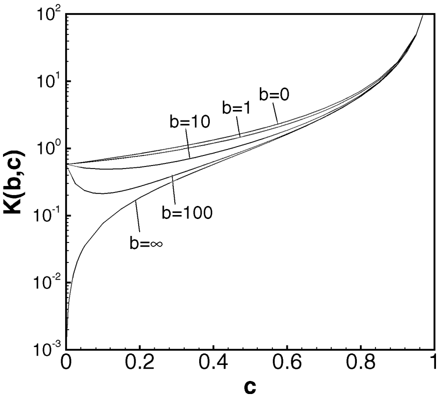

Fig. 1 **Dependency of $K(b,c)$ on c for $b = 0$, 1, 10, 100, ∞, obtained from the last equality in Eq. (19) and from Eq. (23).**

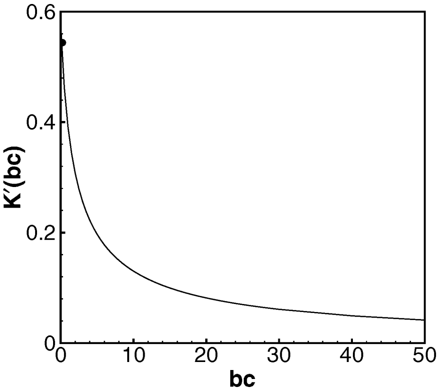

Fig. 2 **Function $K'(bc)$ obtained by evaluating numerically the integral in Eq. (21).**

V. Simplification of Results for Special Cases

It is of interest to consider different limits for the parameters c and b. For hydrogen–oxygen mixtures somewhat above crossover temperatures, branching is much faster than recombination during the induction period, so that $c \to 0$ is a relevant limit. If the ratio of the heat release in recombination to the heat release in branching is high enough that bc can be best assumed not vanish in the limit $c \to 0$, then $\tau_\infty = \ln(1/\epsilon) - K'(bc)$, with

$$K'(bc) = \gamma + \int_0^\infty \left\{ \frac{1}{\theta e^\theta} - \frac{1}{e^\theta + bc}\left[\ln\left(\frac{e^\theta + bc}{1 + bc}\right)\right]^{-1} \right\} \mathrm{d}\theta \qquad (21)$$

which is plotted in Fig. 2. If $bc \to 0$ in the limit $c \to 0$, then heat release by recombination prior to ignition becomes negligible as well, and $K' \to \gamma$ so that the expression $\tau_\infty = \ln(1/\epsilon) - \gamma$, obtained previously,[9] is recovered. The present analysis thus demonstrates explicitly that, to the order to which the expansion in ϵ was carried, the previous results[9] do not depend on the specific choices made for values of a and i, so long as these parameters are of order unity.

In the limit $b \to 0$, heat release by recombination becomes negligible, but radical depletion remains important. The dimensionless induction time in this limit becomes $\tau_\infty = \ln(1/\epsilon)/(1-c) + 2\ln(1-c)/(1-c) - \gamma/(1-c) - K_0(c)$, where

$$K_0(c) = \int_0^\infty \left\{ \frac{1}{(1-c)\theta e^\theta} - \frac{1}{e^\theta[\theta - c(1 - e^{-\theta})]} \right\} \mathrm{d}\theta$$

$$= \frac{c}{1-c}\int_0^\infty \left\{ \frac{\theta - 1 + e^{-\theta}}{\theta[\theta e^\theta - c(e^\theta - 1)]} \right\} \mathrm{d}\theta \qquad (22)$$

The curve for $b = 0$ in Fig. 1 is $K(0, c) = \gamma/(1-c) + K_0(c)$. In the context of the previous analysis,[9] in which there was no recombination heat release, this limit affords an indication of the delay in the ignition time associated with radical depletion.

In the limit $b \to \infty$, branching heat release becomes negligible, and $\tau_\infty = \ln(1/\epsilon)/(1-c) + 2\ln(1-c)/(1-c) - \gamma/(1-c) - K_\infty(c)$, where

$$K_\infty(c) = \int_0^\infty \left[\frac{1}{(1-c)\theta e^\theta} - \frac{1}{e^\theta - c\theta - 1} \right] \mathrm{d}\theta$$

$$= \int_0^\infty \left[\frac{1 - \theta - e^{-\theta} + c\theta(1 - e^{-\theta})}{(1-c)\theta(e^\theta - 1 - c\theta)} \right] \mathrm{d}\theta \qquad (23)$$

The curve for $b = \infty$ in Fig. 1 was obtained as $K(\infty, c) = \gamma/(1-c) + K_\infty(c)$ by evaluating this integral numerically. The first equality in Eq. (23) implies that $K_\infty(0) = -\gamma$, so that $K(\infty, 0) = 0$, unlike the result $K(b, 0) = \gamma$ obtained from Eq. (19) for all finite values of b. The limit $b \to \infty$ might be thought to be more relevant than the limit $b \to 0$ for hydrogen–oxygen systems because $b > 1$ in such mixtures. The resulting ignition time will tend to be an upper bound for hydrogen–oxygen, however, because of the neglect of the accelerating effect of the branching heat release on the branching rate, a substantial influence that can render the upper bound excessively high.

VI. Discussion of Results of the Asymptotic Analysis

To leading order, the ignition time is given by the first term in Eq. (20). The most dominant factor in this term is $(B_0 - cB_0)^{-1}$, the reciprocal of the difference between the branching rate and the recombination rate, these rates being expressed as reciprocal times through division by an appropriate initial reactant-mixture concentration. The timescale for thermal runaway is therefore obtained from the net branching rate. The factor $(1-c)$ multiplying B_0 in Eq. (20) corrects the earlier[9] result for the effect of radical depletion by recombination, to be called here simply radical depletion. This effect is independent of energetics, effects of which appear inside the logarithm at leading order. It causes the induction time to approach infinity at crossover ($c = 1$) in leading order. Even though ignition occurs through thermal explosion in this model, net branching is essential to build up the radicals needed for the important strongly temperature-sensitive step, the branching step, to proceed.

In the leading-order logarithmic term in Eq. (20), the ratio of the initiation rate to the branching rate, A_0/B_0, appears. Increasing A_0/B_0 decreases the ignition time. This logarithmic effect is well known for branched-chain processes.[9] Also well known in the context of Frank–Kamenetskii types of analyses[4] for small $\epsilon = (A_0/B_0)\alpha_b(1 + bc)$ is the dependence on the activation temperature T_a and on the heat release (divided by the heat capacity) q_b through $\alpha_b = q_b T_a / T_0^2$. The present analysis serves to determine the tradeoff between effects of heat release in branching α_b and in recombination $\alpha_r = b\alpha_b$. The parameter that finally appears, $\alpha_b + \alpha_r c = (q_b + c q_r) T_a / T_0^2$, is a kind of Zel'dovich number, in which the effective heat release is that in branching plus the initial ratio of the recombination rate to the branching rate times that in recombination.

If there is no heat release in recombination, then $b = 0$, ϵ is independent of c, and the previous[9] ϵ is recovered, $\epsilon = (A_0/B_0)\alpha_b$, indicating the reduction in the induction time through increasing heat release in branching (from α_b inside the logarithm) at leading order. In the opposite limit in which there is no heat release in branching $b = \infty$, the value of ϵ becomes proportional to c, $\epsilon = (A_0/B_0)\alpha_r c$, so that some recombination is necessary for any heat release at all to be present, enabling the thermal explosion to occur at a finite time. In this limit, the ignition time is infinite at leading order when $c = 0$, and increasing the ratio c of the recombination rate to the branching rate initially decreases the ignition time by increasing the amount of heat release, an effect that continues until reactant depletion begins to dominate the increase in heat release, driving the ignition time to infinity at $c = 1$, as illustrated in Fig. 3 for particular sets of parameters. Figure 3 also shows that this effect, the existence of a minimum ignition time at an optimal value of c in leading order, persists to finite values of b, at which there is some heat release in branching, so long as $b > \ln(1/\epsilon)$.

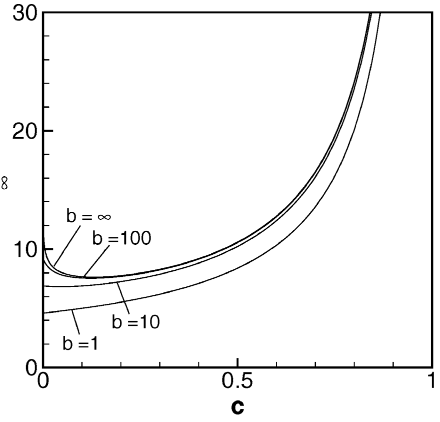

Fig. 3 Dependence of τ_∞ on c at leading order for $\alpha_r A_0/B_0 = 10^{-2}$ and $b = \infty$, 100, 10, and 1.

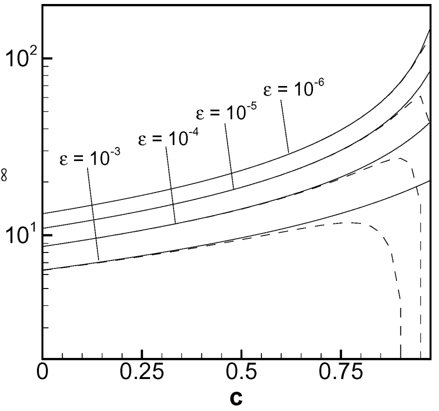

Fig. 4 Variation of τ_∞ with c, obtained by numerical integration of Eq. (6) with $a = 1$, $i = 1$, $b = 1$ (——) and predicted by the asymptotic approximation Eq. (18) with $b = 1$ (- - - -), for $\epsilon = 10^{-3}$, 10^{-4}, 10^{-5}, and 10^{-6}.

The remaining terms in Eq. (20) always have the effect of reducing the ignition time below the value obtained at leading order. As c approaches unity, the higher-order $\ln(1-c)$ term formally becomes dominant and eventually drives τ_∞ negative, but this is unreal and occurs outside the range of validity of the expansion. It reflects the failure of the expansion as crossover is approached. This is illustrated in Fig. 4, which compares values of τ_∞ calculated from Eq. (18) with those obtained by numerical integration of Eq. (6) for various representative cases. In the numerical integration the ignition time was defined by putting $\theta = 10$, which gives a time very near the time at which the solution to Eq. (6) approaches infinity. This figure demonstrates the delay in ignition by radical depletion and shows excellent agreement between the numerical and the asymptotic solutions until crossover is approached too closely. The effective small parameter of expansion actually is $\epsilon/(1-c)^2$, and the agreement is excellent when this parameter is sufficiently small. A different expansion is needed near crossover (see Appendix).

The higher-order term $K(b, c)$ always augments the effect of the $\ln(1-c)$ term in reducing the ignition time. Figure 1 shows that the extent of this augmentation decreases as the ratio b increases, suggesting that heat release in branching is more effective than heat release in recombination in promoting ignition, at least if $\alpha_b + \alpha_r c$ (and hence ϵ) is held fixed as b varies. For $b = \infty$ (all heat release in recombination) and for small b, there is a monotonic variation with c in Fig. 1 augmenting the effect of the $\ln(1-c)$ term, but for higher finite intermediate values of b this variation is nonmonotonic, contributing an increase in ignition time with increasing c for small c as the recombination heat release comes into play, altering the solution from that obtained[9] with $c = 0$ and heat release only in branching. The jump in $K(b, 0)$ at $b = \infty$ is smoothed by the alternative limit of Eq. (21), shown in Fig. 2, which expands the region at $c = 0$ near $b = \infty$ of Fig. 1 to produce a continuous variation from the result[9] with heat release only in branching to the present result ($b = \infty$) for heat release only in recombination. In this continuous variation at $c = 0$, the higher-order reduction in the nondimensional ignition time from the leading-order value $\tau_\infty = \ln[B_0/(A_0\alpha_b)]$ at $bc = 0$, namely, $-\gamma$, decreases to zero as bc increases to infinity, the nondimensional ignition time at leading-order, $\tau_\infty = \ln\{B_0/[A_0\alpha_b(1+bc)]\}$, itself decreasing with increasing total heat release through increasing recombination heat release at constant branching heat release and initiation and branching rates (α_b, A_0, and B_0 fixed).

VII. Comparisons of Results for Hydrogen–Oxygen Systems

As indicated in the Introduction, one motivation for development of the present theory is its potential application to hydrogen–oxygen systems. For ignition in such systems, under fuel-lean conditions only the H-atom concentration obeys an accurate steady-state approximation, and two radicals, OH and O, are out of steady state.[10] This complication precludes an immediate direct comparison for fuel-lean conditions; further analysis would be needed to reduce the concentrations of these two intermediate species to a single effective chain-carrier concentration, and that reduction will not be pursued here. Attention therefore is restricted to fuel-rich and stoichiometric systems, comparisons being given specifically for hydrogen–air mixtures with equivalence ratios of $\phi = 10$ and 1. The resulting comparisons are, however, representative of those that would be obtained in pure hydrogen–oxygen mixtures or at high dilution, over the full near-stoichiometric and fuel-rich range of equivalence ratios.

From the preceding discussion of the model problem it can be seen that A_0 and B_0 are both proportional to the O_2 concentration. It therefore follows from Eq. (20) that it is most convenient to make comparisons on the basis of the variation of the product of the ignition time and the oxygen concentration, $t_\infty[O_2]$, with the initial temperature T_0. Such coordinates are quite common in the literature, extensive citations of which are available.[10] Values of T_0 from about 1000 K to about 2500 K are considered here, and results for pressures of $p = 1$ and 100 bar are shown because they illustrate results that are representative of the general temperature and pressure variations. These selections lead to values of the parameters ϵ between 10^{-7} and 10^{-5} and a between 1.3 and 3.6, with $b = 4.3$ and $i = 3$, so that the ordering adopted in the analysis is applicable. If the elementary initiation reaction $H_2 + O_2 \rightarrow 2OH$ were included in the short mechanism, negative values of a would be obtained at the lower temperatures, arising from the fact that the rate of the exothermic global reaction $3H_2 + O_2 \rightarrow 2H_2O + 2H$ in the two-step reduced mechanism would include twice the rate of this elementary initiation reaction $H_2 + O_2 \rightarrow 2OH$, thereby effectively contributing exothermicity to initiation in the reduced-chemistry description.

Figure 5 compares results of the present theory with those of the earlier[10] approximation that equated the ignition time with the time for radicals to reach partial equilibrium isothermally. These two approximations are quite different because partial equilibrium of H plays no role whatever in the present theory, whereas the temperature change of the present (thermal-runaway) theory is entirely absent for the earlier (isothermal) conditions. Yet it is seen in Fig. 5 that results of the two different approximations are not very different. Ignition times predicted here are less than those obtained from the preceding approximation. This indicates that thermal runaway occurs before partial equilibrium is reached, a situation that in fact persists to very low pressures for stoichiometric and fuel-rich mixtures. The heat release that occurs through branching and recombination during radical buildup increases the temperature sufficiently for the associated increased branching rate to produce thermal runaway before the system can achieve partial equilibrium. The difference is larger at higher equivalence ratios and at higher pressures (approaching a factor of two at 100 bar) because the chemistry and heat release are then faster, causing an earlier departure from the isothermal conditions assumed in applying the partial-equilibrium criterion. This result implies that, even with reactant depletion neglected, the partial-equilibrium criterion always overestimates the temperature-inflection ignition time somewhat in stoichiometric and fuel-rich

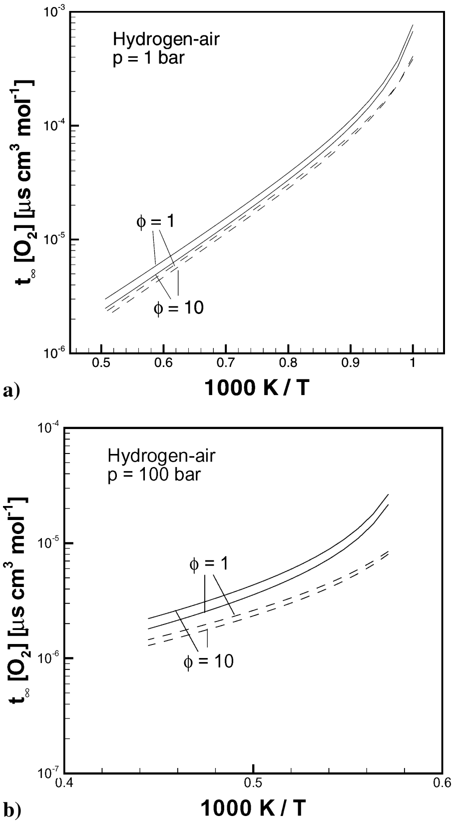

Fig. 5 Variation of the product $t_\infty[O_2]$ with temperature T_0, predicted by Eq. (20) (- - - -) and obtained[10] in the approximation of isothermal branched-chain explosion considering the ignition time to be the time at which radical concentrations reach partial equilibrium (——): a) for hydrogen–air mixtures with equivalence ratios $\phi = 1, 10$ at a pressure of 1 bar and b) for hydrogen–air mixtures with equivalence ratios $\phi = 1$, 10 at a pressure of 100 bar.

systems. The overestimate increases substantially as the system becomes very fuel rich.[10] The present result therefore is a significant improvement over the previous approximation when there is interest in ignition times based on temperature inflection.

It is worthwhile to compare the ignition times predicted here with those obtained by full numerical integrations that employ the temperature-inflection criterion. The computations were performed with the FLAMEMaster code,[16] all results fully converge with error less than 1%. For the high-temperature conditions addressed here, it was previously shown that autoignition times predicted by full detailed chemistry are indistinguishable from those predicted by a six-step short mechanism that retains only the steps $H_2 + O_2 \rightarrow 2OH$, $H_2 + O_2 \rightarrow HO_2 + H$, $H + O_2 \rightarrow O + OH$, $H_2 + O \rightarrow OH + H$, $H_2 + OH \rightarrow H_2O + H$, and $H + O_2 + M \rightarrow HO_2 + M$; all steps were treated as irreversible.[10] Because the first of these steps is no longer viable, this becomes a five-step short mechanism that retains agreement with the corresponding detailed mechanism, giving ignition times that differ by less than 10% until crossover is approached. Results of integrations performed with this five-step mechanism and with the detailed mechanism are compared with the present results of Eq. (20) in Fig. 6, where all conditions are sufficiently far from crossover that Eq. (20) is an excellent approximation to the result of numerical integration of Eq. (6). The small differences between the predictions of the detailed mechanism and of the five-step mechanism are illustrated in Fig. 6 for $\phi = 10$ at 1 bar; these differences are illustrative of those found under other conditions as well. The agreement of the predictions of Eq. (20) with the temperature-inflection criterion in the full mechanism is seen in Fig. 6 to be excellent in stoichiometric mixtures. This is attributable to the fact that the temperature profiles agree quite well nearly up to the inflection point, and the asymptotic approximation diverges rapidly to infinity after that. For fuel-rich conditions at high pressure, however, the asymptotic ignition times are about twice as long. This is a reflection of differences in predicted temperatures profiles early in the induction history resulting from variations in reaction rates with temperature that are not captured well by the Frank–Kameneskii approximation, partially attributable to effects of falloff at high pressures in the recombination step.

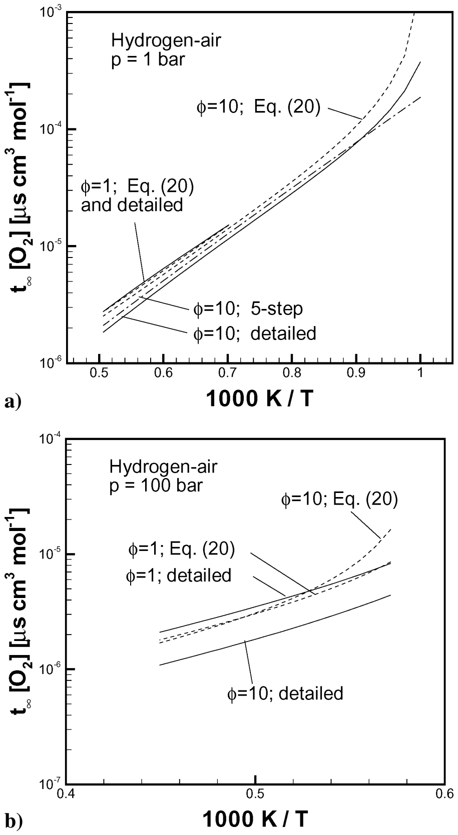

Fig. 6 Variation of the product $t_\infty[O_2]$ with temperature T_0 obtained by numerical calculation with the detailed mechanism using the temperature-inflection criteria for the end of the induction period (——) and predicted by Eq. (20) (- - - -): a) for hydrogen–air mixtures with equivalence ratios $\phi = 1, 10$ at a pressure of 1 bar and b) for hydrogen–air mixtures with equivalence ratios $\phi = 1$, 10 at a pressure of 100 bar. The chain curve for $\phi = 10$ at 1 bar illustrates the difference between the predictions of the detailed and five-step mechanisms.

VIII. Conclusions

Over wide ranges of conditions that include fuel-rich hydrogen–oxygen systems, asymptotic analyses based on thermal runaway yield excellent approximations to ignition times defined in terms of inflection points in temperature-time histories. This has been demonstrated explicitly for a chemical-kinetic model that includes temperature-sensitive branching and temperature-insensitive recombination, with exothermicity in either or both of these steps. The explicit formulas for the ignition times, obtained from the asymptotic analysis, show that the ignition time varies inversely with the net branching rate, thereby exhibiting the strong effect of radical depletion through recombination in delaying ignition. The initiation rate and the heat release accelerate ignition through a logarithmic factor. As crossover is approached, where the recombination rate equals the branching rate, the asymptotic analysis for small initiation rates fails, and different kinds of expansions are needed, which could profitably be investigated in the future. Ignition times become long as crossover is approached, pointing towards the need for a revised nondimensionalization of the time. There are accident scenarios that involve low temperatures and long autoignition times, which motivate future studies in this direction.

At higher temperatures, for stoichiometric and fuel-rich hydrogen–oxygen systems it has been shown that thermal runaway occurs before the shuffle reactions achieve partial equilibrium, even when reactant depletion is neglected. The partial-equilibrium criterion therefore tends to overestimate ignition times for fuel-rich hydrogen–oxygen systems, although this need not necessarily be true for all fuels because the two criteria depend on entirely different chemical-kinetic parameters that will have different values for different systems. Because applications in aerospace propulsion, of the kind encountered in hydrogen-fueled supersonic-combustion ramjets, for example, often encounter quite fuel-lean conditions, it could be of interest to extent the high-temperature analysis, to account for two radicals (O and OH) not being in steady state, with the H atom in steady-state, to obtained well-justified closed-form expressions for autoignition times under those conditions.

Appendix: Asymptotic Behavior near Crossover

The result in Eq. (18) suggests that, when $c < 1$, the most natural nondimensional time and small parameter ϵ for the analysis in the main text are

$$\tau = B_0(1-c)t, \qquad \epsilon = \frac{A_0(\alpha_b + \alpha_r c)}{\left[B_0(1-c)^2\right]} \tag{A1}$$

because then Eq. (18) is simply $\tau_\infty = \ln(1/\epsilon) - K(b, c)$. In terms of the parameters in Eq. (A1), Eq. (6) is

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\tau^2} = -ia\epsilon(1-c)e^{i\theta}\,\frac{\mathrm{d}\theta}{\mathrm{d}\tau} + \epsilon e^{i\theta}\left(\frac{e^\theta + bc}{1+bc}\right) + \left[\left(\frac{e^\theta - c}{1-c}\right) + \left(\frac{e^\theta\,\mathrm{d}\theta/\mathrm{d}\tau}{e^\theta + bc}\right)\right]\left[\frac{\mathrm{d}\theta}{\mathrm{d}\tau} + a\epsilon(1-c)e^{i\theta}\right] \tag{A2}$$

with initial conditions $\theta = 0$ and $\mathrm{d}\theta/\mathrm{d}\tau = a\epsilon(1-c)$ at $\tau = 0$. This modified formulation can facilitate analysis of the limit in which $(1-c)$ becomes small, approaching crossover, but it becomes singular and not useful at crossover ($c = 1$). Different regimes arise as crossover is traversed, necessitating different types of matched asymptotic expansions. Because attempts to explore these regimes systematically would complicate and lengthen the presentation appreciably, and because for aerospace propulsion application there is less interest in the long ignition times encountered near and beyond crossover, the discussion here is restricted to a few general observations.

It is evident from Eq. (4) that, because $X = 0$ at $t = 0$, $\mathrm{d}\theta/\mathrm{d}t$ initially is negative when $a > 0$ and positive when $a < 0$, that is, for endothermic initiation ($a > 0$) there is a small temperature decrease initially, which is of higher order and unimportant when $(1-c)$ is positive and not small. For exothermic initiation ($a < 0$) with $i > 0$, in extreme cases it is possible to encounter thermal runaway in the initiation step itself on the long timescale A_0^{-1}, the branching and recombination playing no role whatever; this simple limit is not of interest for branched-chain explosions. For sufficiently endothermic initiation, specifically for $\alpha_i > \alpha_r$, Eqs. (4) and (5) possess a steady-state solution having both $\mathrm{d}X/\mathrm{d}t = 0$ and $\mathrm{d}\theta/\mathrm{d}t = 0$. This solution, which has $\theta = \ln[c(\alpha_i - \alpha_r)/(\alpha_i + \alpha_b)]$, is most accessible below crossover ($c > 1$) and is irrelevant for $c < 1$, where it corresponds to a negative value of θ that is never reached from the initial state. For $c > 1$, thermal runaway can occur from the steady state on the long timescale A_0^{-1}. Near crossover thermal runaways are possible on shorter timescales, not achieving steady states. For example, for $1 - c \geq 0$ and small, and for small ϵ, there exists a three-zone matched asymptotic expansion that exhibits thermal runaway on a shorter timescale, intermediate between A_0^{-1} and B_0^{-1}. There would be some interest in exploring these regimes further, for example in connection with concerns about hydrogen safety.

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A. Karagozian
Associate Editor