The reduced-kinetic description of hydrogen-air premixed-combustion problems relevant for safety applications

5th Meeting of the Spanish Section of the Combustion Institute

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5th Meeting of the Spanish Section of the Combustion Institute

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Motivation

Context

- H_2 and Syngas are bound to play a predominant role as energy carriers in the foreseable future.
- Safety issues arise concerning hydrogen transport, handling and storage

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Hydrogen combustion characteristics

	L_i	v_l	δ_{QUENCH}	E_{min}	δ_{IGNITION}
H_2	0.3	3 m/s	0.6 mm	0.02 mJ	$\sim$ 50 μm
CH_4	1.0	0.45 m/s	1.8 mm	0.21 mJ	$\sim$ 0.8 mm

Chemistry Reduction

Methodology

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2. Deletion of elementary steps that do not contribute to the chemistry under the conditions of interest
3. Introduction of steady-state approximations for intermediate species with negligible transport rates

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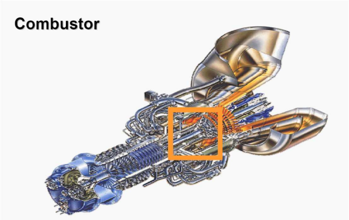
Methodology

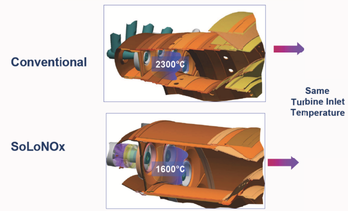
1. Selection of a detailed chemical-kinetic mechanism including a complete set of chemical species and elementary reactions
2. Deletion of elementary steps that do not contribute to the chemistry under the conditions of interest
3. Introduction of steady-state approximations for intermediate species with negligible transport rates
4. Truncation of the steady-state algebraic expressions to facilitate numerical computations

Chemistry Reduction

Methodology

- For selection of the test cases for validation one needs to identify the conditions of interest.
- E.g., in gas-turbine combustion the preheated mixture is burned at elevated pressure.

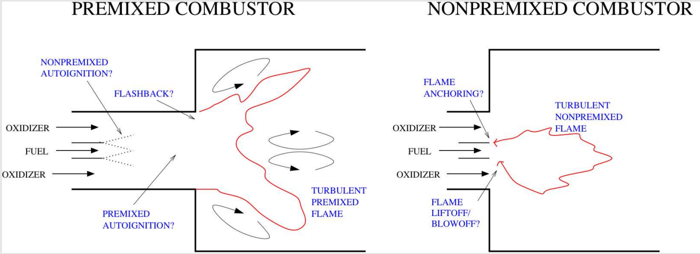




Chemistry Reduction

Methodology

- Validation for lean premixed systems: laminar deflagrations, homogeneous ignition, nonpremixed ignition
- Validation for nonpremixed sytems: laminar strained diffusion flames



Chemistry Reduction

Methodology

- Steady planar adiabatic deflagration ($\rho v = \rho_u v_l$).

$$\begin{aligned}
\rho_u v_l \frac{\mathrm{d} Y_i}{\mathrm{d} x} - \frac{\mathrm{d}}{\mathrm{d} x}\left(\frac{\rho D_T}{L_i}\frac{\mathrm{d} Y_i}{\mathrm{d} x}\right) &= W_i \omega_i \\
\rho_u v_l c_p \frac{\mathrm{d} T}{\mathrm{d} x} - \frac{\mathrm{d}}{\mathrm{d} x}\left(\lambda \frac{\mathrm{d} T}{\mathrm{d} x}\right) &= \sum_i h_i \omega_i
\end{aligned}$$

- Boundary conditions:

$$\begin{aligned}
x \to -\infty : \quad & Y_i - Y_{i\,u} = T - T_u &= 0 \\
x \to -\infty : \quad & \frac{\mathrm{d} Y_i}{\mathrm{d} x} = \frac{\mathrm{d} T}{\mathrm{d} x} &= 0
\end{aligned}$$

Chemistry Reduction

Methodology

- Counterflow diffusion flame ($v = -Ay$).

$$\begin{aligned} \rho A y \frac{\mathrm{d}Y_i}{\mathrm{d}y} + \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\rho D_T}{L_i}\frac{\mathrm{d}Y_i}{\mathrm{d}y}\right) &= -W_i\omega_i \\ \rho A c_p y \frac{\mathrm{d}T}{\mathrm{d}y} + \frac{\mathrm{d}}{\mathrm{d}y}\left(\lambda \frac{\mathrm{d}T}{\mathrm{d}y}\right) &= -\sum_i h_i\omega_i \end{aligned}$$

- Boundary conditions:

$$\begin{aligned} y \to -\infty : \quad Y_i - Y_{i_{-\infty}} = T - T_{-\infty} &= 0 \\ y \to -\infty : \quad Y_i - Y_{i_{\infty}} = T - T_{\infty} &= 0 \end{aligned}$$

Chemistry Reduction

Methodology

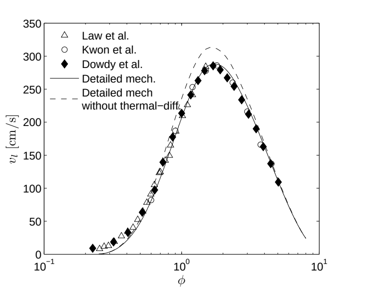
- Adiabatic ignition history in an homogeneous isobaric reactor:

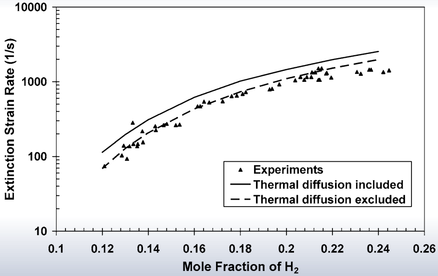
$$\rho \frac{\mathrm{d} Y_i}{\mathrm{d} t} = W_i \omega_i \qquad Y_i(0) = Y_{io}$$

$$\rho c_p \frac{\mathrm{d} T}{\mathrm{d} t} = \sum_i h_i \omega_i \qquad T(0) = T_o$$

Detailed H_2 chemistry

- San-Diego Mechanism: 8 chemical species, 21 reactions, thoroughly tested.





Detailed H_2 chemistry

1.	$H + O_2 \rightleftharpoons OH + O$
2.	$H_2 + O \rightleftharpoons OH + H$
3.	$H_2 + OH \rightleftharpoons H_2O + H$
4.	$H_2O + O \rightleftharpoons 2OH$
5.	$2H + M \rightleftharpoons H_2 + M$
6.	$H + OH + M \rightleftharpoons H_2O + M$
7.	$2O + M \rightleftharpoons O_2 + M$
8.	$H + O + M \rightleftharpoons OH + M$
9.	$O + OH + M \rightleftharpoons HO_2 + M$
10.	$H + O_2 + M \rightleftharpoons HO_2 + M$
11.	$HO_2 + H \rightleftharpoons 2OH$
12.	$HO_2 + H \rightleftharpoons H_2 + O_2$
13.	$HO_2 + H \rightleftharpoons H_2O + O$
14.	$HO_2 + O \rightleftharpoons OH + O_2$
15.	$HO_2 + OH \rightleftharpoons H_2O + O_2$
16.	$2OH + M \rightleftharpoons H_2O_2 + M$
17.	$2HO_2 \rightleftharpoons H_2O_2 + O_2$
18.	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$
19.	$H_2O_2 + H \rightleftharpoons H_2O + OH$
20.	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$
21.	$H_2O_2 + O \rightleftharpoons HO_2 + OH$

21 elementary reactions from a detailed mechanism
(University of California, San Diego)

Detailed H_2 chemistry

1. $H + O_2 \rightleftharpoons OH + O$
2. $H_2 + O \rightleftharpoons OH + H$
3. $H_2 + OH \rightleftharpoons H_2O + H$
4.
5. $2H + M \rightleftharpoons H_2 + M$
6. $H + OH + M \rightleftharpoons H_2O + M$
7.
8.
9.
10. $H + O_2 + M \rightleftharpoons HO_2 + M$
11. $HO_2 + H \rightleftharpoons 2OH$
12. $HO_2 + H \rightleftharpoons H_2 + O_2$
13.
14.
15. $HO_2 + OH \rightleftharpoons H_2O + O_2$
16. $2OH + M \rightleftharpoons H_2O_2 + M$
17. $2HO_2 \rightleftharpoons H_2O_2 + O_2$
18. $H_2O_2 + H \rightleftharpoons HO_2 + H_2$
19.
20.
21.

Crossover Temp.: $k_{1f} C_{\mathrm{O_2}} C_{\mathrm{H}} = k_{10f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}}$

$$k_{1f} = k_{10f} \frac{p}{R_o T} \begin{cases} T_c \simeq 1000\mathrm{K \ at \ } p = 1\mathrm{atm} \\ T_c \simeq 1500\mathrm{K \ at \ } p = 100\mathrm{atm} \end{cases}$$

Skeletal mechanism

Skeletal mechanism
12 elementary steps, 8 species

$$
\begin{array}{rcll}
H + O_2 & \rightleftharpoons & OH + O & (1) \\
H_2 + O & \rightleftharpoons & OH + H & (2) \\
H_2 + OH & \rightleftharpoons & H_2O + H & (3) \\
H + O_2 + M & \rightharpoonup & HO_2 + M & (4) \\
HO_2 + H & \rightharpoonup & 2OH & (5) \\
HO_2 + H & \rightleftharpoons & H_2 + O_2 & (6) \\
HO_2 + OH & \rightharpoonup & H_2O + O_2 & (7) \\
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H + H + M & \rightleftharpoons & H_2 + M & (9) \\
HO_2 + HO_2 & \rightharpoonup & H_2O_2 + O_2 & (10) \\
HO_2 + H_2 & \rightharpoonup & H_2O_2 + H & (11) \\
H_2O_2 + M & \rightharpoonup & 2OH + M & (12)
\end{array}
$$

Justification

Reactions 1-7	describe accurately **lean** premixed combustion (ignition and deflagration) at atmospheric pressures
Reactions 8-9	Adding recombination reactions gives better predictions for **stoichiometric and rich** mixtures. Also allows a good description of the **equilibrium at high temperatures**.
Reactions 10-12	include the chemistry of H_2O_2, important for **high-pressure flames** and **low-temperature ignition**.

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\end{array}
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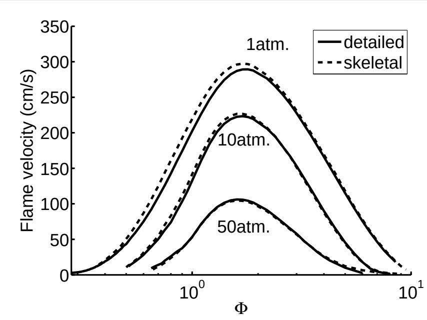
Validation



Laminar flame speed of steady planar flames
$T_0 = 300K$

Skeletal mechanism

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12 elementary steps, 8 species

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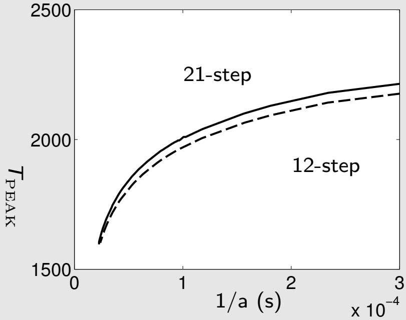

Peak temperature as a function of strain rate for a H_2-air counterflow flame

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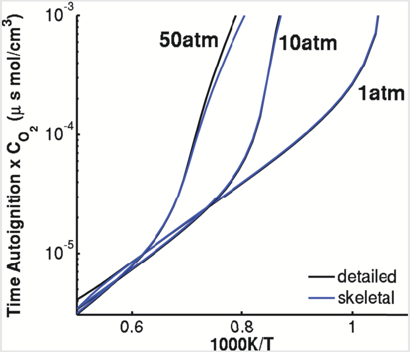
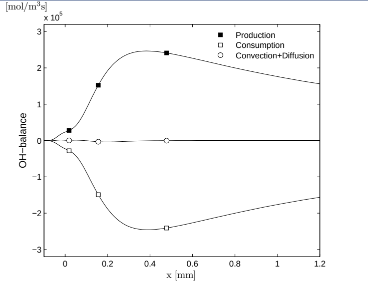


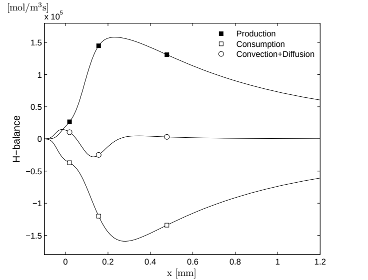
Induction time of a stoichiometric homogeneous mixture

The steady-state approximations

- Laminar premixed flame, $p = 1\text{atm}$, $T_u = 300\text{K}$, and $\phi = 0.8$:



(a) OH



(b) H

$$\underbrace{\rho\frac{\mathrm{D}Y_i}{\mathrm{D}t} - \nabla\cdot(\rho D_i \nabla Y_i)}_{\text{transport}} = \underbrace{\omega_{p,i}W_i}_{\text{production}} - \underbrace{\omega_{c,i}W_i}_{\text{consumption}}$$

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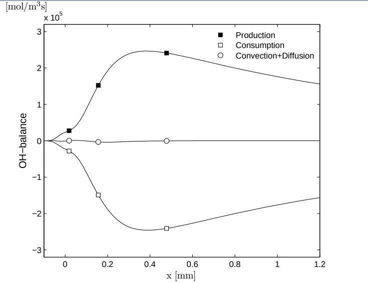

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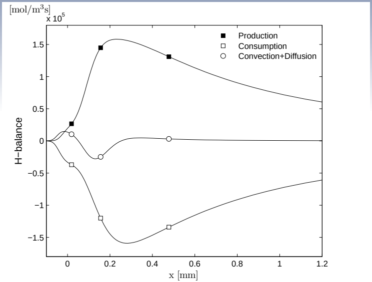

(b) H

$$\underbrace{\cancel{\rho\frac{\mathrm{D}Y_i}{\mathrm{D}t} - \nabla\cdot(\rho D_i \nabla Y_i)}}_{\text{transport}} = \underbrace{\omega_{p,i} W_i}_{\text{production}} - \underbrace{\omega_{c,i} W_i}_{\text{consumption}} \quad \rightarrow \omega_{p,i} = \omega_{c,i}$$

Reduced chemistry in H_2-air flames

Steady-State Analysis

All intermediates but H are in steady state

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Steady-State Analysis

All intermediates but H are in steady state

H_2 reduced mechanism

$$3H_2 + O_2 \overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H, \qquad \omega_{\mathrm{I}} \simeq w_1$$

$$2H + M \overset{\mathrm{II}}{\rightleftharpoons} H_2 + M, \qquad \omega_{\mathrm{II}} \simeq w_{4f}$$

Reduced chemistry in H_2-air flames

Steady-State Analysis

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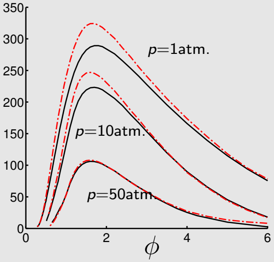
Premixed flame



Laminar flame speed of steady planar flames. $T_0 = 300$K

Reduced chemistry in H_2-air flames

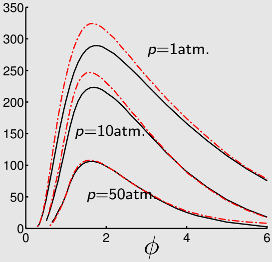
Steady-State Analysis

All intermediates but H are in steady state

H_2 reduced mechanism

$$3\mathrm{H}_2 + \mathrm{O}_2 \overset{\mathrm{I}}{\rightleftharpoons} 2\mathrm{H}_2\mathrm{O} + 2\mathrm{H}, \qquad \omega_{\mathrm{I}} \simeq w_1$$
$$2\mathrm{H} + \mathrm{M} \overset{\mathrm{II}}{\rightleftharpoons} \mathrm{H}_2 + \mathrm{M}, \qquad \omega_{\mathrm{II}} \simeq w_{4f}$$

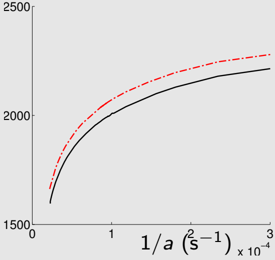
Premixed flame



Laminar flame speed of steady planar flames. $T_0 = 300\mathrm{K}$

Diffusion flame

Variation with strain rate of the maximum temperature in a hydrogen-air counterflow diffusion flame.
$T_0 = 300K, \quad P = 1\mathrm{atm}.$



Reduced chemistry and autoignition

2-step reduced mechanism

$$3H_2 + O_2 \overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H$$
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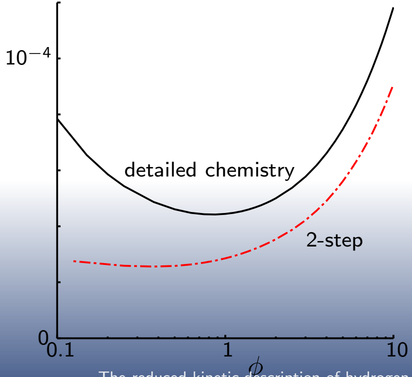

Induction time (s)

of a homogeneous mixture
$T_0 = 1200\mathrm{K}, \quad p = 1\mathrm{atm}.$

Reduced chemistry and autoignition

2-step reduced mechanism

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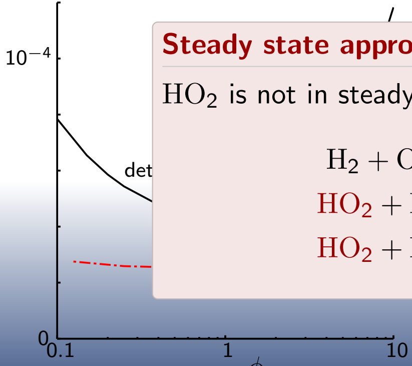

Steady state approximations

HO_2 is not in steady-state during autoignition.

$$H_2 + O_2 \rightharpoonup \color{red}{HO_2} + H$$
$$\color{red}{HO_2} + H \rightharpoonup 2OH$$
$$\color{red}{HO_2} + H \rightharpoonup H_2 + O_2$$

$T_0 = 1200\mathrm{K}, \quad p{=}1\mathrm{atm}.$

Reduced chemistry and autoignition

2-step reduced mechanism

$$3H_2 + O_2 \overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H$$
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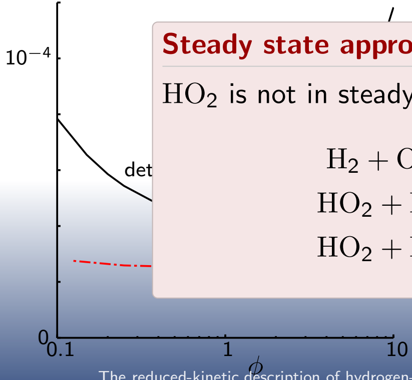
3-step including HO_2

$$H_2 + O_2 \overset{\mathrm{III}}{\rightleftharpoons} HO_2 + H$$



Steady state approximations

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$$H_2 + O_2 \rightharpoonup HO_2 + H$$
$$HO_2 + H \rightharpoonup 2OH$$
$$HO_2 + H \rightharpoonup H_2 + O_2$$

$T_0 = 1200\mathrm{K}$, p=1atm.

Reduced chemistry and autoignition

2-step reduced mechanism

$$3H_2 + O_2 \overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H$$
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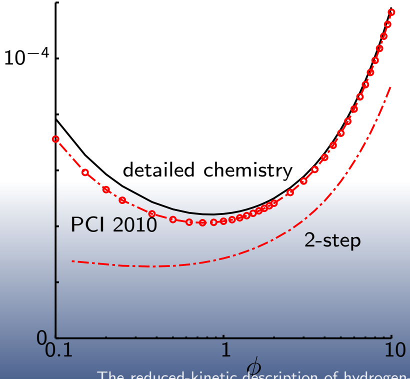


3-step including HO_2

$$H_2 + O_2 \overset{\mathrm{III}}{\rightleftharpoons} HO_2 + H$$

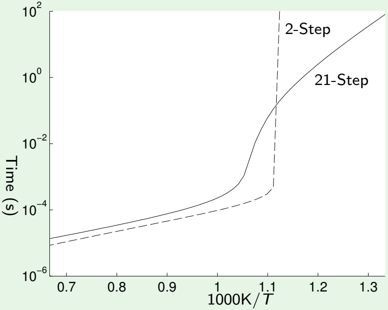
Good agreement is obtained in induction time for all ϕ by including HO_2 out of steady state **and a correction for the branching time** accounting for departures of O and OH from steady state.

Induction time (s)

of a homogeneous mixture
$T_0 = 1200$K, p=1atm.

Combustion problems relevant for safety applications

Low-Temperature Ignition



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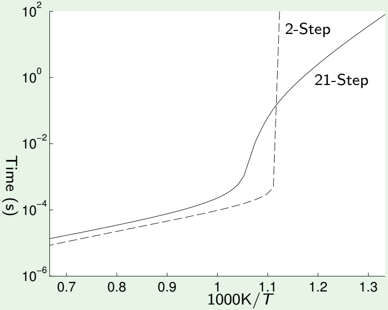
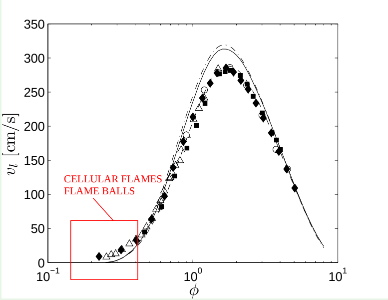


Very fuel-lean flames



Ignition above crossover

H_2 reduced mechanism

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Ignition above crossover

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2H + M &\overset{\mathrm{II}}{\rightleftharpoons} H_2 + M
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}} &= k_{6b} C_{\mathrm{H}_2} C_{\mathrm{O}_2} + k_{1f} C_{\mathrm{O}_2} C_{\mathrm{H}} \\
\omega_{\mathrm{II}} &= k_{4f} C_{\mathrm{M}} C_{\mathrm{O}_2} C_{\mathrm{H}}
\end{aligned}
$$

Ignition above crossover

H_2 reduced mechanism

$$
\begin{aligned}
3\mathrm{H_2} + \mathrm{O_2} &\overset{\mathrm{I}}{\rightleftharpoons} 2\mathrm{H_2O} + 2\mathrm{H} \\
2\mathrm{H} + \mathrm{M} &\overset{\mathrm{II}}{\rightleftharpoons} \mathrm{H_2} + \mathrm{M}
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}} &= k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_{1f} C_{\mathrm{O_2}} C_{\mathrm{H}} \\
\omega_{\mathrm{II}} &= k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}}
\end{aligned}
$$

Branched-chain explosion

$$
\frac{\mathrm{d} C_{\mathrm{H}}}{\mathrm{d} t} = 2 k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + 2(k_{1f} - k_{4f} C_{\mathrm{M}}) C_{\mathrm{O_2}} C_{\mathrm{H}}; \quad C_{\mathrm{H}}(0) = 0
$$

Ignition above crossover

H_2 reduced mechanism

$$\begin{aligned} 3H_2 + O_2 &\overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H \\ 2H + M &\overset{\mathrm{II}}{\rightleftharpoons} H_2 + M \end{aligned}$$

$$\begin{aligned} \omega_{\mathrm{I}} &= k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_{1f} C_{\mathrm{O_2}} C_{\mathrm{H}} \\ \omega_{\mathrm{II}} &= k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}} \end{aligned}$$

Branched-chain explosion

$$\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}t} = 2k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + 2(k_{1f} - k_{4f} C_{\mathrm{M}}) C_{\mathrm{O_2}} C_{\mathrm{H}}; \quad C_{\mathrm{H}}(0) = 0$$

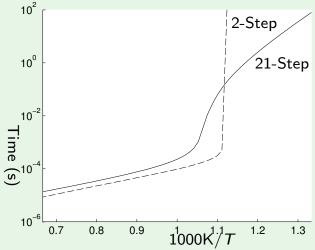
$$C_{\mathrm{H}} = \varepsilon C_{\mathrm{H_2}} \left[e^{2(k_{1f} - k_{4f} C_{\mathrm{M}}) C_{\mathrm{O_2}} t} - 1 \right]; \quad \varepsilon = \frac{k_{6b}}{k_{1f} - k_{4f} C_{\mathrm{M}}} \sim 10^{-6}$$

Ignition above crossover

H_2 reduced mechanism

$$
\begin{aligned}
3H_2 + O_2 &\overset{\mathrm{I}}{\rightleftharpoons} 2H_2O + 2H \\
2H + M &\overset{\mathrm{II}}{\rightleftharpoons} H_2 + M
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}} &= k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_{1f} C_{\mathrm{O_2}} C_{\mathrm{H}} \\
\omega_{\mathrm{II}} &= k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}}
\end{aligned}
$$



Branched-chain explosion

$$
\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}t} = 2k_{6b} C_{\mathrm{H_2}} C_{\mathrm{O_2}} + 2(k_{1f} - k_{4f} C_{\mathrm{M}}) C_{\mathrm{O_2}} C_{\mathrm{H}}; \quad C_{\mathrm{H}}(0) = 0
$$

$$
C_{\mathrm{H}} = \varepsilon C_{\mathrm{H_2}} \left[e^{2(k_{1f} - k_{4f} C_{\mathrm{M}}) C_{\mathrm{O_2}} t} - 1 \right]; \quad \varepsilon = \frac{k_{6b}}{k_{1f} - k_{4f} C_{\mathrm{M}}} \sim 10^{-6}
$$

Low-temperature ignition

Initial skeletal mechanism

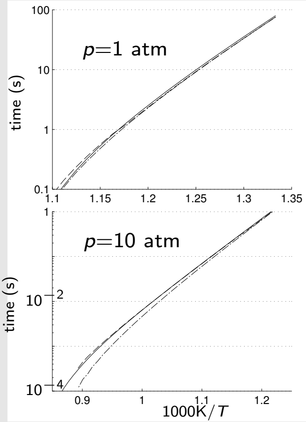
$$
\begin{array}{rcl}
H + O_2 & \overset{1}{\rightleftharpoons} & OH + O \\
H_2 + O & \overset{2}{\rightleftharpoons} & OH + H \\
H_2 + OH & \overset{3}{\rightleftharpoons} & H_2O + H \\
H + O_2 + M & \overset{4}{\rightharpoonup} & HO_2 + M \\
HO_2 + H & \overset{5}{\rightharpoonup} & 2OH \\
HO_2 + H & \overset{6}{\rightleftharpoons} & H_2 + O_2 \\
HO_2 + OH & \overset{7}{\rightharpoonup} & H_2O + O_2 \\
H + OH + M & \overset{8}{\rightleftharpoons} & H_2O + M \\
H + H + M & \overset{9}{\rightleftharpoons} & H_2 + M \\
HO_2 + HO_2 & \overset{10}{\rightharpoonup} & H_2O_2 + O_2 \\
HO_2 + H_2 & \overset{11}{\rightharpoonup} & H_2O_2 + H \\
H_2O_2 + M & \overset{12}{\rightharpoonup} & 2OH + M
\end{array}
$$

Low-temperature ignition

Initial skeletal mechanism

$$
\begin{array}{rcl}
H + O_2 & \overset{1}{\rightleftharpoons} & OH + O \\
H_2 + O & \overset{2}{\rightleftharpoons} & OH + H \\
H_2 + OH & \overset{3}{\rightleftharpoons} & H_2O + H \\
H + O_2 + M & \overset{4}{\rightharpoonup} & HO_2 + M \\
 & & \\
HO_2 + H & \overset{6}{\leftharpoondown} & H_2 + O_2 \\
 & & \\
 & & \\
HO_2 + HO_2 & \overset{10}{\rightharpoonup} & H_2O_2 + O_2 \\
HO_2 + H_2 & \overset{11}{\rightharpoonup} & H_2O_2 + H \\
H_2O_2 + M & \overset{12}{\rightharpoonup} & 2OH + M
\end{array}
$$

Validation



21 (solid), 8 (dashed), 3 (dot-dashed)

3-step Reduced Mechanism (Treviño, 1991)

Initial skeletal mechanism

$$
\begin{aligned}
H + O_2 &\xrightarrow{1} OH + O \\
H_2 + O &\xrightarrow{2} OH + H \\
H_2 + OH &\xrightarrow{3} H_2O + H \\
H + O_2 + M &\xrightarrow{4} HO_2 + M \\
H_2 + O_2 &\xrightarrow{5} HO_2 + H \\
HO_2 + HO_2 &\xrightarrow{6} H_2O_2 + O_2 \\
HO_2 + H_2 &\xrightarrow{7} H_2O_2 + H \\
H_2O_2 + M &\xrightarrow{8} 2OH + M
\end{aligned}
$$

3-step Reduced Mechanism (Treviño, 1991)

Initial skeletal mechanism

$$
\begin{aligned}
H + O_2 &\xrightarrow{1} OH + O \\
H_2 + O &\xrightarrow{2} OH + H \\
H_2 + OH &\xrightarrow{3} H_2O + H \\
H + O_2 + M &\xrightarrow{4} HO_2 + M \\
H_2 + O_2 &\xrightarrow{5} HO_2 + H \\
HO_2 + HO_2 &\xrightarrow{6} H_2O_2 + O_2 \\
HO_2 + H_2 &\xrightarrow{7} H_2O_2 + H \\
H_2O_2 + M &\xrightarrow{8} 2OH + M
\end{aligned}
$$

Steady-state intermediates

H, O, OH

3-step Reduced Mechanism (Treviño, 1991)

Initial skeletal mechanism

$$\begin{aligned}
H + O_2 &\xrightarrow{1} OH + O \\
H_2 + O &\xrightarrow{2} OH + H \\
H_2 + OH &\xrightarrow{3} H_2O + H \\
H + O_2 + M &\xrightarrow{4} HO_2 + M \\
H_2 + O_2 &\xrightarrow{5} HO_2 + H \\
HO_2 + HO_2 &\xrightarrow{6} H_2O_2 + O_2 \\
HO_2 + H_2 &\xrightarrow{7} H_2O_2 + H \\
H_2O_2 + M &\xrightarrow{8} 2OH + M
\end{aligned}$$

Steady-state intermediates

H, O, OH

3-step reduced mechanism

$$\begin{aligned}
2H_2 + O_2 &\xrightarrow{I^*} 2H_2O \\
H_2O_2 + H_2 &\overset{II^*}{\rightleftharpoons} 2H_2O \\
H_2 + 2O_2 &\overset{III^*}{\rightleftharpoons} 2HO_2
\end{aligned}$$

3-step Reduced Mechanism (Treviño, 1991)

Initial skeletal mechanism

$$
\begin{aligned}
H + O_2 &\xrightarrow{1} OH + O \\
H_2 + O &\xrightarrow{2} OH + H \\
H_2 + OH &\xrightarrow{3} H_2O + H \\
H + O_2 + M &\xrightarrow{4} HO_2 + M \\
H_2 + O_2 &\xrightarrow{5} HO_2 + H \\
HO_2 + HO_2 &\xrightarrow{6} H_2O_2 + O_2 \\
HO_2 + H_2 &\xrightarrow{7} H_2O_2 + H \\
H_2O_2 + M &\xrightarrow{8} 2OH + M
\end{aligned}
$$

Steady-state intermediates

H, O, OH

3-step reduced mechanism

$$
\begin{aligned}
2H_2 + O_2 &\xrightarrow{\mathrm{I}^*} 2H_2O \\
H_2O_2 + H_2 &\overset{\mathrm{II}^*}{\rightleftharpoons} 2H_2O \\
H_2 + 2O_2 &\overset{\mathrm{III}^*}{\rightleftharpoons} 2HO_2
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}^*} &= w_1 + w_6 + w_7 \\
\omega_{\mathrm{II}^*} &= -w_6 - w_7 + w_8 \\
\omega_{\mathrm{III}^*} &= \frac{w_4 + w_5 - 2w_6 - w_7}{2}
\end{aligned}
$$

3-step Reduced Mechanism (Treviño, 1991)

Initial skeletal mechanism

$$
\begin{aligned}
H + O_2 &\xrightarrow{1} OH + O \\
H_2 + O &\xrightarrow{2} OH + H \\
H_2 + OH &\xrightarrow{3} H_2O + H \\
H + O_2 + M &\xrightarrow{4} HO_2 + M \\
H_2 + O_2 &\xrightarrow{5} HO_2 + H \\
HO_2 + HO_2 &\xrightarrow{6} H_2O_2 + O_2 \\
HO_2 + H_2 &\xrightarrow{7} H_2O_2 + H \\
H_2O_2 + M &\xrightarrow{8} 2OH + M
\end{aligned}
$$

Steady-state expression for H

$$
C_H = \frac{k_5 C_{H_2} C_{O_2} + k_7 C_{H_2} C_{HO_2} + 2k_8 C_{H_2O_2} C_M}{(k_4 C_M - k_1) C_{O_2}}
$$

Steady-state intermediates

H, O, OH

3-step reduced mechanism

$$
\begin{aligned}
2H_2 + O_2 &\xrightarrow{I^*} 2H_2O \\
H_2O_2 + H_2 &\overset{II^*}{\rightleftharpoons} 2H_2O \\
H_2 + 2O_2 &\overset{III^*}{\rightleftharpoons} 2HO_2
\end{aligned}
$$

$$
\begin{aligned}
\omega_{I^*} &= w_1 + w_6 + w_7 \\
\omega_{II^*} &= -w_6 - w_7 + w_8 \\
\omega_{III^*} &= \frac{w_4 + w_5 - 2w_6 - w_7}{2}
\end{aligned}
$$

3-step Reduced Mechanism (Treviño, 1991)

3-step reduced mechanism

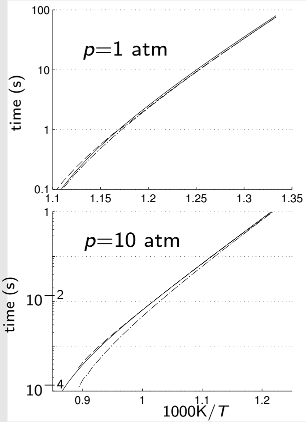
$$
\begin{aligned}
2\mathrm{H_2} + \mathrm{O_2} &\xrightarrow{\mathrm{I}^*} 2\mathrm{H_2O} \\
\mathrm{H_2O_2} + \mathrm{H_2} &\overset{\mathrm{II}^*}{\rightleftharpoons} 2\mathrm{H_2O} \\
\mathrm{H_2} + 2\mathrm{O_2} &\overset{\mathrm{III}^*}{\rightleftharpoons} 2\mathrm{HO_2}
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}^*} &= w_1 + w_6 + w_7 \\
\omega_{\mathrm{II}^*} &= -w_6 - w_7 + w_8 \\
\omega_{\mathrm{III}^*} &= \frac{w_4 + w_5 - 2w_6 - w_7}{2}
\end{aligned}
$$

$$
C_{\mathrm{H}} = \frac{k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_7 C_{\mathrm{H_2}} C_{\mathrm{HO_2}} + 2k_8 C_{\mathrm{H_2O_2}} C_{\mathrm{M}}}{(k_4 C_{\mathrm{M}} - k_1) C_{\mathrm{O_2}}}
$$

3-step Reduced Mechanism (Treviño, 1991)

Validation



21 (solid), 8 (dashed), 3 (dot-dashed)

3-step reduced mechanism

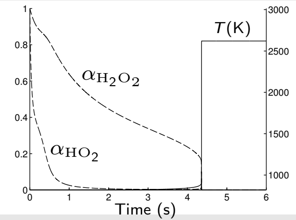
$$
\begin{aligned}
2H_2 + O_2 &\xrightarrow{\mathrm{I}^*} 2H_2O \\
H_2O_2 + H_2 &\overset{\mathrm{II}^*}{\rightleftharpoons} 2H_2O \\
H_2 + 2O_2 &\overset{\mathrm{III}^*}{\rightleftharpoons} 2HO_2
\end{aligned}
$$

$$
\begin{aligned}
\omega_{\mathrm{I}^*} &= w_1 + w_6 + w_7 \\
\omega_{\mathrm{II}^*} &= -w_6 - w_7 + w_8 \\
\omega_{\mathrm{III}^*} &= \frac{w_4 + w_5 - 2w_6 - w_7}{2}
\end{aligned}
$$

$$
C_{\mathrm{H}} = \frac{k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_7 C_{\mathrm{H_2}} C_{\mathrm{HO_2}} + 2k_8 C_{\mathrm{H_2O_2}} C_{\mathrm{M}}}{(k_4 C_{\mathrm{M}} - k_1) C_{\mathrm{O_2}}}
$$

3-step Reduced Mechanism (Treviño, 1991)

Thermal explosion



$$\alpha_i = \frac{|\dot{C}_{i_P} - \dot{C}_{i_C}|}{\dot{C}_{i_P}}$$

3-step reduced mechanism

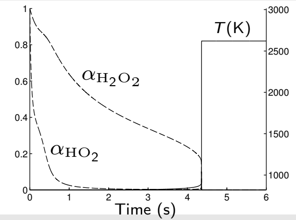
$$\begin{array}{rcl} 2\mathrm{H_2} + \mathrm{O_2} & \xrightarrow{\mathrm{I}^*} & 2\mathrm{H_2O} \\ \mathrm{H_2O_2} + \mathrm{H_2} & \overset{\mathrm{II}^*}{\rightleftharpoons} & 2\mathrm{H_2O} \\ \mathrm{H_2} + 2\mathrm{O_2} & \overset{\mathrm{III}^*}{\rightleftharpoons} & 2\mathrm{HO_2} \end{array}$$

$$\begin{aligned} \omega_{\mathrm{I}^*} &= w_1 + w_6 + w_7 \\ \omega_{\mathrm{II}^*} &= -w_6 - w_7 + w_8 \\ \omega_{\mathrm{III}^*} &= \frac{w_4 + w_5 - 2w_6 - w_7}{2} \end{aligned}$$

$$C_{\mathrm{H}} = \frac{k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}} + k_7 C_{\mathrm{H_2}} C_{\mathrm{HO_2}} + 2k_8 C_{\mathrm{H_2O_2}} C_{\mathrm{M}}}{(k_4 C_{\mathrm{M}} - k_1) C_{\mathrm{O_2}}}$$

3-step Reduced Mechanism (Treviño, 1991)

Thermal explosion



$$\alpha_i = \frac{|\dot{C}_{i_P} - \dot{C}_{i_C}|}{\dot{C}_{i_P}}$$

HO_2 reaches steady state after a short initial period

3-step reduced mechanism

$$2H_2 + O_2 \xrightarrow{I^*} 2H_2O$$
$$H_2O_2 + H_2 \overset{II^*}{\rightleftharpoons} 2H_2O$$
$$H_2 + 2O_2 \overset{III^*}{\rightleftharpoons} 2HO_2$$

$$\omega_{I^*} = w_1 + w_6 + w_7$$
$$\omega_{II^*} = -w_6 - w_7 + w_8$$
$$\omega_{III^*} = \frac{w_4 + w_5 - 2w_6 - w_7}{2}$$

$$C_H = \frac{k_5 C_{H_2} C_{O_2} + k_7 C_{H_2} C_{HO_2} + 2k_8 C_{H_2O_2} C_M}{(k_4 C_M - k_1) C_{O_2}}$$

2-step Reduced Mechanism

$$\dot{C}_{\mathrm{HO_2}} = w_4 + w_5 - 2w_6 - w_7 = 0$$

2-step Reduced Mechanism

$$\dot{C}_{\mathrm{HO_2}} = w_4 + w_5 - 2w_6 - w_7 = 0$$

2-step reduced mechanism

$$\mathrm{2H_2 + O_2 \xrightarrow{I} 2H_2O}$$
$$\mathrm{2H_2O \xrightarrow{II} H_2O_2 + H_2}$$

Global rates

$$\omega_{\mathrm{I}} = \frac{w_5 + w_7 + (1+\alpha)w_8}{1-\alpha}$$
$$\omega_{\mathrm{II}} = \frac{(1-\frac{1}{2}\alpha)(w_5 + w_7) + \alpha w_8}{1-\alpha}$$

$$\alpha = \frac{2k_1}{k_4 C_{\mathrm{M_4}}},\ w_5 = k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}},\ w_6 = k_6 C^2_{\mathrm{HO_2}},\ w_7 = k_7 C_{\mathrm{HO_2}} C_{\mathrm{H_2}},\ w_8 = k_8 C_{\mathrm{M}} C_{\mathrm{H_2O_2}}$$

2-step Reduced Mechanism

$$\dot{C}_{\mathrm{HO_2}} = w_4 + w_5 - 2w_6 - w_7 = 0$$

2-step reduced mechanism

$$\begin{aligned} 2\mathrm{H_2} + \mathrm{O_2} &\xrightarrow{\mathrm{I}} 2\mathrm{H_2O} \\ 2\mathrm{H_2O} &\xrightarrow{\mathrm{II}} \mathrm{H_2O_2} + \mathrm{H_2} \end{aligned}$$

Global rates

$$\omega_{\mathrm{I}} = \frac{w_5 + w_7 + (1+\alpha)w_8}{1-\alpha}$$

$$\omega_{\mathrm{II}} = \frac{(1-\frac{1}{2}\alpha)(w_5 + w_7) + \alpha w_8}{1-\alpha}$$

$$\alpha = \frac{2k_1}{k_4 C_{\mathrm{M_4}}},\ w_5 = k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}},\ w_6 = k_6 C^2_{\mathrm{HO_2}},\ w_7 = k_7 C_{\mathrm{HO_2}} C_{\mathrm{H_2}},\ w_8 = k_8 C_{\mathrm{M}} C_{\mathrm{H_2O_2}}$$

Conservation equations

$$\frac{\mathrm{d}C_{\mathrm{H_2O_2}}}{\mathrm{d}t} = \omega_{\mathrm{II}}$$

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}t} = -2h_{\mathrm{H_2O}}(\omega_{\mathrm{I}} - \omega_{\mathrm{II}}) - h_{\mathrm{H_2O_2}}\omega_{\mathrm{II}}$$

Init. Conditions

$$C_{\mathrm{H_2O_2}}(0) = T(0) - T_o = 0$$

2-step Reduced Mechanism

$$\dot{C}_{\mathrm{HO_2}} = w_4 + w_5 - 2w_6 - w_7 = 0 \Rightarrow C_{\mathrm{HO_2}} \simeq \left(\frac{(2-\alpha)w_5 + 2w_8}{2(1-\alpha)k_6}\right)^{1/2}$$

2-step reduced mechanism

$$\begin{aligned} 2\mathrm{H_2} + \mathrm{O_2} &\xrightarrow{\mathrm{I}} 2\mathrm{H_2O} \\ 2\mathrm{H_2O} &\xrightarrow{\mathrm{II}} \mathrm{H_2O_2} + \mathrm{H_2} \end{aligned}$$

Global rates

$$\omega_{\mathrm{I}} = \frac{w_5 + w_7 + (1+\alpha)w_8}{1-\alpha}$$

$$\omega_{\mathrm{II}} = \frac{(1-\frac{1}{2}\alpha)(w_5 + w_7) + \alpha w_8}{1-\alpha}$$

$$\alpha = \frac{2k_1}{k_4 C_{\mathrm{M_4}}},\ w_5 = k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}},\ w_6 = k_6 C_{\mathrm{HO_2}}^2,\ w_7 = k_7 C_{\mathrm{HO_2}} C_{\mathrm{H_2}},\ w_8 = k_8 C_{\mathrm{M}} C_{\mathrm{H_2O_2}}$$

Conservation equations

$$\frac{\mathrm{d}C_{\mathrm{H_2O_2}}}{\mathrm{d}t} = \omega_{\mathrm{II}}$$

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}t} = -2h_{\mathrm{H_2O}}(\omega_{\mathrm{I}} - \omega_{\mathrm{II}}) - h_{\mathrm{H_2O_2}}\omega_{\mathrm{II}}$$

Init. Conditions

$$C_{\mathrm{H_2O_2}}(0) = T(0) - T_o = 0$$

2-step Reduced Mechanism

Using the approximations $w_5 = 0$ and $(w_8 - \frac{1}{2} w_7)\alpha = 0$ yields

Reduced global rates

$$\begin{aligned}
\omega_{\mathrm{I}} - \omega_{\mathrm{II}} &= = \frac{1+\alpha}{1-\alpha} k_8 C_{\mathrm{M}_8} C_{\mathrm{H}_2\mathrm{O}_2} \\
\omega_{\mathrm{II}} &= \frac{k_7 k_8^{1/2}}{k_6^{1/2}} \frac{C_{\mathrm{H}_2} C_{\mathrm{M}_8}}{(1-\alpha)^{3/2}} \left[\left(1 - \frac{\alpha}{2}\right) \frac{k_5 C_{\mathrm{H}_2} C_{\mathrm{O}_2}}{k_8 C_{\mathrm{M}_8}^2} + \frac{C_{\mathrm{H}_2\mathrm{O}_2}}{C_{\mathrm{M}_8}} \right]^{1/2}
\end{aligned}$$

2-step Reduced Mechanism

Using the approximations $w_5 = 0$ and $(w_8 - \frac{1}{2}w_7)\alpha = 0$ yields

Reduced global rates

$$\omega_{\mathrm{I}} - \omega_{\mathrm{II}} = = \frac{1+\alpha}{1-\alpha} k_8 C_{\mathrm{M}_8} C_{\mathrm{H_2O_2}}$$

$$\omega_{\mathrm{II}} = \frac{k_7 k_8^{1/2}}{k_6^{1/2}} \frac{C_{\mathrm{H_2}} C_{\mathrm{M}_8}}{(1-\alpha)^{3/2}} \left[\left(1 - \frac{\alpha}{2}\right) \frac{k_5 C_{\mathrm{H_2}} C_{\mathrm{O_2}}}{k_8 C_{\mathrm{M}_8}^2} + \frac{C_{\mathrm{H_2O_2}}}{C_{\mathrm{M}_8}} \right]^{1/2}$$

$$k_8 \propto e^{-\frac{E_8}{R_o T}}, \quad \frac{k_7 k_8^{1/2}}{k_6^{1/2}} \propto e^{-\frac{E_7 + \frac{1}{2}E_8 - \frac{1}{2}E_6}{R_o T}}$$

$$\text{with} \quad \beta = \frac{E_8}{R_o T_o} \simeq \frac{E_7 + \frac{1}{2}E_8 - \frac{1}{2}E_6}{R_o T_o} \simeq 30 \quad \text{for} \quad T_o = 800\mathrm{K}$$

Dimensionless Problem

Dimensionless variables

$$\varphi = \left[(1-\alpha)^{1/2}(1+\alpha)\beta q\right]^{2/3}\left(\frac{k_7}{(k_6 k_8)^{1/2}}\right)^{-2/3}\left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{-2/3}\frac{C_{\mathrm{H_2O_2}}}{C_{\mathrm{M_8}}}$$

$$\tau = \frac{(1+\alpha)^{1/3}}{(1-\alpha)^{4/3}}(\beta q)^{1/3} k_8 C_{\mathrm{M_8}}\left(\frac{k_7}{(k_6 k_8)^{1/2}}\right)^{2/3}\left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{2/3} t$$

$$\theta = \beta\frac{T-T_o}{T_o}, \qquad q = \frac{-2h_{\mathrm{H_2O}}C_{\mathrm{M_8}}}{\rho c_p T_o}$$

Dimensionless Problem

Dimensionless variables

$$\varphi = \left[(1-\alpha)^{1/2}(1+\alpha)\beta q\right]^{2/3}\left(\frac{k_7}{(k_6 k_8)^{1/2}}\right)^{-2/3}\left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{-2/3}\frac{C_{\mathrm{H_2O_2}}}{C_{\mathrm{M_8}}}$$

$$\tau = \frac{(1+\alpha)^{1/3}}{(1-\alpha)^{4/3}}(\beta q)^{1/3} k_8 C_{\mathrm{M_8}}\left(\frac{k_7}{(k_6 k_8)^{1/2}}\right)^{2/3}\left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{2/3} t$$

$$\theta = \beta\frac{T-T_o}{T_o}, \qquad q = \frac{-2h_{\mathrm{H_2O}}C_{\mathrm{M_8}}}{\rho c_p T_o}$$

Conservation equations

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2}e^{\theta}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda(a+\varphi)^{1/2}e^{\theta}$$

Init. Conditions

$$\varphi(0) = \theta = 0$$

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2} e^{\theta};\ \varphi(0) = 0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda (a+\varphi)^{1/2} e^{\theta};\ \theta(0) = 0$$

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2} e^{\theta};\ \varphi(0) = 0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda (a+\varphi)^{1/2} e^{\theta};\ \theta(0) = 0$$

$$a = \left(1 - \frac{\alpha}{2}\right)^{1/3} (1-\alpha)^{1/3} (1+\alpha)^{2/3} (\beta q)^{2/3} \frac{k_5 k_6^{1/3}}{(k_7 k_8)^{2/3}} \left(\frac{C_{\mathrm{H}_2}}{C_{\mathrm{M}_8}}\right)^{1/3} \left(\frac{C_{\mathrm{O}_2}}{C_{\mathrm{M}_8}}\right) \sim 10^{-5}$$

Initiation counts for $\tau \sim a^{1/2}$ when $\varphi \sim \theta \sim a$ but it is negligible at later times

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2} e^{\theta};\ \varphi(0) = 0$$
$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda (a+\varphi)^{1/2} e^{\theta};\ \theta(0) = 0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\varphi} = \Lambda + \varphi^{1/2}$$
$$\theta = (2/3)\varphi^{3/2} + \Lambda\varphi$$

$$a = \left(1 - \frac{\alpha}{2}\right)^{1/3} (1-\alpha)^{1/3} (1+\alpha)^{2/3} (\beta q)^{2/3} \frac{k_5 k_6^{1/3}}{(k_7 k_8)^{2/3}} \left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{1/3} \left(\frac{C_{\mathrm{O_2}}}{C_{\mathrm{M_8}}}\right) \sim 10^{-5}$$

Initiation counts for $\tau \sim a^{1/2}$ when $\varphi \sim \theta \sim a$ but it is negligible at later times

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2}e^{\theta};\ \varphi(0)=0$$
$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda(a+\varphi)^{1/2}e^{\theta};\ \theta(0)=0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\varphi} = \Lambda + \varphi^{1/2}$$
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$$a = \left(1-\frac{\alpha}{2}\right)^{1/3}(1-\alpha)^{1/3}(1+\alpha)^{2/3}(\beta q)^{2/3}\frac{k_5 k_6^{1/3}}{(k_7 k_8)^{2/3}}\left(\frac{C_{\mathrm{H}_2}}{C_{\mathrm{M}_8}}\right)^{1/3}\left(\frac{C_{\mathrm{O}_2}}{C_{\mathrm{M}_8}}\right) \sim 10^{-5}$$

Initiation counts for $\tau \sim a^{1/2}$ when $\varphi \sim \theta \sim a$ but it is negligible at later times

$$\tau_i = \int_0^{\infty} \frac{\mathrm{d}\varphi}{\varphi^{1/2}\exp\left(\frac{2}{3}\varphi^{3/2}+\Lambda\varphi\right)}$$

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2} e^{\theta};\ \varphi(0)=0$$
$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda (a+\varphi)^{1/2} e^{\theta};\ \theta(0)=0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\varphi} = \Lambda + \varphi^{1/2}$$
$$\theta = (2/3)\varphi^{3/2} + \Lambda\varphi$$

$$a = \left(1-\frac{\alpha}{2}\right)^{1/3} (1-\alpha)^{1/3}(1+\alpha)^{2/3}(\beta q)^{2/3} \frac{k_5 k_6^{1/3}}{(k_7 k_8)^{2/3}} \left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{1/3} \left(\frac{C_{\mathrm{O_2}}}{C_{\mathrm{M_8}}}\right) \sim 10^{-5}$$

Initiation counts for $\tau \sim a^{1/2}$ when $\varphi \sim \theta \sim a$ but it is negligible at later times

$\tau_i = \int_0^\infty \frac{\mathrm{d}\varphi}{\varphi^{1/2} \exp\left(\frac{2}{3}\varphi^{3/2} + \Lambda\varphi\right)}$

$$\Lambda = \left[\frac{k_7/(k_6 k_8)^{1/2}}{(1-\alpha)^{1/2}(1+\alpha)}\right]^{2/3} (\beta q)^{1/3} \left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{2/3} \frac{h_{\mathrm{H_2O_2}}}{2 h_{\mathrm{H_2O}}} \simeq 0.1$$

Ignition time

$$\frac{\mathrm{d}\varphi}{\mathrm{d}\tau} = (a+\varphi)^{1/2} e^{\theta};\ \varphi(0)=0$$
$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \varphi e^{\theta} + \Lambda (a+\varphi)^{1/2} e^{\theta};\ \theta(0)=0$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\varphi} = \Lambda + \varphi^{1/2}$$
$$\theta = (2/3)\varphi^{3/2} + \Lambda\varphi$$

$$a = \left(1-\frac{\alpha}{2}\right)^{1/3} (1-\alpha)^{1/3}(1+\alpha)^{2/3}(\beta q)^{2/3} \frac{k_5 k_6^{1/3}}{(k_7 k_8)^{2/3}} \left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{1/3} \left(\frac{C_{\mathrm{O_2}}}{C_{\mathrm{M_8}}}\right) \sim 10^{-5}$$

Initiation counts for $\tau \sim a^{1/2}$ when $\varphi \sim \theta \sim a$ but it is negligible at later times

$$\tau_i = \int_0^{\infty} \frac{\mathrm{d}\varphi}{\varphi^{1/2} \exp\left(\frac{2}{3}\varphi^{3/2} + \Lambda\varphi\right)} = (2/3)^{2/3}\Gamma(1/3) \simeq 2.0444$$

$$\Lambda = \left[\frac{k_7/(k_6 k_8)^{1/2}}{(1-\alpha)^{1/2}(1+\alpha)}\right]^{2/3} (\beta q)^{1/3} \left(\frac{C_{\mathrm{H_2}}}{C_{\mathrm{M_8}}}\right)^{2/3} \frac{h_{\mathrm{H_2O_2}}}{2 h_{\mathrm{H_2O}}} \simeq 0.1$$

Ignition time

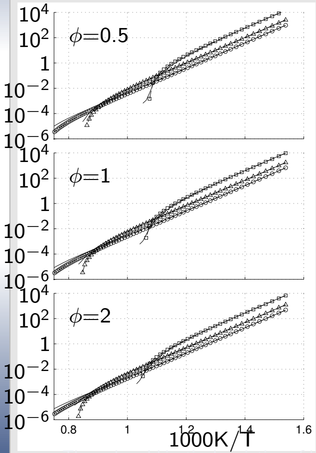
Explicit analytic prediction

$$t_i \quad = \quad 2.0444\frac{(1-\alpha)^{4/3}}{(1+\alpha)^{1/3}}(\beta q)^{-1/3}(k_8 C_{\mathrm{M}_8})^{-1}\left(\frac{k_7}{(k_6 k_8)^{1/2}}\right)^{-2/3}\left(\frac{C_{\mathrm{H}_2}}{C_{\mathrm{M}_8}}\right)^{-2/3}$$

Ignition time

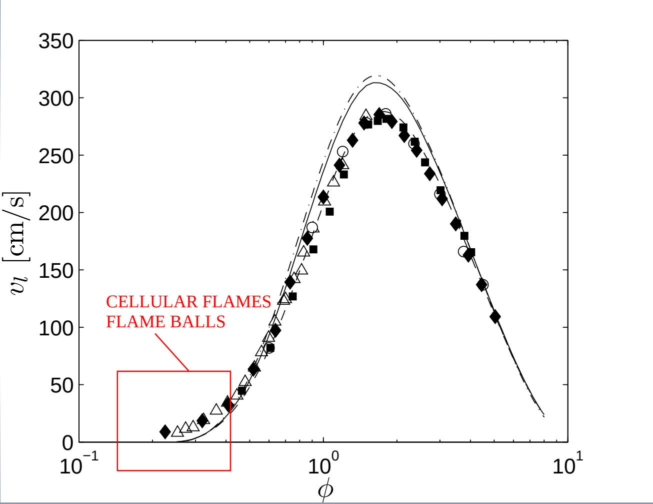
Explicit analytic prediction

$$t_i = 2.0444 \frac{(1-\alpha)^{4/3}}{(1+\alpha)^{1/3}} (\beta q)^{-1/3} (k_8 C_{\mathrm{M}_8})^{-1} \left(\frac{k_7}{(k_6 k_8)^{1/2}} \right)^{-2/3} \left(\frac{C_{\mathrm{H}_2}}{C_{\mathrm{M}_8}} \right)^{-2/3}$$



21-step (solid curves)
t_i for $p=$ 1 atm (squares)
t_i for $p=$ 10 atm (triangles)
t_i for $p=$ 50 atm (circles)

Very lean flames and flammability limit



Skeletal mechanism for very lean flames

Skeletal mechanism
12 elementary steps, 8 species

$$
\begin{aligned}
H + O_2 &\overset{1}{\rightleftharpoons} OH + O \\
H_2 + O &\overset{2}{\rightleftharpoons} OH + H \\
H_2 + OH &\overset{3}{\rightleftharpoons} H_2O + H \\
H + O_2 + M &\overset{4}{\rightharpoonup} HO_2 + M \\
HO_2 + H &\overset{5}{\rightharpoonup} 2OH \\
HO_2 + H &\overset{6}{\rightleftharpoons} H_2 + O_2 \\
HO_2 + OH &\overset{7}{\rightharpoonup} H_2O + O_2 \\
H + OH + M &\overset{8}{\rightleftharpoons} H_2O + M \\
H + H + M &\overset{9}{\rightleftharpoons} H_2 + M \\
HO_2 + HO_2 &\overset{10}{\rightharpoonup} H_2O_2 + O_2 \\
HO_2 + H_2 &\overset{11}{\rightharpoonup} H_2O_2 + H \\
H_2O_2 + M &\overset{12}{\rightharpoonup} 2OH + M
\end{aligned}
$$

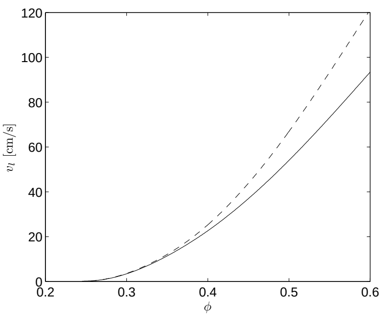
Skeletal mechanism for very lean flames

Skeletal mechanism
12 elementary steps, 8 species

$$\begin{array}{rcl}
H + O_2 & \stackrel{1}{\rightleftharpoons} & OH + O \\
H_2 + O & \stackrel{2}{\rightleftharpoons} & OH + H \\
H_2 + OH & \stackrel{3}{\rightleftharpoons} & H_2O + H \\
H + O_2 + M & \stackrel{4}{\rightharpoondown} & HO_2 + M \\
HO_2 + H & \stackrel{5}{\rightharpoondown} & 2OH \\
HO_2 + H & \stackrel{6}{\rightleftharpoons} & H_2 + O_2 \\
HO_2 + OH & \stackrel{7}{\rightharpoondown} & H_2O + O_2
\end{array}$$

Simplification

Reactions 1-7 describe accurately **lean** deflagrations at atmospheric and moderately elevated pressures



One-step reduced mechanism

1. $H+O_2 \rightleftharpoons OH+O$
2. $H_2+O \rightleftharpoons OH+H$
3. $H_2+OH \rightleftharpoons H_2O+H$

4f. $H+O_2+M \rightarrow HO_2+M$

5f. $HO_2+H \rightarrow OH+OH$

6f. $HO_2+H \rightarrow H_2+O_2$

7f. $HO_2+OH \rightarrow H_2O+O_2$

$$\dot{C}_{\mathrm{H_2}} = -\omega_2 - \omega_3 + \omega_{6f}$$
$$\dot{C}_{\mathrm{O_2}} = -\omega_1 - \omega_{4f} + \omega_{6f} + \omega_{7f}$$
$$\dot{C}_{\mathrm{H_2O}} = \omega_3 + \omega_{7f}$$
$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f}$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f}$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f}$$

One-step reduced mechanism

1. $H + O_2 \rightleftharpoons OH + O$
2. $H_2 + O \rightleftharpoons OH + H$
3. $H_2 + OH \rightleftharpoons H_2O + H$

4f. $H + O_2 + M \rightarrow HO_2 + M$

5f. $HO_2 + H \rightarrow OH + OH$

6f. $HO_2 + H \rightarrow H_2 + O_2$

7f. $HO_2 + OH \rightarrow H_2O + O_2$

$$\dot{C}_{\mathrm{H_2}} = -\omega_2 - \omega_3 + \omega_{6f}$$
$$\dot{C}_{\mathrm{O_2}} = -\omega_1 - \omega_{4f} + \omega_{6f} + \omega_{7f}$$
$$\dot{C}_{\mathrm{H_2O}} = \omega_3 + \omega_{7f}$$
$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f}$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f}$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f}$$

$$\dot{C}_{\mathrm{H_2}} + \left\{ \dot{C}_{\mathrm{O}} + \frac{1}{2}\dot{C}_{\mathrm{OH}} + \frac{3}{2}\dot{C}_{\mathrm{H}} - \frac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\} = -2\omega_{4f}$$
$$\dot{C}_{\mathrm{O_2}} + \left\{ \dot{C}_{\mathrm{O}} + \frac{1}{2}\dot{C}_{\mathrm{OH}} + \frac{1}{2}\dot{C}_{\mathrm{H}} + \frac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\} = -\omega_{4f}$$
$$\dot{C}_{\mathrm{H_2O}} - \left\{ \dot{C}_{\mathrm{O}} + \dot{C}_{\mathrm{H}} - \dot{C}_{\mathrm{HO_2}} \right\} = 2\omega_{4f}$$

One-step reduced mechanism

1. $H+O_2 \rightleftharpoons OH+O$
2. $H_2+O \rightleftharpoons OH+H$
3. $H_2+OH \rightleftharpoons H_2O+H$
4f. $H+O_2+M \rightarrow HO_2+M$
5f. $HO_2+H \rightarrow OH+OH$
6f. $HO_2+H \rightarrow H_2+O_2$
7f. $HO_2+OH \rightarrow H_2O+O_2$

$$\dot{C}_{\mathrm{H_2}} = -\omega_2 - \omega_3 + \omega_{6f}$$
$$\dot{C}_{\mathrm{O_2}} = -\omega_1 - \omega_{4f} + \omega_{6f} + \omega_{7f}$$
$$\dot{C}_{\mathrm{H_2O}} = \omega_3 + \omega_{7f}$$
$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2 \; = 0$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f} \; = 0$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f} \; =$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f} \; = 0$$

$$\dot{C}_{\mathrm{H_2}} + \cancel{\left\{ \dot{C}_{\mathrm{O}} + \tfrac{1}{2}\dot{C}_{\mathrm{OH}} + \tfrac{3}{2}\dot{C}_{\mathrm{H}} - \tfrac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\}} = -2\omega_{4f}$$
$$\dot{C}_{\mathrm{O_2}} + \cancel{\left\{ \dot{C}_{\mathrm{O}} + \tfrac{1}{2}\dot{C}_{\mathrm{OH}} + \tfrac{1}{2}\dot{C}_{\mathrm{H}} + \tfrac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\}} = -\omega_{4f}$$
$$\dot{C}_{\mathrm{H_2O}} - \cancel{\left\{ \dot{C}_{\mathrm{O}} + \dot{C}_{\mathrm{H}} - \dot{C}_{\mathrm{HO_2}} \right\}} = 2\omega_{4f}$$

- One-step reaction among the main chemical species

$$2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\mathrm{H_2O} \quad (\omega_{4f} = k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}})$$

One-step reduced mechanism

1. $H + O_2 \rightleftharpoons OH + O$
2. $H_2 + O \rightleftharpoons OH + H$
3. $H_2 + OH \rightleftharpoons H_2O + H$

4f. $H + O_2 + M \rightarrow HO_2 + M$

5f. $HO_2 + H \rightarrow OH + OH$

6f. $HO_2 + H \rightarrow H_2 + O_2$

7f. $HO_2 + OH \rightarrow H_2O + O_2$

$$\dot{C}_{\mathrm{H_2}} = -\omega_2 - \omega_3 + \omega_{6f}$$
$$\dot{C}_{\mathrm{O_2}} = -\omega_1 - \omega_{4f} + \omega_{6f} + \omega_{7f}$$
$$\dot{C}_{\mathrm{H_2O}} = \omega_3 + \omega_{7f}$$
$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2 = 0$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f} = 0$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f} =$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f} = 0$$

$$\dot{C}_{\mathrm{H_2}} + \cancel{\left\{ \dot{C}_{\mathrm{O}} + \tfrac{1}{2}\dot{C}_{\mathrm{OH}} + \tfrac{3}{2}\dot{C}_{\mathrm{H}} - \tfrac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\}} = -2\omega_{4f}$$
$$\dot{C}_{\mathrm{O_2}} + \cancel{\left\{ \dot{C}_{\mathrm{O}} + \tfrac{1}{2}\dot{C}_{\mathrm{OH}} + \tfrac{1}{2}\dot{C}_{\mathrm{H}} + \tfrac{1}{2}\dot{C}_{\mathrm{HO_2}} \right\}} = -\omega_{4f}$$
$$\dot{C}_{\mathrm{H_2O}} - \cancel{\left\{ \dot{C}_{\mathrm{O}} + \dot{C}_{\mathrm{H}} - \dot{C}_{\mathrm{HO_2}} \right\}} = 2\omega_{4f}$$

- One-step reaction among the main chemical species

$$2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\mathrm{H_2O} \quad (\omega_{4f} = k_{4f}\, C_{\mathrm{M}}\, C_{\mathrm{O_2}}\, C_{\mathrm{H}})$$

One-step reduced mechanism

$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2 = 0$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f} = 0$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f} = 0$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f} = 0$$

One-step reduced mechanism

$$\dot{C}_{\mathrm{O}} = \omega_1 - \omega_2 = 0 = k_{1f} C_{\mathrm{O_2}} C_{\mathrm{H}} - k_{1b} C_{\mathrm{OH}} C_{\mathrm{O}} - k_{2f} C_{\mathrm{H_2}} C_{\mathrm{O}} + k_{2b} C_{\mathrm{OH}} C_{\mathrm{H}}$$
$$\dot{C}_{\mathrm{OH}} = \omega_1 + \omega_2 - \omega_3 + 2\omega_{5f} - \omega_{7f} = 0$$
$$\dot{C}_{\mathrm{H}} = -\omega_1 + \omega_2 + \omega_3 - \omega_{4f} - \omega_{5f} - \omega_{6f} = 0$$
$$\dot{C}_{\mathrm{HO_2}} = \omega_{4f} - \omega_{5f} - \omega_{6f} - \omega_{7f} = 0$$

One-step reduced mechanism

- $C_{\mathrm{H}} = \dfrac{1}{HG} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$

One-step reduced mechanism

- $C_{\mathrm{H}} = \dfrac{1}{HG} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{OH}} = \dfrac{k_{2f} C_{\mathrm{H_2}}}{H k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$

One-step reduced mechanism

- $C_{\mathrm{H}} = \dfrac{1}{HG} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{OH}} = \dfrac{k_{2f} C_{\mathrm{H_2}}}{H k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{O}} = \dfrac{\bar{\alpha} k_{3f} C_{\mathrm{H_2}}}{G k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$

One-step reduced mechanism

- $C_{\mathrm{H}} = \dfrac{1}{HG} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{OH}} = \dfrac{k_{2f} C_{\mathrm{H_2}}}{H k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{O}} = \dfrac{\bar{\alpha} k_{3f} C_{\mathrm{H_2}}}{G k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{HO_2}} = \dfrac{k_{3f}}{(f + G) k_{7f}} C_{\mathrm{H_2}}$

One-step reduced mechanism

- $C_{\mathrm{H}} = \dfrac{1}{HG} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{OH}} = \dfrac{k_{2f} C_{\mathrm{H_2}}}{H k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{O}} = \dfrac{\bar{\alpha} k_{3f} C_{\mathrm{H_2}}}{G k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{HO_2}} = \dfrac{k_{3f}}{(f+G) k_{7f}} C_{\mathrm{H_2}}$

$$f = \frac{k_{5f} + k_{6f}}{k_{7f}} \frac{k_{3f}}{k_{4f} C_{\mathrm{M}}} \frac{C_{\mathrm{H_2}}}{C_{\mathrm{O_2}}} \qquad H = \frac{1}{2} + \frac{1}{2} \left[1 + 4\gamma_{2b} f \frac{1}{\bar{\alpha}} \left(\frac{k_{1f}}{\alpha k_{4f} C_{\mathrm{M}}} - 1 \right) \right]^{1/2}$$

$$G = \frac{1+\gamma_{3b}}{2} + \frac{f}{2} \left\{ [1 + 2(3+\gamma_{3b})/f + (1+\gamma_{3b})^2/f^2]^{1/2} - 1 \right\}$$

$$\bar{\alpha} = \frac{k_{6f} f / (k_{5f} + k_{6f}) + G}{f + G} \qquad \gamma_{3b} = \frac{k_{3b} C_{\mathrm{H_2O}}}{k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \qquad \gamma_{2b} = \frac{k_{7f}}{k_{5f} + k_{6f}} \frac{k_{2b} k_{2f}}{k_{1b} k_{3f}}$$

One-step reduced mechanism

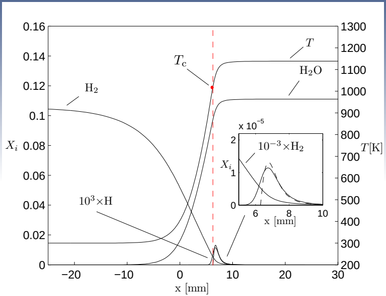
- $C_{\mathrm{H}} = \dfrac{1}{\cancel{H}G} \dfrac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{OH}} = \dfrac{k_{2f} C_{\mathrm{H_2}}}{\cancel{H} k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{O}} = \dfrac{\bar{\alpha} k_{3f} C_{\mathrm{H_2}}}{G k_{1b}} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$
- $C_{\mathrm{HO_2}} = \dfrac{k_{3f}}{(f+G) k_{7f}} C_{\mathrm{H_2}}$

$$f = \frac{k_{5f} + k_{6f}}{k_{7f}} \frac{k_{3f}}{k_{4f} C_{\mathrm{M}}} \frac{C_{\mathrm{H_2}}}{C_{\mathrm{O_2}}} \qquad H = \frac{1}{2} + \frac{1}{2} \left[1 + 4 \gamma_{2b} f \frac{1}{\bar{\alpha}} \left(\frac{k_{1f}}{\alpha k_{4f} C_{\mathrm{M}}} - 1 \right) \right]^{1/2} \simeq 1$$

$$G = \frac{1 + \gamma_{3b}}{2} + \frac{f}{2} \left\{ \left[1 + 2(3 + \gamma_{3b})/f + (1 + \gamma_{3b})^2 / f^2 \right]^{1/2} - 1 \right\}$$

$$\bar{\alpha} = \frac{k_{6f} f / (k_{5f} + k_{6f}) + G}{f + G} \qquad \gamma_{3b} = \frac{k_{3b} C_{\mathrm{H_2O}}}{k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \qquad \gamma_{2b} = \frac{k_{7f}}{k_{5f} + k_{6f}} \frac{k_{2b} k_{2f}}{k_{1b} k_{3f}} \ll 1$$

One-step reduced mechanism



$$\omega_{4f} = k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}} C_{\mathrm{H}}$$

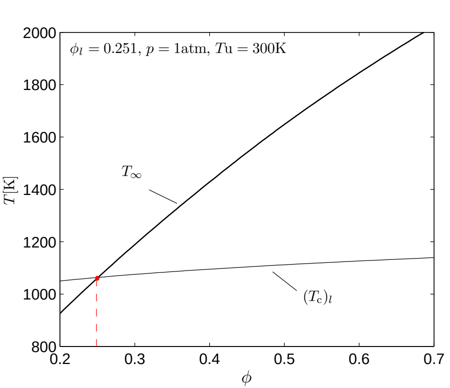
$$C_{\mathrm{H}} = \frac{1}{HG} \frac{k_{2f} k_{3f} C_{\mathrm{H_2}}^2}{k_{1b} k_{4f} C_{\mathrm{M}} C_{\mathrm{O_2}}} \left(\frac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right)$$

$$\mathrm{H} + \mathrm{O_2} \xrightarrow{1f} \mathrm{OH} + \mathrm{O}$$

$$\mathrm{H} + \mathrm{O_2} + \mathrm{M} \xrightarrow{4f} \mathrm{HO_2} + \mathrm{M}$$

- The concentration of the radicals H, O and OH vanish at a crossover temperature T_c defined by $k_{1f} = \bar{\alpha} k_{4f} C_{\mathrm{M}}$.
- $\omega = \dfrac{1}{HG} \left(\dfrac{k_{1f}}{\bar{\alpha} k_{4f} C_{\mathrm{M}}} - 1 \right) \dfrac{k_{2f} k_{3f}}{k_{1b}} C_{\mathrm{H_2}}^2 \quad$ if $k_{1f} > \bar{\alpha} k_{4f} C_{\mathrm{M}}$
- $\omega = 0 \quad$ if $k_{1f} < \bar{\alpha} k_{4f} C_{\mathrm{M}}$

Kinetically-controlled lean flammability limit



$$k_{1f} = \bar{\alpha} k_{4f} C_{\mathrm{M}} \quad \rightarrow \quad T_c$$

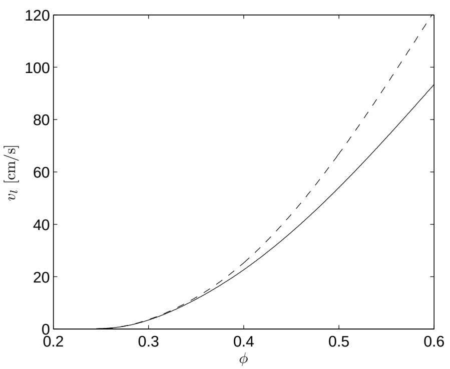
$$\bar{\alpha} = \frac{k_{6f} f / (k_{5f} + k_{6f}) + G}{f + G}$$

$$f = \frac{k_{5f} + k_{6f}}{k_{7f}} \frac{k_{3f}}{k_{4f} C_{\mathrm{M}}} \frac{C_{\mathrm{H_2}}}{C_{\mathrm{O_2}}}$$

- The crossover temperature at the lean flammability limit $(T_c)_l$ is defined by $k_{1f} = k_{4f} C_{\mathrm{M}}$ because $\bar{\alpha} = 1$ for $C_{\mathrm{H_2}} \ll 1$.
- Flames can not exist for values of the equivalence ratio $\phi < \phi_l$, such that $T_\infty < (T_c)_l$.

Numerical computation of planar flames

- H_2-air at $p = 1$ atm and $T_u = 300$ K

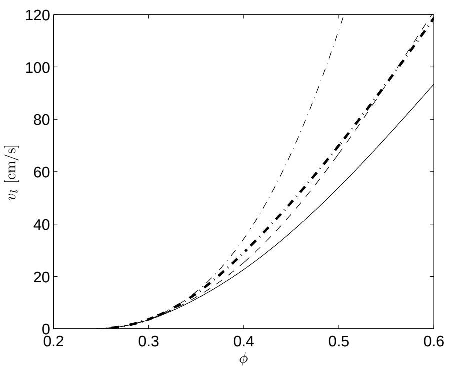


Solid curve: 21-step mech.
Dashed curve: 7-step mech.

$$\omega = \frac{1}{HG}\left(\frac{k_{1f}}{\bar{\alpha}k_{4f}C_{\mathrm{M}}} - 1\right)\frac{k_{2f}k_{3f}}{k_{1b}}C_{\mathrm{H_2}}^2$$

Numerical computation of planar flames

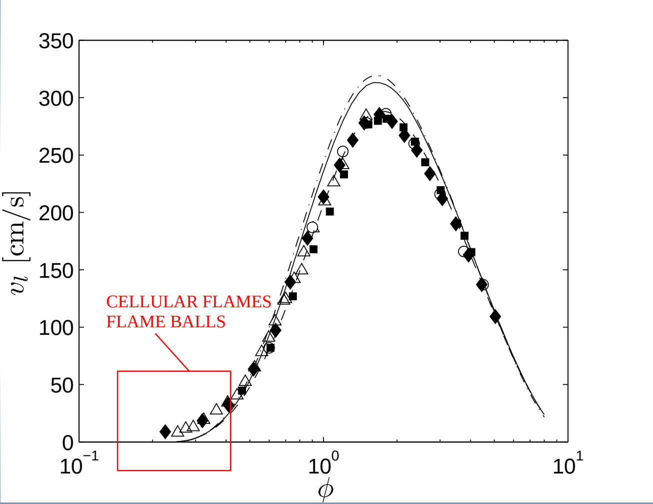
- H_2-air at $p = 1$ atm and $T_u = 300$ K



Solid curve: 21-step mech.
Dashed curve: 7-step mech.
Thick dot-dashed: 1-step
Thin dot-dashed: 1-step ($H = 1$)

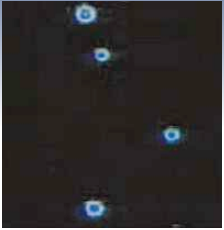
$$\omega = \frac{1}{HG}\left(\frac{k_{1f}}{\bar{\alpha}k_{4f}C_{\mathrm{M}}} - 1\right)\frac{k_{2f}k_{3f}}{k_{1b}}C_{\mathrm{H_2}}^2$$

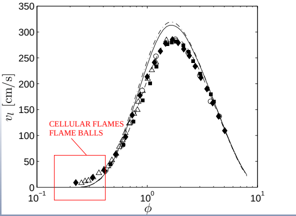
Very lean flames and flammability limit

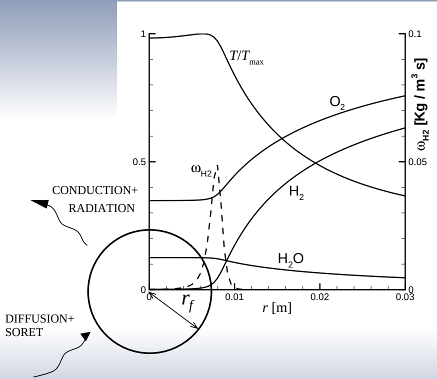


Lean hydrogen-air flame balls

Ronney's experiments
on space shuttle (1997)







Detailed numerical description of steady flame balls

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}[\lambda r^2 \frac{\mathrm{d}T}{\mathrm{d}r}] = Q_R - \sum_i h_i^o \dot{m}_i$$

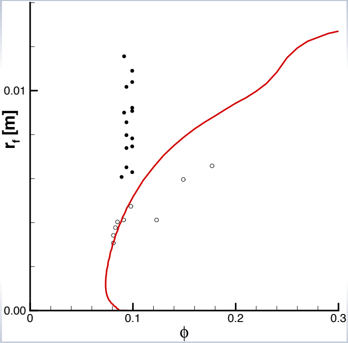
$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}[\rho D_i r^2 (\frac{\mathrm{d}Y_i}{\mathrm{d}r} + \frac{\alpha_i Y_i}{T}\frac{\mathrm{d}T}{\mathrm{d}r})] = \dot{m}_i$$

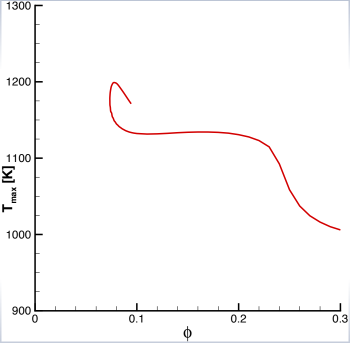
$$\begin{cases} \frac{\mathrm{d}T}{\mathrm{d}r} = \frac{\mathrm{d}Y_i}{\mathrm{d}r} = 0 \ \text{ at } \ r = 0 \\ T(\infty) - T_\infty = Y_i(\infty) - Y_{i\infty} = 0 \end{cases}$$

- $\dot{m}_i$: San Diego 21-step mechanism with 8 reacting species (O_2, H_2, H_2O, O, H, OH, HO_2, H_2O_2)
- Molecular diffusion: Fick's Law with Smooke's model: $(\lambda/c_p)/(\lambda/c_p)_0 = (T/T_0)^{0.7}$, $Le_i = constant$
- Thermal diffusion with $\alpha_{\mathrm{H}} = -0.23$ and $\alpha_{\mathrm{H_2}} = -0.29$
- Q_R: **S**tatistical **N**arrow **B**and model (SNB)

Detailed numerical description of steady flame balls

Detailed chemistry + SNB radiation model





One-step chemistry description

For H_2-air mixtures near the lean flammability limit (Fernández-Galisteo et al, C&F 156, 985-996, 2009) all chemical intermediates have very small concentrations and are in steady state, while the main species react according to

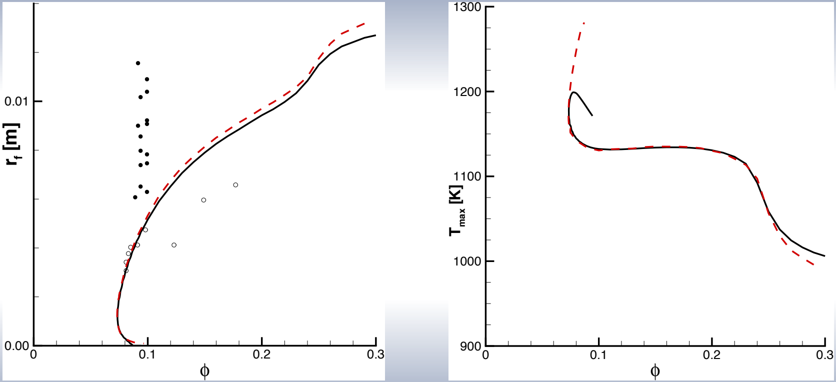
$$2H_2 + O_2 \rightarrow 2H_2O$$

with a rate given by

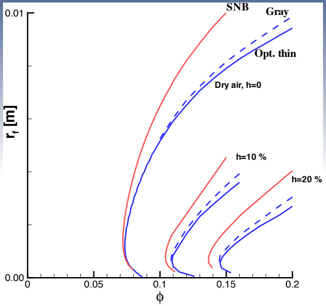
$$\begin{cases} \mathrm{IF} k_{1f} > \alpha k_{4f} C_{\mathrm{M}} : \omega = \frac{1}{GH} \left(\frac{k_{1f}}{\alpha k_{4f} C_{\mathrm{M}}} - 1 \right) \frac{k_{2f} k_{3f}}{k_{1b}} (\rho Y_{\mathrm{H}_2} / W_{\mathrm{H}_2})^2 \\ \mathrm{IF} k_{1f} \leq \alpha k_{4f} C_{\mathrm{M}} : \omega = 0 \end{cases}$$

The **crossover temperature**, T_c, is defined from $k_{1f} = \alpha k_{4f} C_{\mathrm{M}}$ in terms of the rates of the elementary reactions $H + O_2 \overset{1}{\rightleftharpoons} OH + O$ and $H + O_2 + M \xrightarrow{4f} HO_2 + M$ with a factor $1/6 \leq \alpha \leq 1$ that depends on the local hydrogen content. Nondimensional activation energy $\beta \sim \mathbf{10}$ for $k_{1f}/(\alpha k_{4f} C_{\mathrm{M}})$.

One-step chemistry description



Radiation models



- Characteristic absorption length $\alpha_a^{-1} \sim 10\mathrm{cm}$ ($\alpha_a \equiv$ absorption coefficient
- Optically thin approximation is accurate enough for description of flame-balls near extinction

$$\boxed{Q_R = 4\sigma\alpha_a(T^4 - T_\infty^4)}$$

Steady flame balls

The identity $\nabla Y_{\mathrm{H_2}} + \alpha_{\mathrm{H_2}} Y_{\mathrm{H_2}} \nabla T/T = T^{-\alpha_{\mathrm{H_2}}} \nabla (T^{\alpha_{\mathrm{H_2}}} Y_{\mathrm{H_2}})$ enables thermal diffusion to be incorporated in a single Fickian-like diffusion term as a function of $Y = (T/T_\infty)^{\alpha_{\mathrm{H_2}}} Y_{\mathrm{H_2}}$ with **increased diffusivity** $D = (T/T_\infty)^{-\alpha_{\mathrm{H_2}}} D_{\mathrm{H_2}}$, so that

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\lambda r^2 \frac{\mathrm{d}T}{\mathrm{d}r}\right) = 4\kappa_{\mathrm{H_2O}} \sigma p (W/W_{\mathrm{H_2O}}) Y_{\mathrm{H_2O}} (T^4 - T_\infty^4) - 2W_{\mathrm{H_2}} q \omega$$
$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D_{\mathrm{O_2}} r^2}{W_{\mathrm{O_2}}}\frac{\mathrm{d}Y_{\mathrm{O_2}}}{\mathrm{d}r}\right) = -\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D_{\mathrm{H_2O}} r^2}{2W_{\mathrm{H_2O}}}\frac{\mathrm{d}Y_{\mathrm{H_2O}}}{\mathrm{d}r}\right) = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D r^2}{2W_{\mathrm{H_2}}}\frac{\mathrm{d}Y}{\mathrm{d}r}\right) = \omega$$

with boundary conditions

$$\begin{cases} r = 0: & \mathrm{d}T/\mathrm{d}r = \mathrm{d}Y_i/\mathrm{d}r = 0 \\ r = \infty: & T - T_\infty = Y - Y_{\mathrm{H_2}\infty} = Y_{\mathrm{O_2}} - Y_{\mathrm{O_2}\infty} = Y_{\mathrm{H_2O}} = 0 \end{cases}$$

Steady flame balls

The identity $\nabla Y_{\mathrm{H_2}} + \alpha_{\mathrm{H_2}} Y_{\mathrm{H_2}} \nabla T / T = T^{-\alpha_{\mathrm{H_2}}} \nabla (T^{\alpha_{\mathrm{H_2}}} Y_{\mathrm{H_2}})$ enables thermal diffusion to be incorporated in a single Fickian-like diffusion term as a function of $Y = (T/T_\infty)^{\alpha_{\mathrm{H_2}}} Y_{\mathrm{H_2}}$ with **increased diffusivity** $D = (T/T_\infty)^{-\alpha_{\mathrm{H_2}}} D_{\mathrm{H_2}}$, so that

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\lambda r^2 \frac{\mathrm{d}T}{\mathrm{d}r}\right) = 4\kappa_{\mathrm{H_2O}}\sigma p (W/W_{\mathrm{H_2O}}) Y_{\mathrm{H_2O}} (T^4 - T_\infty^4) - 2W_{\mathrm{H_2}} q\omega$$

$$\cancel{\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D_{\mathrm{O_2}} r^2}{W_{\mathrm{O_2}}}\frac{\mathrm{d}Y_{\mathrm{O_2}}}{\mathrm{d}r}\right)} = \cancel{-\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D_{\mathrm{H_2O}} r^2}{2W_{\mathrm{H_2O}}}\frac{\mathrm{d}Y_{\mathrm{H_2O}}}{\mathrm{d}r}\right)} = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho D r^2}{2W_{\mathrm{H_2}}}\frac{\mathrm{d}Y}{\mathrm{d}r}\right) = \omega$$

with boundary conditions

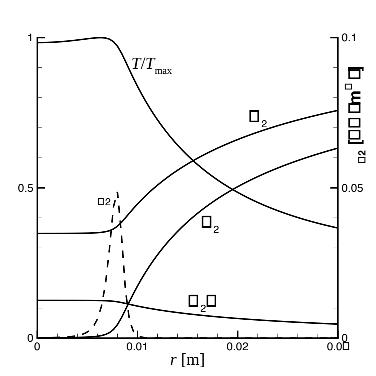
$$\begin{cases} r = 0: & \mathrm{d}T/\mathrm{d}r = \mathrm{d}Y_i/\mathrm{d}r = 0 \\ r = \infty: & T - T_\infty = Y - Y_{\mathrm{H_2}\infty} = 0 \end{cases}$$

Assuming for simplicity $D_{\mathrm{H_2O}} \propto D_{\mathrm{O_2}} \propto D$ leads to

$$Y_{\mathrm{H_2O}} = 2\frac{W_{\mathrm{H_2O}}}{W_{\mathrm{O_2}}}\frac{D_{\mathrm{O_2}}}{D_{\mathrm{H_2O}}}(Y_{\mathrm{O_2}\infty} - Y_{\mathrm{O_2}}) = \frac{W_{\mathrm{H_2O}}}{W_{\mathrm{H_2}}}\frac{D}{D_{\mathrm{H_2O}}}(Y_{\mathrm{H_2}\infty} - Y)$$

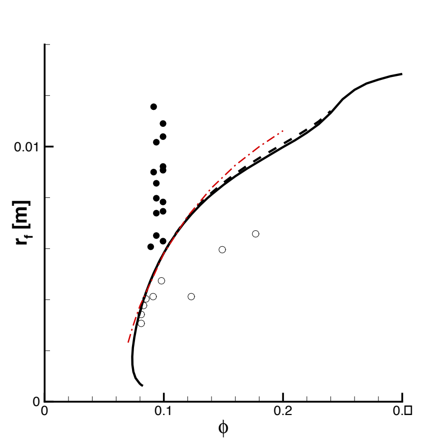
The thin reaction-layer description

$\phi = 0.15$



For $\beta \gg 1$ the reaction occurs in a thin layer where $Y_{\mathrm{H}_2}/Y_{\mathrm{H}_{2\infty}} \sim (T - T_c)/T_c \sim \beta^{-1}$

The reaction-sheet approximation with $T_{\max} = T_c$



Characteristic scales near turning point

$$\left.\begin{array}{l}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\lambda r^2\frac{\mathrm{d}T}{\mathrm{d}r}\right) = \cancel{Q_R} - 2W_{\mathrm{H}_2}q\omega \\ \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\rho D r^2\frac{\mathrm{d}Y}{\mathrm{d}r}\right) = 2W_{\mathrm{H}_2}\omega\end{array}\right\} \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\lambda r^2\frac{\mathrm{d}T}{\mathrm{d}r} + \rho D q r^2\frac{\mathrm{d}Y}{\mathrm{d}r}\right) = 0$$

Integrating with boundary conditions

$\frac{\mathrm{d}T}{\mathrm{d}r} = \frac{\mathrm{d}Y}{\mathrm{d}r} = 0$ at $r = 0$ and $T - T_\infty = Y - Y_{\mathrm{H}_2\infty} = 0$ as $r \to \infty$

leads to ($\lambda \propto T^\nu$, $\rho D \propto T^\gamma$)

$$\frac{L_{\mathrm{H}_2} c_{p_\infty} T_\infty}{1+\nu-\gamma}\left(\frac{T}{T_\infty}\right)^{1+\nu-\gamma} + qY = \frac{L_{\mathrm{H}_2} c_{p_\infty} T_\infty}{1+\nu-\gamma} + qY_{\mathrm{H}_{2\infty}}$$

at the flame ($Y = 0$): $\boxed{\left(\frac{T_f}{T_\infty}\right)^{1+\nu-\gamma} = 1 + \frac{(1+\nu-\gamma)qY_{\mathrm{H}_{2\infty}}}{L_{\mathrm{H}_2} c_{p_\infty} T_\infty}.}$

Integrating for $r > r_f$ with $\omega = 0$:

$$\boxed{\left(\frac{\partial Y}{\partial r}\right)_{f+} = \frac{1+\nu-\gamma}{1+\nu}\frac{(T_f/T_\infty)^{1+\nu}-1}{(T_f/T_\infty)^\gamma[(T_f/T_\infty)^{1+\nu-\gamma}-1]}\frac{Y_{\mathrm{H}_{2\infty}}}{r_f}}$$

Across the flame: $\boxed{\frac{\rho D}{4W_{\mathrm{H}_2}}\left(\frac{\partial Y}{\partial r}\right)^2_{f+} = \int_0^\infty \omega \mathrm{d}Y}$

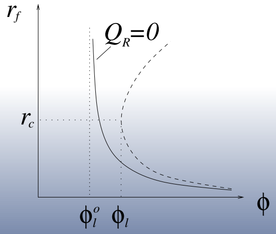
Characteristic scales

$$\boxed{\left(\frac{T_f}{T_\infty}\right)^{1+\nu-\gamma} = 1 + \frac{(1+\nu-\gamma)qY_{\mathrm{H_2}\infty}}{L_{\mathrm{H_2}}c_{p\infty}T_\infty}.}$$

$$\boxed{\left(\frac{\partial Y}{\partial r}\right)_{f+} = \frac{1+\nu-\gamma}{1+\nu}\frac{(T_f/T_\infty)^{1+\nu}-1}{(T_f/T_\infty)^{\gamma}[(T_f/T_\infty)^{1+\nu-\gamma}-1]}\frac{Y_{\mathrm{H_2}\infty}}{r_f}}$$

$$\boxed{\frac{\rho D}{4W_{\mathrm{H_2}}}\left(\frac{\partial Y}{\partial r}\right)^2_{f+} = \int_0^\infty \omega \mathrm{d}Y} \quad \boxed{\omega = \frac{1}{GH}\left(\frac{k_{1f}}{\alpha k_{4f}C_{\mathrm{M}}} - 1\right)\frac{k_{2f}k_{3f}}{k_{1b}}\left(\frac{\rho Y_{\mathrm{H_2}}}{W_{\mathrm{H_2}}}\right)^2}$$

As $T_f \to T_c$, $\frac{k_{1f}}{\alpha k_{4f}C_{\mathrm{M}}} \to 1$, $\left(\frac{\partial Y}{\partial r}\right)_{f+} \to 0$, $r_f \to \infty$

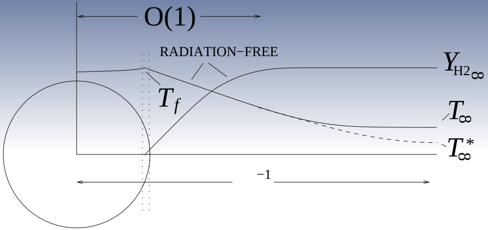


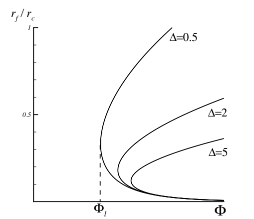
Extinction occurs for $T_f - T_c \sim \beta^{-1}T_c$ $(\phi_l - \phi_l^o \sim \beta^{-1})$

$$r_c = \left(\frac{\beta^3 D_c G_c H_c}{2(k_{2f}k_{3f}/k_{1b})_c(\rho_c Y_{\mathrm{H_2}\infty}/W_{\mathrm{H_2}})}\right)^{1/2}$$

$$\begin{aligned}\varepsilon &= \frac{O[Q_R]}{O[(\nabla(\lambda\nabla T)]} \\ &= 4\kappa_{\mathrm{H_2O}_c}\sigma p\frac{W_{\mathrm{air}}}{W_{\mathrm{H_2O}}}\frac{Y_{\mathrm{H_2O}_r}T_c^3 r_c^2}{\lambda_c} \ll 1\end{aligned}$$

Extinction limit analysis for $\beta^{-1} \sim \varepsilon \ln(\varepsilon^{-1})$





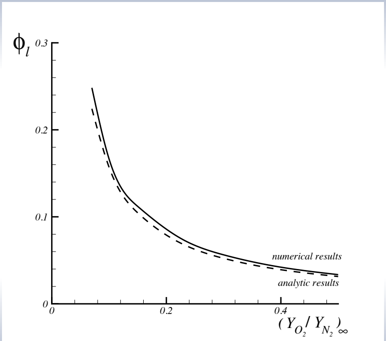
The effect of far-field radiation introduces an apparent ambient temperature $T_\infty^* < T_\infty$ such that

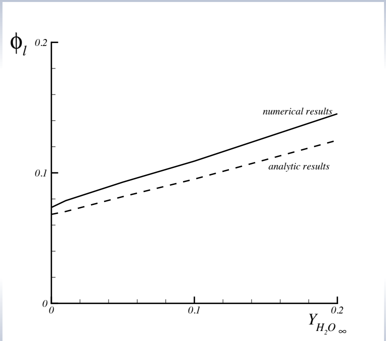
$$(T_\infty - T_\infty^*)/T_\infty \sim \varepsilon \ln(\varepsilon^{-1}) \sim \beta^{-1}$$

$$\boxed{R_f = r_f/r_c,\ \Phi = \beta(\phi - \phi_l^o),\ \Delta = \beta(T_\infty - T_\infty^*)/T_\infty \sim O(1)}$$

Extinction limit results

$$\boxed{\phi_l = \phi_l^o + \beta^{-1}\Phi_l}$$





(Some) Conclusions

- Reduced-kinetic mechanisms appropriate for low-temperature ignition and ultra-lean premixed combustion have been derived and used to develop explicit analytic expressions for quantities of practical interest in connection with safety applications (i.e., ignition times and flammability limits).
- The reduced-kinetic descriptions can be used to shorten computational times in numerical calculations and can also aid further analytical work on deflagration and flame-ball stability.