HYDROGEN THERMOCHEMISTRY

Module Fundamentals of Hydrogen Safety

Lecture 3

COMBUSTION REACTION OF HYDROGEN IN AIR
STOICHIOMETRIC EQUATION

Stoichiometric equation of the hydrogen-oxygen reaction:

$$\boxed{\nu'_{\mathrm{H_2}}\,\mathrm{H_2} + \nu'_{\mathrm{O_2}}\,\mathrm{O_2} + \nu'_{\mathrm{H_2O}}\,\mathrm{H_2O} \xrightarrow{k} \nu''_{\mathrm{H_2}}\,\mathrm{H_2} + \nu''_{\mathrm{O_2}}\,\mathrm{O_2} + \nu''_{\mathrm{H_2O}}\,\mathrm{H_2O}} \tag{1}$$

where ν'_i and ν''_i respectively denote the stoichiometric coefficients before and after the reaction.

$$\nu'_{\mathrm{H_2}} = 2,\ \nu'_{\mathrm{O_2}} = 1,\ \nu'_{\mathrm{H_2O}} = 0$$
$$\nu''_{\mathrm{H_2}} = 0,\ \nu''_{\mathrm{O_2}} = 0,\ \nu''_{\mathrm{H_2O}} = 2$$

$$\Longrightarrow \quad 2\,\mathrm{H_2} + \mathrm{O_2} \xrightarrow{k} 2\,\mathrm{H_2O} \tag{2}$$

Stoichiometric equation of the hydrogen-air reaction:

$$\boxed{\nu'_{\mathrm{H_2}}\,\mathrm{H_2} + \nu'_{\mathrm{O_2}}\,\mathrm{O_2} + \nu'_{\mathrm{N_2}}\,\mathrm{N_2} + \nu'_{\mathrm{H_2O}}\,\mathrm{H_2O} \xrightarrow{k} \nu''_{\mathrm{H_2}}\,\mathrm{H_2} + \nu''_{\mathrm{O_2}}\,\mathrm{O_2} + \nu''_{\mathrm{N_2}}\,\mathrm{N_2} + \nu''_{\mathrm{H_2O}}\,\mathrm{H_2O}} \tag{3}$$

$$\nu'_{\mathrm{H_2}} = 2,\ \nu'_{\mathrm{O_2}} = 1,\ \nu'_{\mathrm{N_2}} = 7.524,\ \nu'_{\mathrm{H_2O}} = 0$$
$$\nu''_{\mathrm{H_2}} = 0,\ \nu''_{\mathrm{O_2}} = 0,\ \nu'_{\mathrm{N_2}} = 7.524,\ \nu''_{\mathrm{H_2O}} = 2$$

$$\Longrightarrow \quad 2\,\mathrm{H_2} + \mathrm{O_2} + 3.762\,\mathrm{N_2} \xrightarrow{k} 3.762\,\mathrm{N_2} + 2\,\mathrm{H_2O} \tag{4}$$

COMBUSTION REACTION OF HYDROGEN IN AIR
STOICHIOMETRIC AIR-FUEL RATIO AND EQUIVALENCE RATIO

The stoichiometric equation of the hydrogen-air reaction (3) may be written as:

$$\nu'_{\mathrm{H_2}}\,\mathrm{H_2} + \nu'_{\mathrm{Air}}\left[\mathrm{O_2} + (\nu'_{\mathrm{N_2}}/\nu'_{\mathrm{O_2}})\,\mathrm{N_2}\right]\nu'_{\mathrm{H_2O}}\,\mathrm{H_2O} \xrightarrow{k} \nu''_{\mathrm{H_2}}\,\mathrm{H_2} + \nu''_{\mathrm{O_2}}\,\mathrm{O_2} + \nu''_{\mathrm{N_2}}\,\mathrm{N_2} + \nu''_{\mathrm{H_2O}}\,\mathrm{H_2O} \quad (5)$$

$$\nu'_{\mathrm{H_2}} = 2,\ \nu'_{\mathrm{Air}} = 1.0,\ \nu'_{\mathrm{N_2}}/\nu'_{\mathrm{O_2}} = 3.762,\ \nu'_{\mathrm{H_2O}} = 0,\ \nu''_{\mathrm{H_2}} = 0,\ \nu''_{\mathrm{O_2}} = 0,\ \nu''_{\mathrm{N_2}} = 0,\ \nu''_{\mathrm{H_2O}} = 2$$

$$\Longrightarrow \quad 2\,\mathrm{H_2} + (\mathrm{O_2} + 3.762\,\mathrm{N_2}) \xrightarrow{k} 3.762\,\mathrm{N_2} + 2\,\mathrm{H_2O} \quad (6)$$

The **stoichiometric air-fuel ratio** is defined as:

$$\lambda_{\mathrm{AF}} \equiv \left[\frac{M_{\mathrm{Air}}}{M_{\mathrm{Fuel}}}\right]_{\mathrm{St}} = \left[\frac{M_{\mathrm{Air}}}{M_{\mathrm{H_2}}}\right]_{\mathrm{St}} = \left[1 + \frac{\nu'_{\mathrm{N_2}}}{\nu'_{\mathrm{O_2}}}\right]\left[\frac{\nu'_{\mathrm{Air}}}{\nu'_{\mathrm{H_2}}}\right]_{\mathrm{St}} \frac{\mathcal{M}_{\mathrm{Air}}}{\mathcal{M}_{\mathrm{H_2}}} = 4.762\left[\frac{\nu'_{\mathrm{Air}}}{\nu'_{\mathrm{H_2}}}\right]_{\mathrm{St}} \frac{\mathcal{M}_{\mathrm{Air}}}{\mathcal{M}_{\mathrm{H_2}}} \quad (7)$$

where M_i denotes the total mass of the i-th species, and $\mathcal{M}_i$ its molecular mass.
The **equivalence ratio of the fuel-air system**, $0 \leq \phi < \infty$, is defined as

$$\phi \equiv \frac{[M_{\mathrm{Fuel}}/M_{\mathrm{Air}}]}{[M_{\mathrm{Fuel}}/M_{\mathrm{Air}}]_{\mathrm{St}}} = \frac{\left[\nu'_{\mathrm{H_2}}/\nu'_{\mathrm{Air}}\right]}{\left[\nu'_{\mathrm{H_2}}/\nu'_{\mathrm{Air}}\right]_{\mathrm{St}}} = \frac{[\mathrm{vol.\%\,H_2}/(100 - \mathrm{vol.\%\,H_2})]}{[\mathrm{vol.\%\,H_2}/(100 - \mathrm{vol.\%\,H_2})]_{\mathrm{St}}} \quad (8)$$

where $\phi < 1$ denotes fuel-lean, $\phi = 1$ stoichiometric, and $\phi > 1$ fuel-rich mixtures.

The equivalence ratio of a fuel-oxidiser system is independent of the amount of inert species!

COMBUSTION REACTION OF HYDROGEN IN AIR
OVERALL REACTION RATE EXPRESSION

- For a chemical reaction,

$$\sum_{i=1}^{i=N} \nu'_{\mathrm{M}_i}\,\mathrm{M}_i \xrightarrow{k} \sum_{i=1}^{i=N} \nu''_{\mathrm{M}_i}\,\mathrm{M}_i, \tag{9}$$

  the **law of mass action** states that the **overall rate of reaction**, RR, is proportional to the product of the reactant concentrations.

$$\mathrm{RR} = k \prod_{i=1}^{i=n} [\mathrm{M}_i]^{\nu'_{\mathrm{M}_i}}\,. \tag{10}$$

- The net production rate of each species is

$$\frac{d\,[\mathrm{M}_i]}{dt} = \left(\nu''_{\mathrm{M}_i} - \nu'_{\mathrm{M}_i}\right)\,\mathrm{RR} = \left(\nu''_{\mathrm{M}_i} - \nu'_{\mathrm{M}_i}\right)\,k \prod_{i=1}^{i=n} [\mathrm{M}_i]^{\nu'_{\mathrm{M}_i}}\,. \tag{11}$$

- The specific reaction rate constant, k, is independent of the concentrations $[\mathrm{M}_i]$, and depends only on the temperature (equation of Arrhenius)

$$k = A\,T^b \exp\left(-\mathrm{E_a}/RT\right), \tag{12}$$

  where $A\,T^b$ represents the collision frequency, and the exponential term is called the Boltzmann factor. The values of A, b and $\mathrm{E_a}$ are characteristic to the nature of the reaction, and, independent of pressure, temperature and concentration in case of an elementary reaction.

COMBUSTION REACTION OF HYDROGEN IN AIR
OVERALL REACTION RATE EXPRESSION

- For the overall hydrogen-air reaction (3), the law of mass action (10) becomes:

$$\mathrm{RR} = k\ [\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\ [\mathrm{O_2}]^{\nu'_{\mathrm{O_2}}}\,, \tag{13}$$

  and the net production rate of species (11) becomes

$$-\frac{1}{2}\frac{d\,[\mathrm{H_2}]}{dt} = -\frac{d\,[\mathrm{O_2}]}{dt} = \frac{1}{2}\frac{d\,[\mathrm{H_2O}]}{dt} = k\ [\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\ [\mathrm{O_2}]^{\nu'_{\mathrm{O_2}}}\,; \qquad \frac{d\,[\mathrm{N_2}]}{dt} = 0 \tag{14}$$

- For the overall hydrogen-air reaction (5), the law of mass action (10) becomes:

$$\mathrm{RR} = k\ [\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\ [\mathrm{Air}]^{\nu'_{\mathrm{Air}}}\,, \tag{15}$$

  and the net production rate of species (11) becomes

$$-\frac{1}{2}\frac{d\,[\mathrm{H_2}]}{dt} = -\frac{d\,[\mathrm{O_2}]}{dt} = \frac{1}{2}\frac{d\,[\mathrm{H_2O}]}{dt} = k\ [\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\ [\mathrm{O_2}]^{\nu'_{\mathrm{Air}}}\,; \qquad \frac{d\,[\mathrm{N_2}]}{dt} = 0 \tag{16}$$

- The overall hydrogen-air reaction (cf. equations (3) and (11)) is the sum of a large number of elementary reactions. Unlike with elementary reactions, the values of A, b and $\mathrm{E_a}$ in the expression for the specific rate constant (12) do depend on pressure and concentration.

COMBUSTION REACTION OF HYDROGEN IN AIR
OVERALL REACTION ORDER

The overall reaction order of a chemical system of arbitrary complexity follows from its representation as a one-step overall reaction

$$\sum_{i=1}^{i=N} \nu'_{\mathrm{M}_i}\,\mathrm{M}_i \xrightarrow{k} \sum_{i=1}^{i=N} \nu''_{\mathrm{M}_i}\,\mathrm{M}_i, \tag{17}$$

where ν'_{M_i} are the stoichiometric coefficients of the reactants, ν''_{M_i} are the stoichiometric coefficients of the products, M_i the specification of the i-th species, and N the total number of compounds involved.

- The overall process represented by equation (17) is said to be of order ν'_{M_i} with respect to M_i.
- The **overall reaction order** of the process represented by equation (17) is equal to the sum of ν'_{M_i},

  $$n = \sum_{i=1}^{i=N} \nu'_{\mathrm{M}_i}, \tag{18}$$

  i.e. the sum of the exponents in the reactant concentration term.
- With hydrogen-air mixtures in the equivalence ratio range $0.6 < \phi < 1.1$ at 1 atm, Marinov, Wetbrook & Pitz (1996) [1] observed that the constants in the overall reaction rate

  $$\mathrm{RR_{ov}} = k\;[\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\;[\mathrm{O_2}]^{\nu'_{\mathrm{O_2}}} = A\,T^b \exp\left(-\mathrm{E_a}/RT\right)[\mathrm{H_2}]^{\nu'_{\mathrm{H_2}}}\;[\mathrm{O_2}]^{\nu'_{\mathrm{O_2}}}\,, \tag{19}$$

  assume values of
  $A = 1.8 * 10^{13}\,\mathrm{mol\,cm^{-3}\,s^{-1}}$, $b = 0$, $\mathrm{E_a} = 73745\,\mathrm{cal\,mol^{-1}}$, $\nu'_{\mathrm{H_2}} = 1.0$, and $\nu'_{\mathrm{O_2}} = 0.5$.

COMBUSTION REACTION OF HYDROGEN IN AIR

EFFECT OF EQUIVALENCE RATIO AND PRESSURE ON OVERALL REACTION ORDER

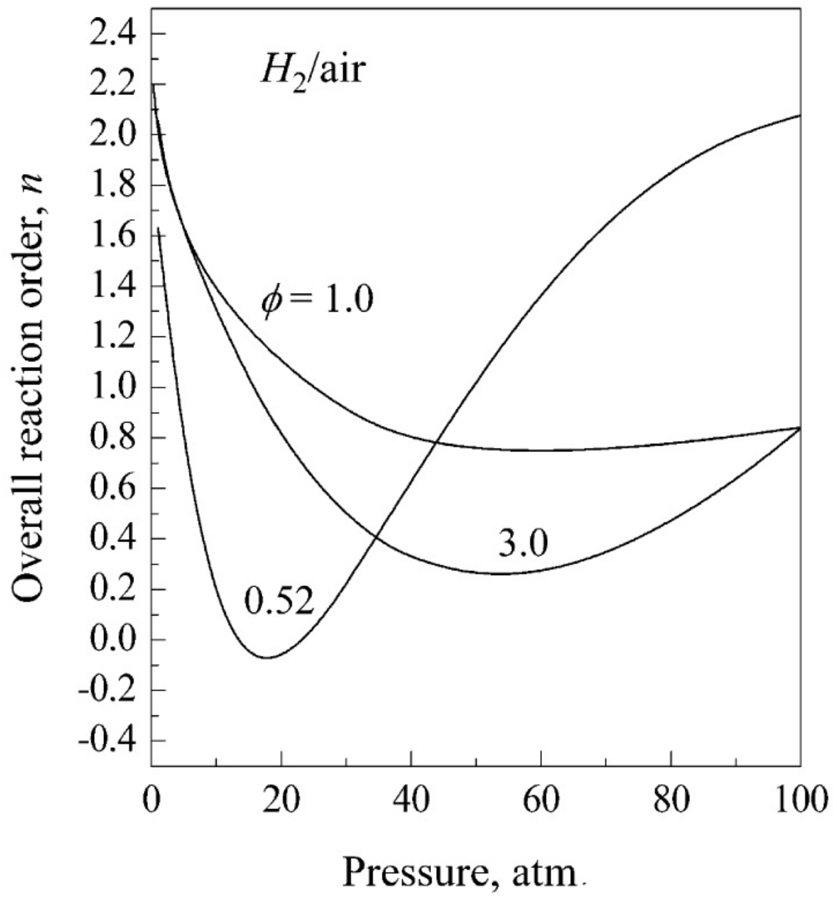

Figure 1. Overall reaction order for lean, stoichiometric and rich hydrogen-air mixtures, showing a decreasing, and then an increasing trend with increasing pressure. After Law (2006) [2].

COMBUSTION REACTION OF HYDROGEN IN AIR

EFFECT OF EQUIVALENCE RATIO AND PRESSURE ON OVERALL ACTIVATION ENERGY

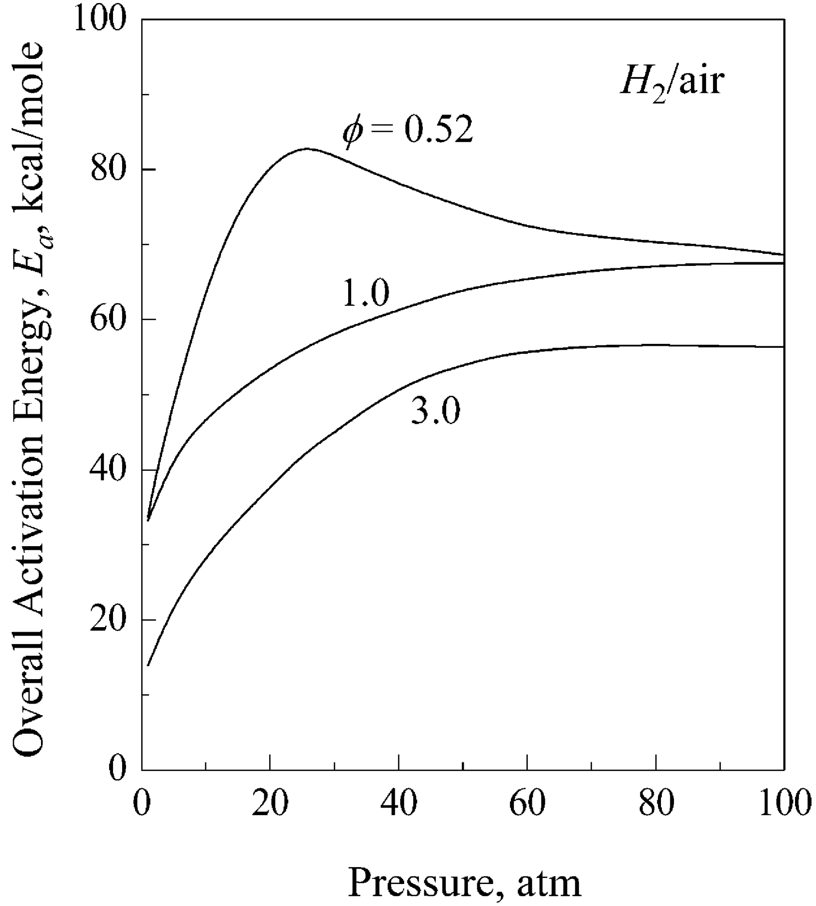

Figure 2. Overall activation energy for hydrogen-air mixtures, showing its strong variation with pressure. After Law (2006) [2].

COMBUSTION REACTION OF HYDROGEN IN AIR

EFFECT OF EQUIVALENCE RATIO AND PRESSURE ON OVERALL ACTIVATION ENERGY

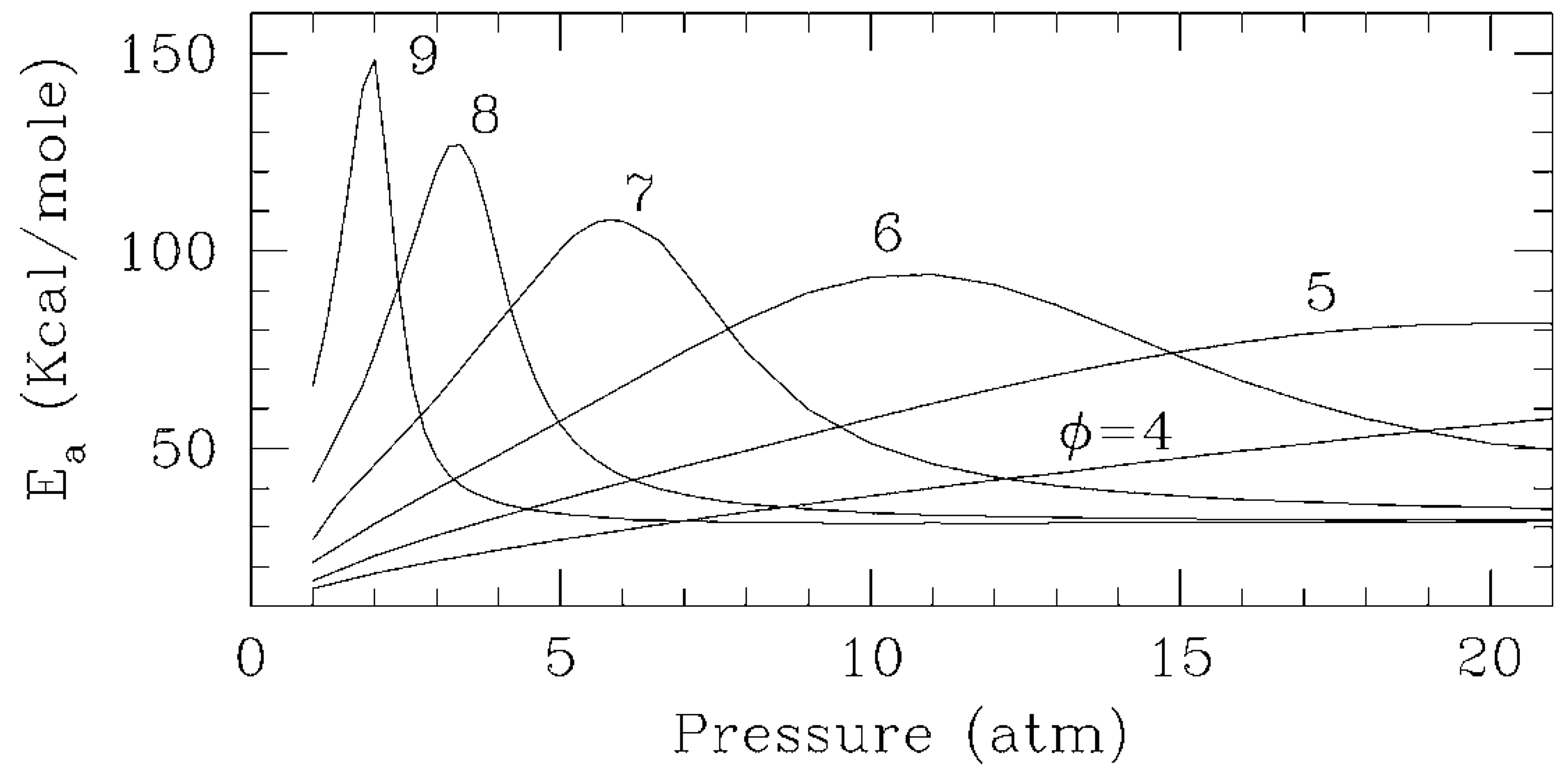

Figure 3. Overall activation energy for rich hydrogen=air mixtures as a function of pressure, for various equivalence ratios. After Christiansen, Law & Sung (2000) [3] and Law (2006) [2].

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: THE MILLER MECHANISM

Table 1. Elementary reactions and forward rate constants of the mechanism by Miller, Mitchell, Smooke & Kee (1982) [4] with 23 reactions and 9 species. Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; E_a: $[\mathrm{cal\,mol}^{-1}]$.

Reaction	A	b	E_a
$H_2 + OH \rightleftharpoons H_2O + H$	$2.16{*}10^{18}$	1.51	3430
$H + O_2 \rightleftharpoons OH + O$	$2.65{\cdot}10^{16}$	-0.6707	17041
$O + H_2 \rightleftharpoons OH + H$	$3.87{\cdot}10^{4}$	2.7	6260
$H + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$2.08{\cdot}10^{19}$	-1.24	0
$OH + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$1.45{\cdot}10^{13}$	0	-500
	$5{\cdot}10^{15}$	0	17330
$H + 2\,HO_2 \rightleftharpoons OH + OH$	$8.4{\cdot}10^{13}$	0	635
$O + 2\,HO_2 \rightleftharpoons O_2 + OH$	$2{\cdot}10^{13}$	0	0
$H_2 + M \rightleftharpoons H + H + M$	$2.2{\cdot}10^{22}$	-2	0
$H + OH + M \rightleftharpoons H_2O + M$	$4.48{\cdot}10^{13}$	0	1068
$H_2O_2 + M \rightleftharpoons OH + OH + M$	$1.21{\cdot}10^{7}$	2	5200
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	$2{\cdot}10^{12}$	0	427
	$1.7{\cdot}10^{18}$	0	29410
$O + H + M \rightleftharpoons OH + M$	$5{\cdot}10^{17}$	-1	0
$O + H_2O_2 + M \rightleftharpoons OH + HO_2$	$9.63{\cdot}10^{6}$	2	4000

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COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: THE MILLER MECHANISM

Table 1. Elementary reactions and forward rate constants of the mechanism by Miller, Mitchell, Smooke & Kee (1982) [4] with 23 reactions and 9 species. Units are: A: [$\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}$]; b: [-]; $\mathrm{E_a}$: [$\mathrm{cal\,mol^{-1}}$].

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Reaction	A	b	$\mathrm{E_a}$
$H + HO_2 \rightleftharpoons O + H_2O$	$3.97{\cdot}10^{12}$	0	671
$H + H_2O_2 \rightleftharpoons OH + H_2O$	$1{\cdot}10^{13}$	0	3600
$2\,OH + M \rightleftharpoons H_2O_2 + M$	$2.3{\cdot}10^{18}$	-0.9	-1700
$H + O_2 + H_2O \rightleftharpoons HO_2 + H_2O$	$1.126{\cdot}10^{19}$	-0.76	0
$H + O_2 + Ar \rightleftharpoons HO_2 + Ar$	$7{\cdot}10^{17}$	-0.8	0
$2\,OH \rightleftharpoons O + H_2O$	$3.57{\cdot}10^{4}$	2.4	-2110
$O_2 + M \rightleftharpoons 2\,O + M$	$1.2{\cdot}10^{17}$	-1	0
$2\,HO_2 \rightleftharpoons H_2O_2 + O_2$	$1.3{\cdot}10^{11}$	0	-1630
	$4.2{\cdot}10^{14}$	0	12000
$2\,H + H_2O \rightleftharpoons H_2 + H_2O$	$6{\cdot}10^{19}$	-1.25	0
$2\,H + H_2 \rightleftharpoons 2\,H_2$	$9{\cdot}10^{16}$	-0.6	0

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: THE MARINOV MECHANISM

Table 2. Elementary reactions and forward rate constants of the mechanism by Marinov, Westbrook & Pitz (1996) [1] with 24 reactions and 9 species. Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; E_a: $[\mathrm{cal\,mol}^{-1}]$.

Reaction	A	b	E_a
$H_2 + OH \rightleftharpoons H_2O + H$	$2.14{*}10^8$	1.52	3449
$H + O_2 \rightleftharpoons OH + O$	$2.02{\cdot}10^{14}$	-0.4	0
$O + H_2 \rightleftharpoons OH + H$	$5.06{\cdot}10^4$	2.67	6290
$H + O_2 + M \rightleftharpoons HO_2 + M$	$1.05{\cdot}10^{19}$	-1.257	0
$OH + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$2.89{\cdot}10^{13}$	0	-497
$H + 2\,HO_2 \rightleftharpoons OH + OH$	$1.5{\cdot}10^{14}$	0	1000
$O + 2\,HO_2 \rightleftharpoons O_2 + OH$	$3.25{\cdot}10^{13}$	0	0
$H_2 + M \rightleftharpoons H + H + M$	$2.21{\cdot}10^{22}$	-2	0
$H + OH + M \rightleftharpoons H_2O + M$	$8.45{\cdot}10^{11}$	0.65	1241
$H_2O_2 + M \rightleftharpoons OH + OH + M$	$1.98{\cdot}10^6$	2	2435
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	2.4	4.042	-2162
$O + H + M \rightleftharpoons OH + M$	$4.71{\cdot}10^{18}$	-1	0
$O + H_2O_2 + M \rightleftharpoons OH + HO_2$	$9.55{\cdot}10^6$	2	3970

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Table 2. Elementary reactions and forward rate constants of the mechanism by Marinov, Westbrook & Pitz (1996) [1] with 24 reactions and 9 species. Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; E_a: $[\mathrm{cal\,mol}^{-1}]$.

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Reaction	A	b	E_a
$H + HO_2 \rightleftharpoons O + H_2O$	$3.01{\cdot}10^{13}$	0	1721
$H + H_2O_2 \rightleftharpoons OH + H_2O$	$3.07{\cdot}10^{13}$	0	4217
$2\,OH + M \rightleftharpoons H_2O_2 + M$	$3.041{\cdot}10^{30}$	-4.63	2049
$H + O_2 + H_2 \rightleftharpoons HO_2 + H_2$	$1.52{\cdot}10^{19}$	-1.133	0
$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	$2.031{\cdot}10^{20}$	-1.590	0
$H + O_2 + H_2O \rightleftharpoons HO_2 + H_2O$	$2.1{\cdot}10^{23}$	-2.437	0
$2\,OH \rightleftharpoons O + H_2O$	$3.57{\cdot}10^{4}$	2.4	-2112
$O_2 + M \rightleftharpoons 2\,O + M$	$1.89{\cdot}10^{13}$	0	-1788
$2\,HO_2 \rightleftharpoons H_2O_2 + O_2$	$4.2{\cdot}10^{14}$	0	-11980
	$1.3{\cdot}10^{11}$	0	-1629
$2\,H + H_2O \rightleftharpoons H_2 + H_2O$	$6{\cdot}10^{19}$	-1.25	0
$2\,H + H_2 \rightleftharpoons 2\,H_2$	$9.27{\cdot}10^{16}$	-0.6	0

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: THE CANTERA MECHANISM

Table 3. Elementary reactions and forward rate constants of the CANTERA mechanism with 18 reactions and 9 species. Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; E_a: $[\mathrm{cal\,mol}^{-1}]$.

Reaction	A	b	E_a
$H_2 + OH \rightleftharpoons H_2O + H$	$1.17{*}10^{9}$	1.3	3626
$H + O_2 \rightleftharpoons OH + O$	$5.13{\cdot}10^{9}$	-0.816	16507
$O + H_2 \rightleftharpoons OH + H$	$1.8{\cdot}10^{10}$	1	8826
$H + O_2 + M \rightleftharpoons HO_2 + M$	$2.10{\cdot}10^{19}$	1	0
$H + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$6.7{\cdot}10^{19}$	-1.42	0
$OH + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$5{\cdot}10^{13}$	0	1000
$H + 2\,HO_2 \rightleftharpoons OH + OH$	$2.5{\cdot}10^{14}$	0	1900
$O + 2\,HO_2 \rightleftharpoons O_2 + OH$	$4.8{\cdot}10^{13}$	0	1000
$H_2 + M \rightleftharpoons H + H + M$	$7.5{\cdot}10^{23}$	-2.6	0
$H + OH + M \rightleftharpoons H_2O + M$	$2.5{\cdot}10^{13}$	0	700
$HO_2 + H \rightleftharpoons H_2 + O_2$	$1.3{\cdot}10^{17}$	0	45500
$H_2O_2 + M \rightleftharpoons OH + OH + M$	$1.6{\cdot}10^{12}$	0	3800
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	$1{\cdot}10^{13}$	0	1800
$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	$6.7{\cdot}10^{19}$	-1.42	0
$H_2 + O_2 \rightleftharpoons 2\,OH$	$1.7{\cdot}10^{13}$	0	47780
$2\,OH \rightleftharpoons O + H_2O$	$6{\cdot}10^{8}$	1.3	0
$O_2 + M \rightleftharpoons 2\,O + M$	$1.85{\cdot}10^{11}$	0.5	95560
$2\,HO_2 \rightleftharpoons H_2O_2 + O_2$	$2{\cdot}10^{12}$	0	0

Table 4. Elementary reactions and forward rate constants of the mechanisms by Miller, Mitchell, Smooke & Kee (1982) [4], Marinov, Westbrook & Pitz (1996) [1], and CANTERA.
Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; $\mathrm{E_a}$: $[\mathrm{cal\,mol}^{-1}]$.

Reaction	Miller mechanism			Marinov mechanism			CANTERA mechanism		
	A	b	$\mathrm{E_a}$	A	b	$\mathrm{E_a}$	A	b	$\mathrm{E_a}$
$H_2 + OH \rightleftharpoons H_2O + H$	$2.16{*}10^{18}$	1.51	3430	$2.14{*}10^{8}$	1.52	3449	$1.17{*}10^{9}$	1.3	3626
$H + O_2 \rightleftharpoons OH + O$	$2.65{\cdot}10^{16}$	-0.6707	17041	$2.02{\cdot}10^{14}$	-0.4	0	$5.13{\cdot}10^{9}$	-0.816	16507
$O + H_2 \rightleftharpoons OH + H$	$3.87{\cdot}10^{4}$	2.7	6260	$5.06{\cdot}10^{4}$	2.67	6290	$1.8{\cdot}10^{10}$	1	8826
$H + O_2 + M \rightleftharpoons HO_2 + M$	-	-	-	$1.05{\cdot}10^{19}$	-1.257	0	$2.10{\cdot}10^{19}$	1	0
$H + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$2.08{\cdot}10^{19}$	-1.24	0	-	-	-	$6.7{\cdot}10^{19}$	-1.42	0
$OH + 2\,O_2 \rightleftharpoons HO_2 + O_2$	$1.45{\cdot}10^{13}$ $5{\cdot}10^{15}$	0 0	-500 17330	$2.89{\cdot}10^{13}$	0	-497	$5{\cdot}10^{13}$	0	1000
$H + 2\,HO_2 \rightleftharpoons OH + OH$	$8.4{\cdot}10^{13}$	0	635	$1.5{\cdot}10^{14}$	0	1000	$2.5{\cdot}10^{14}$	0	1900
$O + 2\,HO_2 \rightleftharpoons O_2 + OH$	$2{\cdot}10^{13}$	0	0	$3.25{\cdot}10^{13}$	0	0	$4.8{\cdot}10^{13}$	0	1000
$H_2 + M \rightleftharpoons H + H + M$	$2.2{\cdot}10^{22}$	-2	0	$2.21{\cdot}10^{22}$	-2	0	$7.5{\cdot}10^{23}$	-2.6	0
$H + OH + M \rightleftharpoons H_2O + M$	$4.48{\cdot}10^{13}$	0	1068	$8.45{\cdot}10^{11}$	0.65	1241	$2.5{\cdot}10^{13}$	0	700
$HO_2 + H \rightleftharpoons H_2 + O_2$	-	-	-	-	-	-	$1.3{\cdot}10^{17}$	0	45500
$H_2O_2 + M \rightleftharpoons OH + OH + M$	$1.21{\cdot}10^{7}$	2	5200	$1.98{\cdot}10^{6}$	2	2435	$1.6{\cdot}10^{12}$	0	3800
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	$2{\cdot}10^{12}$ $1.7{\cdot}10^{18}$	0 0	427 29410	2.4	4.042	-2162	$1{\cdot}10^{13}$	0	1800
$O + H + M \rightleftharpoons OH + M$	$5{\cdot}10^{17}$	-1	0	$4.71{\cdot}10^{18}$	-1	0	-	-	-
$O + H_2O_2 + M \rightleftharpoons OH + HO_2$	$9.63{\cdot}10^{6}$	2	4000	$9.55{\cdot}10^{6}$	2	3970	-	-	-

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Table 4. Elementary reactions and forward rate constants of the mechanisms by Miller, Mitchell, Smooke & Kee (1982) [4], Marinov, Westbrook & Pitz (1996) [1], and CANTERA.
Units are: A: $[\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}]$; b: [-]; $\mathrm{E_a}$: $[\mathrm{cal\,mol}^{-1}]$.

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Reaction	Miller mechanism			Marinov mechanism			CANTERA mechanism		
	A	b	$\mathrm{E_a}$	A	b	$\mathrm{E_a}$	A	b	$\mathrm{E_a}$
$H + HO_2 \rightleftharpoons O + H_2O$	$3.97{\cdot}10^{12}$	0	671	$3.01{\cdot}10^{13}$	0	1721	-	-	-
$H + H_2O_2 \rightleftharpoons OH + H_2O$	$1{\cdot}10^{13}$	0	3600	$3.07{\cdot}10^{13}$	0	4217	-	-	-
$2\,OH + M \rightleftharpoons H_2O_2 + M$	$2.3{\cdot}10^{18}$	-0.9	-1700	$3.041{\cdot}10^{30}$	-4.63	2049	-	-	-
$H + O_2 + H_2 \rightleftharpoons HO_2 + H_2$	-	-	-	$1.52{\cdot}10^{19}$	-1.133	0	-	-	-
$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	-	-	-	$2.031{\cdot}10^{20}$	-1.590	0	$6.7{\cdot}10^{19}$	-1.42	0
$H + O_2 + H_2O \rightleftharpoons HO_2 + H_2O$	$1.126{\cdot}10^{19}$	-0.76	0	$2.1{\cdot}10^{23}$	-2.437	0	-	-	-
$H + O_2 + Ar \rightleftharpoons HO_2 + Ar$	$7{\cdot}10^{17}$	-0.8	0	-	-	-	-	-	-
$H_2 + O_2 \rightleftharpoons 2\,OH$	-	-	-	-	-	-	$1.7{\cdot}10^{13}$	0	47780
$2\,OH \rightleftharpoons O + H_2O$	$3.57{\cdot}10^{4}$	2.4	-2110	$3.57{\cdot}10^{4}$	2.4	-2112	$6{\cdot}10^{8}$	1.3	0
$O_2 + M \rightleftharpoons 2\,O + M$	$1.2{\cdot}10^{17}$	-1	0	$1.89{\cdot}10^{13}$	0	-1788	$1.85{\cdot}10^{11}$	0.5	95560
$2\,HO_2 \rightleftharpoons H_2O_2 + O_2$	$1.3{\cdot}10^{11}$	0	-1630	$4.2{\cdot}10^{14}$	0	-11980	$2{\cdot}10^{12}$	0	0
	$4.2{\cdot}10^{14}$	0	12000	$1.3{\cdot}10^{11}$	0	-1629			
$2\,H + H_2O \rightleftharpoons H_2 + H_2O$	$6{\cdot}10^{19}$	-1.25	0	$6{\cdot}10^{19}$	-1.25	0	-	-	-
$2\,H + H_2 \rightleftharpoons 2\,H_2$	$9{\cdot}10^{16}$	-0.6	0	$9.27{\cdot}10^{16}$	-0.6	0	-	-	-

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: REDUCED MECHANISM BY LU, JU & LAW DERIVED FROM THE DETAILED MECHANISM BY KIM, YETTER & DRYER

Table 5. Elementary reactions and forward rate constants of the mechanism by Kim, Yetter & Dryer (1994) [5] with 19 reactions and 9 species. Units are: A: [$\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}$]; b: [-]; $\mathrm{E_a}$: [$\mathrm{cal\,mol^{-1}}$].

	Reaction	${}^{10}\log A$	b	$10^{-3}\times\mathrm{E_a}$
	$H_2 - O_2$ chain reactions			
1	$H + O_2 \rightleftharpoons O + OH$	14.28	0.0	16.44
2	$O + H_2 \rightleftharpoons H + OH$	4.71	2.67	6.29
3	$OH + H_2 \rightleftharpoons H + H_2O$	8.33	1.51	3.43
4	$O + H_2O \rightleftharpoons OH + OH$	6.47	2.02	13.40
	$H_2 - O_2$ dissociation/recombination reactions			
5	$H_2 + M \rightleftharpoons H + H + M$	19.66	-1.40	104.38
	$H_2 + Ar \rightleftharpoons H + H + Ar$	18.77	-1.10	104.38
6	$O + O + M \rightleftharpoons O_2 + M$	15.79	-0.50	0.00
	$O + O + Ar \rightleftharpoons O_2 + Ar$	13.28	0.0	-1.79
7	$O + H_2 \rightleftharpoons OH + H$	18.67	-1.0	0.00
8	$O + OH + M \rightleftharpoons H_2O + M$	22.35	-2.0	0.00
	$H + OH + Ar \rightleftharpoons H_2O + Ar$	21.92	-2.0	0.00

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COMBUSTION REACTION OF HYDROGEN IN AIR

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	Reaction	${}^{10}\log A$	b	$10^{-3}\times E_a$
Formation and consumption of HO_2				
9	$H + O_2 + M \rightleftharpoons HO_2 + M$	19.79	-1.42	0.00
	$H + O_2 + Ar \rightleftharpoons HO_2 + Ar$	15.18	0.0	-1.00
	$H + O_2 \rightleftharpoons HO_2$	13.65	0.0	0.00
10	$HO_2 + H \rightleftharpoons H_2 + O_2$	13.82	0.0	2.13
11	$HO_2 + H \rightleftharpoons OH + OH$	14.23	0.0	0.87
12	$HO_2 + O \rightleftharpoons O_2$	13.24	0.0	-0.40
13	$HO_2 + OH \rightleftharpoons H_2O + O_2$	16.28	-1.00	0.00

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Table 5. Elementary reactions and forward rate constants of the mechanism by Kim, Yetter & Dryer (1994) [5] with 19 reactions and 9 species. Units are: A: [$\mathrm{mol}^{1-n}\,\mathrm{cm}^{3n-3}\,\mathrm{s}^{-1}\,\mathrm{K}^{-b}$]; b: [-]; $\mathrm{E_a}$: [$\mathrm{cal\,mol}^{-1}$].

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	Reaction	${}^{10}\log A$	b	$10^{-3}\times\mathrm{E_a}$
Formation and consumption of H_2O_2				
14	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	14.62	0.0	11.98
		11.11	0.0	-1.629
15	$H_2O_2 + M \rightleftharpoons OH + OH + M$	17.08	0.0	45.50
	$H_2O_2 + Ar \rightleftharpoons OH + OH + Ar$	16.28	0.0	43.00
	$H_2O_2 \rightleftharpoons OH + OH$	14.47	0.0	48.40
16	$H_2O_2 + H \rightleftharpoons H_2O + OH$	13.00	0.0	3.59
17	$H_2O_2 + H \rightleftharpoons H_2 + HO_2$	13.68	0.0	7.95
18	$H_2O_2 + O \rightleftharpoons OH + HO_2$	6.98	2.0	3.97
19	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	12.00	0.0	0.00
		14.76	0.0	9.56

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: REDUCED MECHANISM BY LU, JU & LAW DERIVED FROM THE DETAILED MECHANISM BY KIM, YETTER & DRYER

Reduced kinetic scheme for hydrogen-air combustion by Lu, Ju & Law (2001) [6]:

$$\mathrm{O} + \mathrm{H_2} \rightleftharpoons \mathrm{H} + \mathrm{OH} \tag{20}$$

$$\mathrm{H} + \mathrm{O_2} \rightleftharpoons \mathrm{O} + \mathrm{OH} \tag{21}$$

$$\mathrm{OH} + \mathrm{H_2} \rightleftharpoons \mathrm{H} + \mathrm{H_2O} \tag{22}$$

$$\mathrm{H_2} + \mathrm{M} \rightleftharpoons \mathrm{H} + \mathrm{H} + \mathrm{M} \tag{23}$$

Reactions (20) to (22) are H_2–O_2 chain reactions.
Reaction (23) is a H_2–O_2 recombination reaction.

COMBUSTION REACTION OF HYDROGEN IN AIR

REACTION MECHANISMS: REDUCED MECHANISM BY LU, JU & LAW DERIVED FROM THE DETAILED MECHANISM BY KIM, YETTER & DRYER

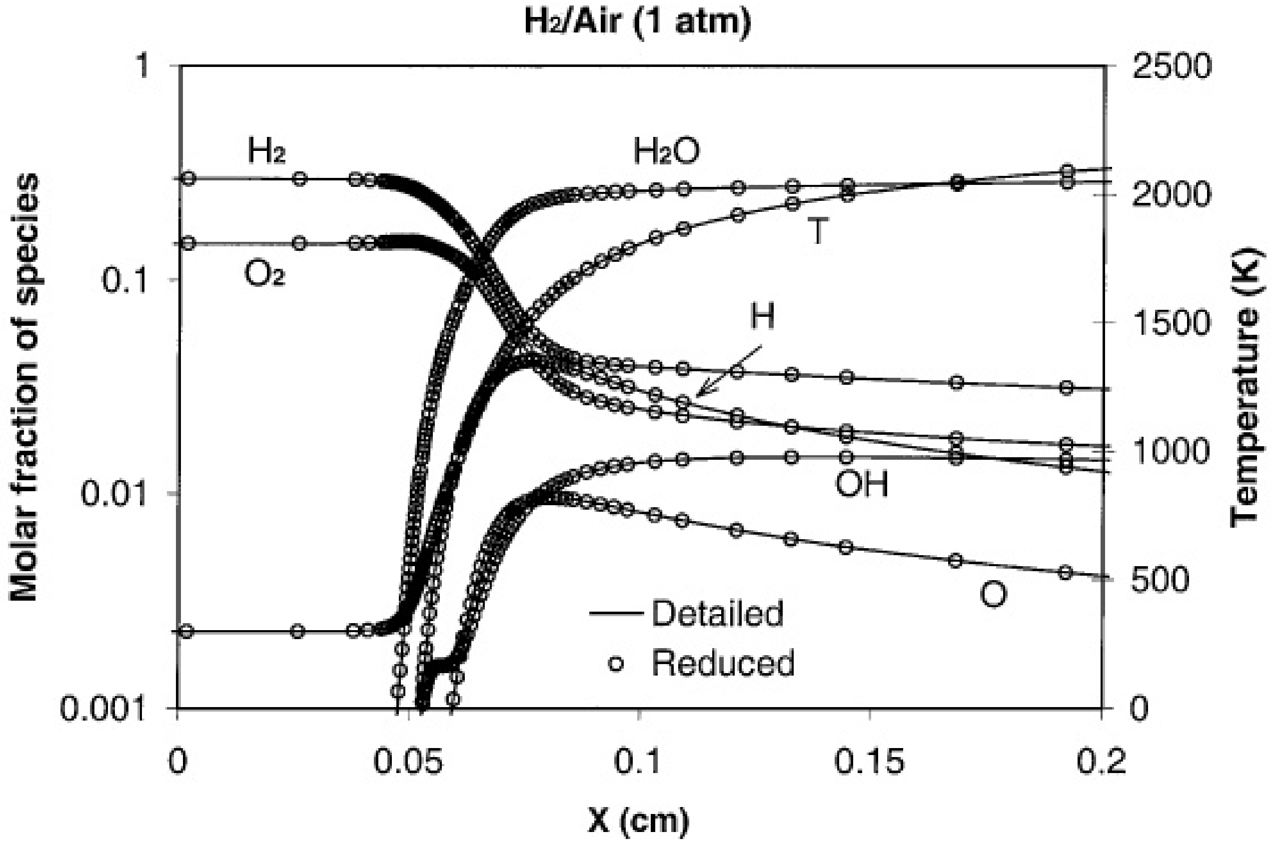

Figure 4. Comparison of the temperature and species flame structure as predicted by the reduced mechanism of Lu, Ju & Law (2001) [6] and the detailed mechanism of Kim, Yetter & Dryer (1994) [5] for a stoichiometric H_2–air flame at 1 atm.

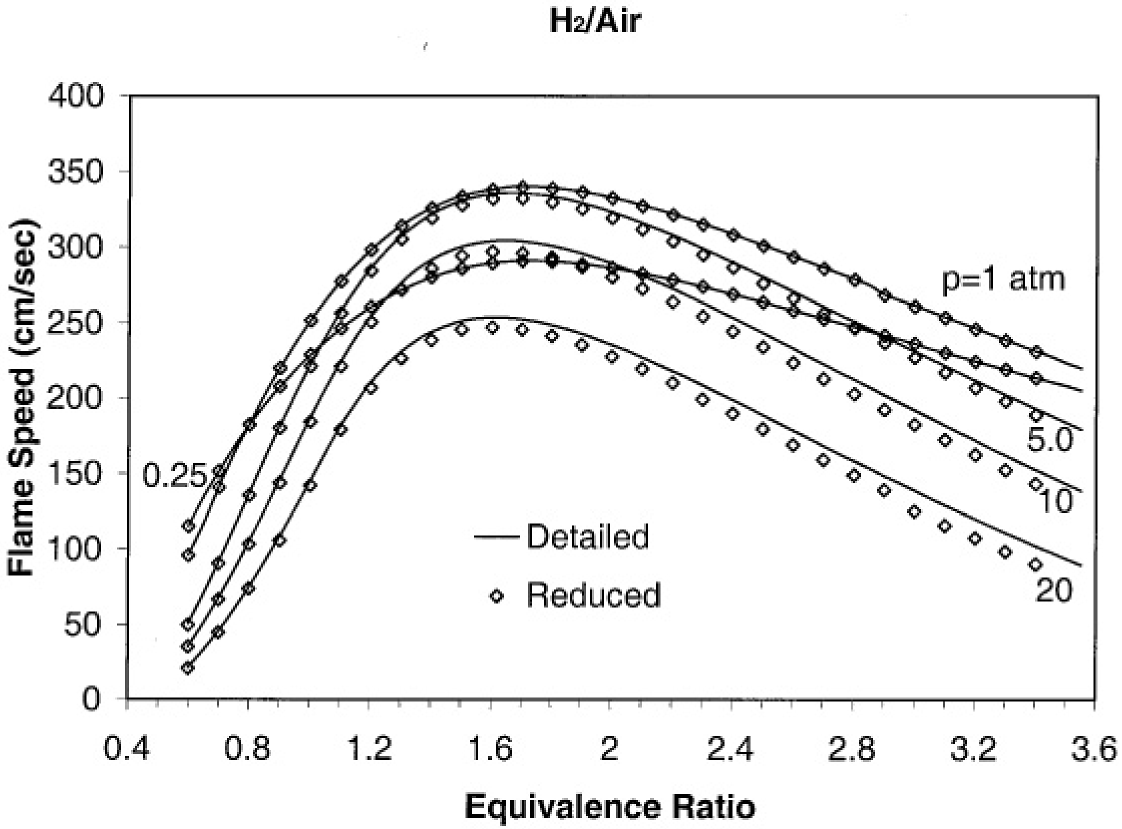

Figure 5. Comparison of the laminar burning velocity as predicted by the reduced mechanism of Lu, Ju & Law (2001) [6] and the detailed mechanism of Kim, Yetter & Dryer (1994) [5] for a stoichiometric H_2–air flame at 1 atm.

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