Chemical Kinetics in Support of Syngas Turbine Combustion

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Research Motivation and Objectives

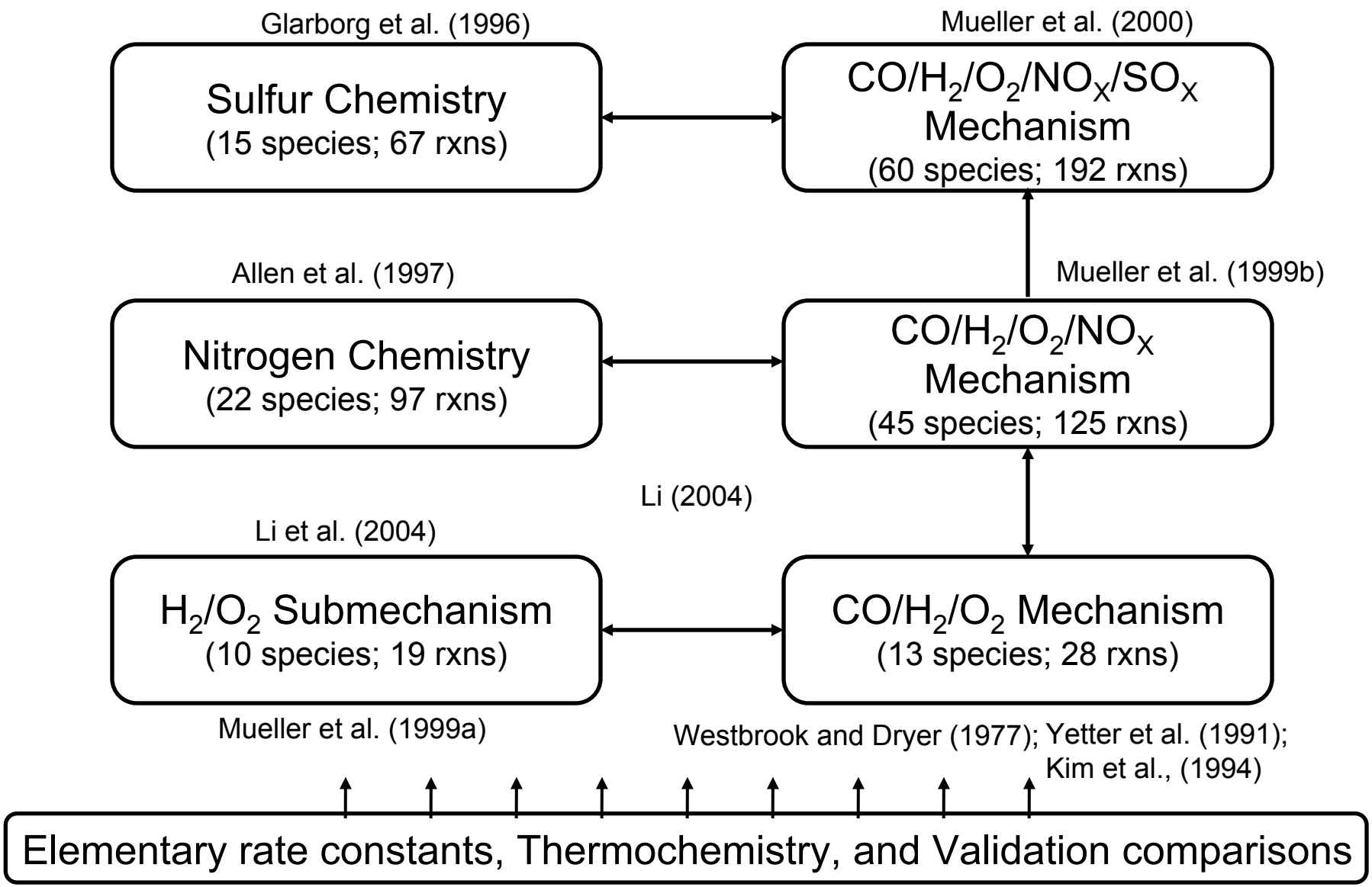
Motivation:

- Syngas turbine combustion conditions span a range of pressures, temperatures, and compositions atypical of those more generally encompassed by fundamental chemical kinetic validation and combustion experiments.
- More accurate computational design tools will require chemical kinetic models to be used either directly or as a skeletal model from which lower dimensional representations for CFD can be derived.

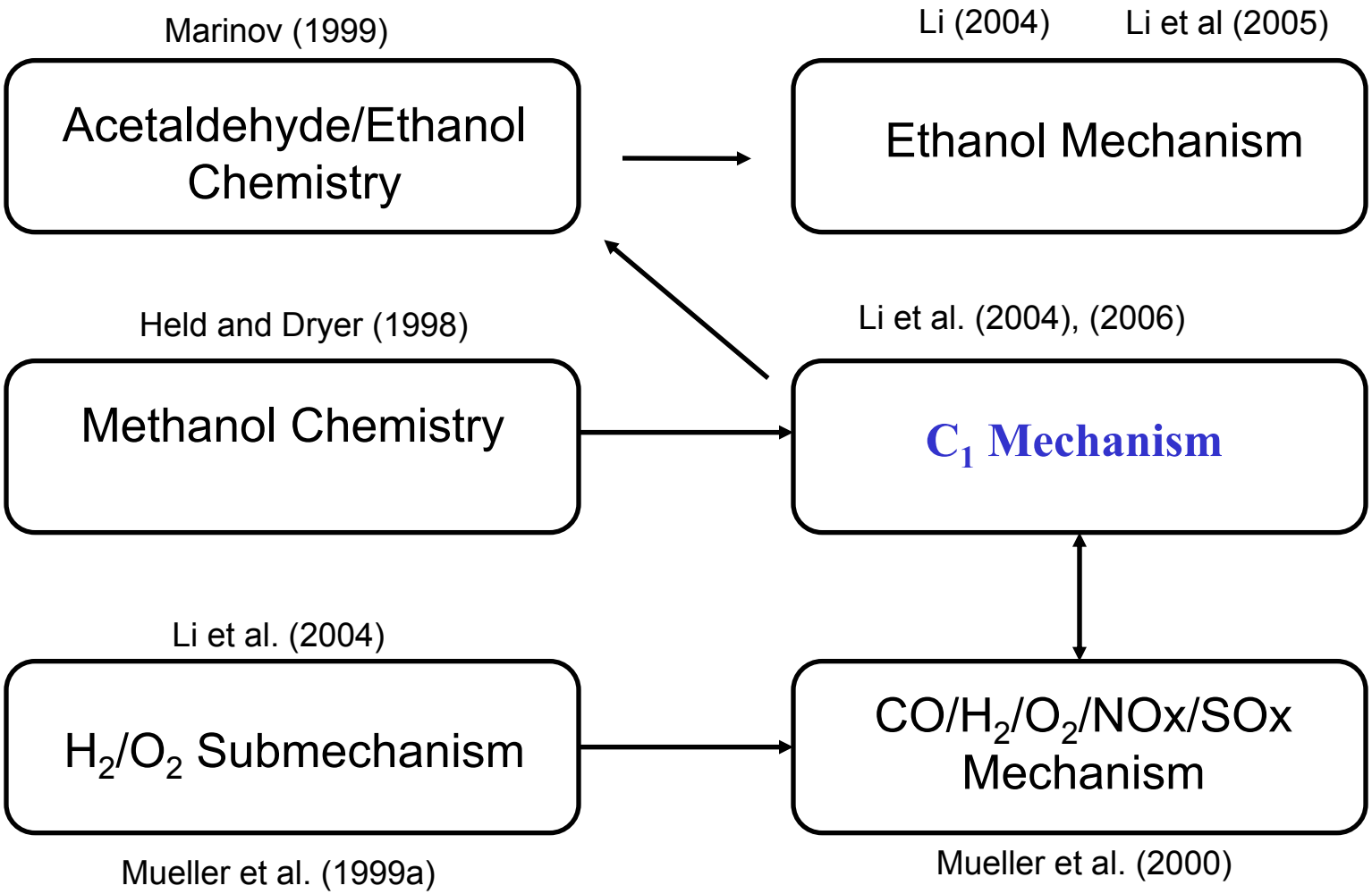
Objectives

- Further investigate fundamental chemical kinetic characteristics of CO/H_2/Air/diluent/contaminant mixtures at pressures, temperatures, and diluent concentrations of CO_2 and H_2O typical of syngas combustion in gas turbines.
- Further evaluate third body collisional properties of major diluents, carbon dioxide and water, in the $H + O_2 + M = HO_2 + M$ reaction.
- Extend our own prior work in developing and validating kinetic models for the CO/hydrogen/oxygen/contaminant systems.
- Provide additional experimental data using a Variable Pressure Flow Reactor (VPFR) for mixture oxidation.
- Analyze the individual and interactive behavior of specific elementary and subsets of elementary reactions at the conditions of interest.

Mechanism Development



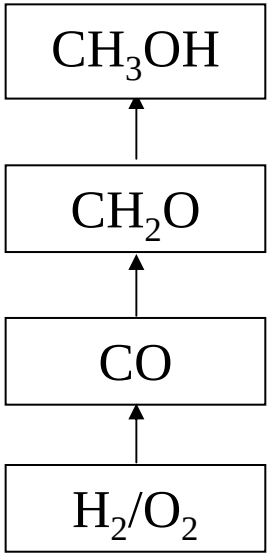
C_1 Mechanism Development



Available on the web at http://www.princeton.edu/~combust/

C_1 Mechanism Used in This Work

- The mechanism consists of 85 elementary reactions among 21 species, and is based on the CH_3OH/O_2 mechanism of Held and Dryer (1998) and new H_2/O_2 mechanism of Li et al. (2004).
- Revisions encompass recently published kinetic and thermochemical information, while continuing to predict both new experiments and the experimental targets investigated by the original mechanism.
- It is developed in a hierarchical manner:



At each level, the sub-mechanism is tested against a wide range of experimental data:

- Species time histories in flow reactors
- Ignition delay data from shock tubes, etc.
- Laminar premixed flame speeds
- Other data (stirred reactor, burner-stabilized flame, etc.)
- New validations as they become available

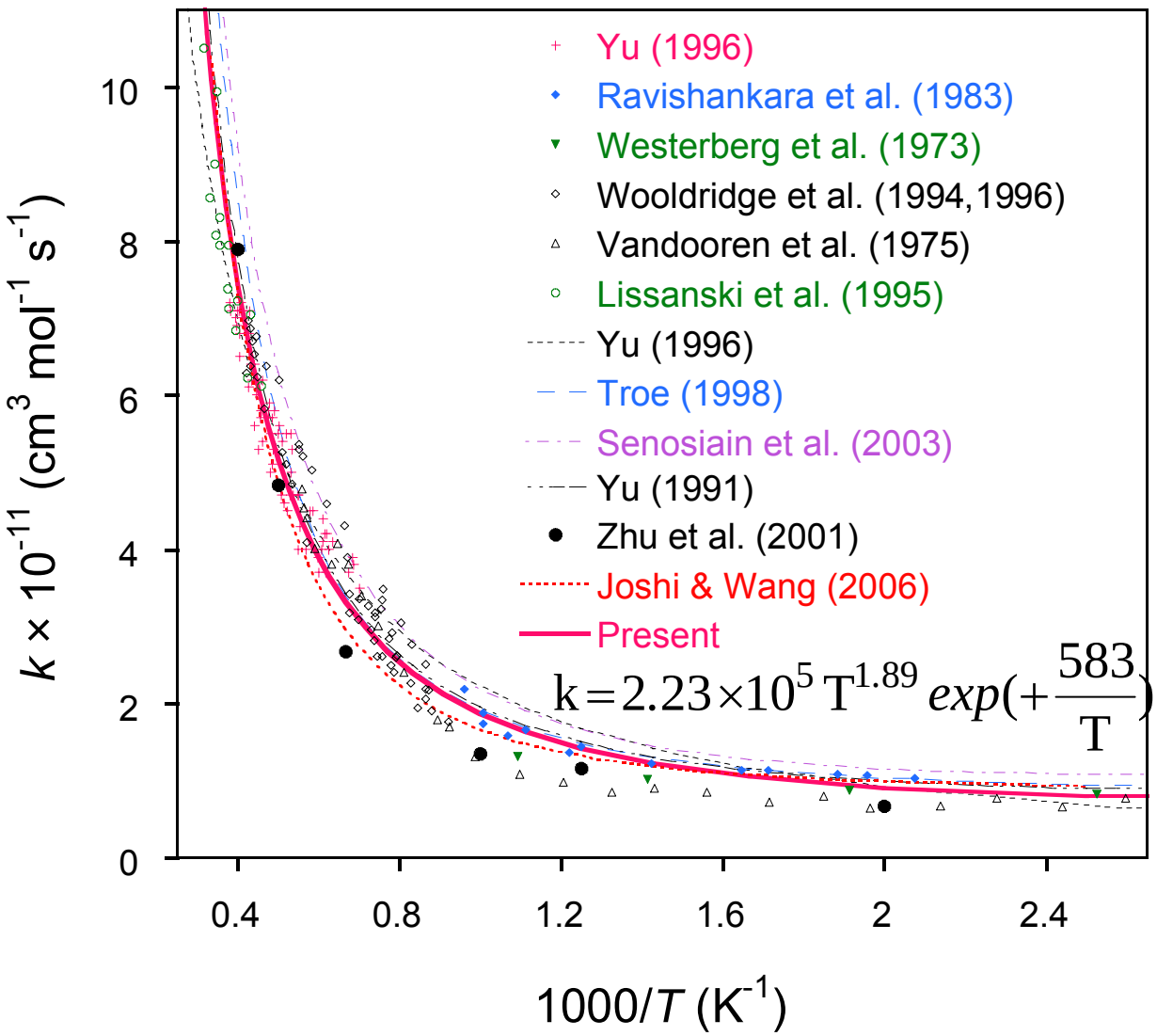
Key C_1 Mechanism Refinements

Part I: $CO + OH = CO_2 + H$

- This reaction is the main pathway to convert CO to CO_2 and is responsible for a major fraction of the energy release derived in hydrocarbon oxidation
- Recent theoretical calculations predict higher rates than experimental measurements at low to intermediate temperature range
- The temperature-dependent sensitivity analysis of Zhao et al. (2005) demonstrates that the laminar flame speed of H_2/CO oxidation systems is most sensitive to this reaction at 300-1900 K, depending on H_2/CO ratio
- The C_1 mechanism uses a new, weighted least squares fit of all of the experimentally measured rate constants available in literature.

$$k = 2.23 \times 10^5 \, T^{1.89} \, exp(+\frac{583}{T})$$

Weighted Fit for CO + OH = CO_2 + H



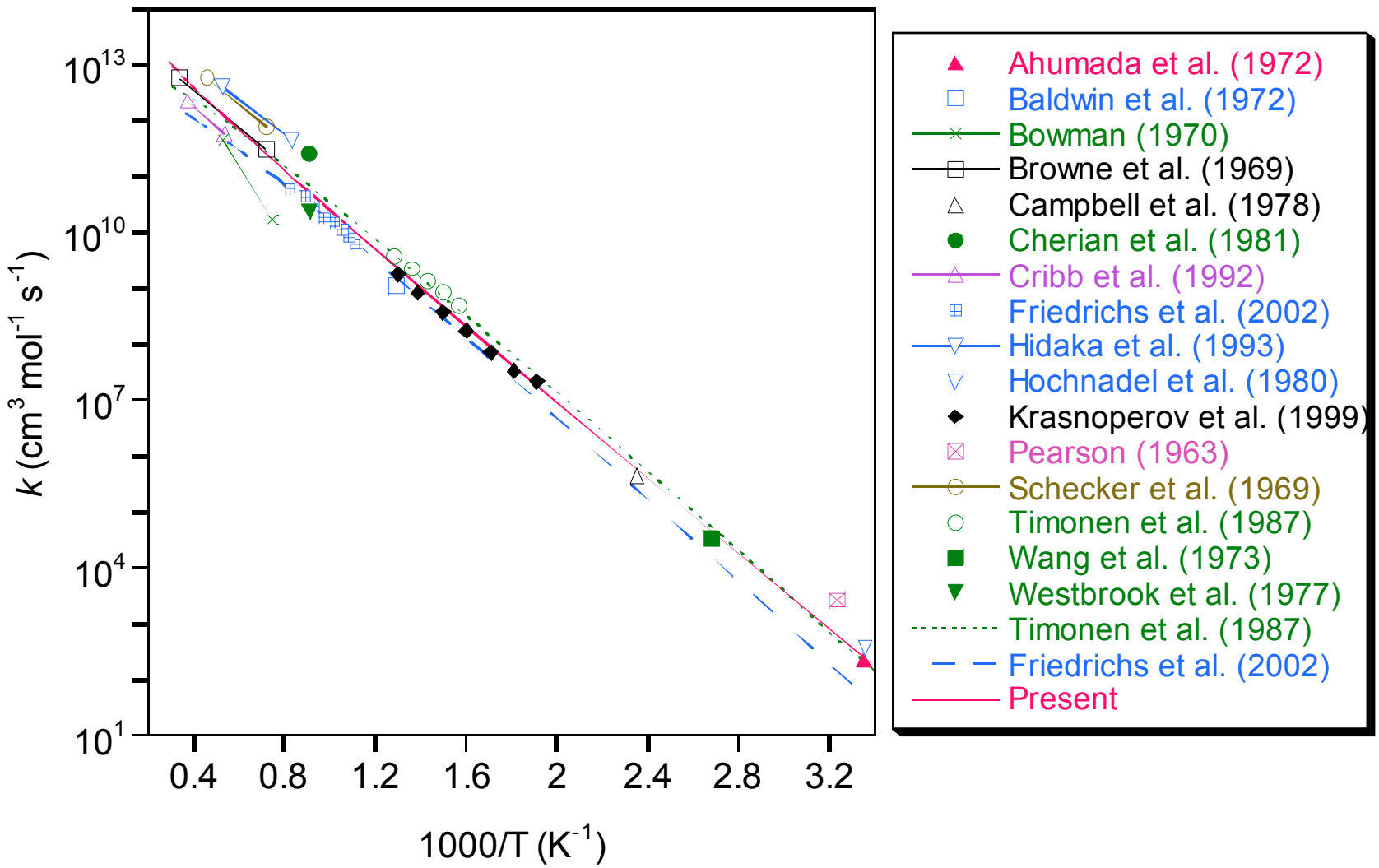
Key C_1 Mechanism Refinements

Part II: HCO + M = H + CO + M

- This reaction is the main pathway generating CO during the high temperature combustion of hydrocarbons.
- The temperature-dependent sensitivity analysis of Zhao et al. (2005) demonstrates that the laminar flame speed of hydrocarbon combustion systems is most sensitive to this reaction at 1300-2000 K, which is above the temperature range of recent experimental studies of this reaction (Friedrichs et al., 2002).
- Extrapolation of Friedrichs et al. causes difficulties in reproducing flame speed and flow reactor results for numerous hydrocarbons
- In the present study, a new rate correlation was developed by a weighted least squares fitting of literature experimental data

$$k = 4.75 \times 10^{11} T^{0.66} \exp(-\frac{7485}{T})$$

Weighted Fit for HCO + M = CO + H + M



Full Set of Updated Kinetic Parameters

❖ Reaction rate coefficients:

- H_2/O_2 sub-mechanism: Li et al. (Int. J. Chem. Kinet. 2004)
- $CO + OH = CO_2 + H$: this study
  - weighted least squares fitting of experimental results in literature
- $HCO + M = H + CO + M$: this study
  - weighted least squares fitting of experimental results in literature
- CH_2O decomposition: Friedrichs et al. (Int. J. Chem. Kinet. 2004, 36, 157)
- $CH_2O + H = HCO + H_2$: Irdam et al. (Int. J. Chem. Kinet. 1993, 25, 285)
- $CH_2O + HO_2 = HCO + H_2O_2$: Eiteneer et al. (J. Phys. Chem. A 1998, 102, 5196)
- CH_3OH decomposition reactions: GRI-MECH 3.0 (1999)

❖ Thermodynamic data:

- OH: Ruscic et al. (J. Phys. Chem. A 2002, 106, 2727)
- HO_2: Ruscic et al. (J. Phys. Chem. A 2006, In press)
- CH_3: Ruscic et al. (J. Phys. Chem. A 1999, 103, 8625)
- CH_2OH: Johnson and Hudgens (J. Phys. Chem. 1996, 100, 19874)

Literature CO Experiments Used for Validation

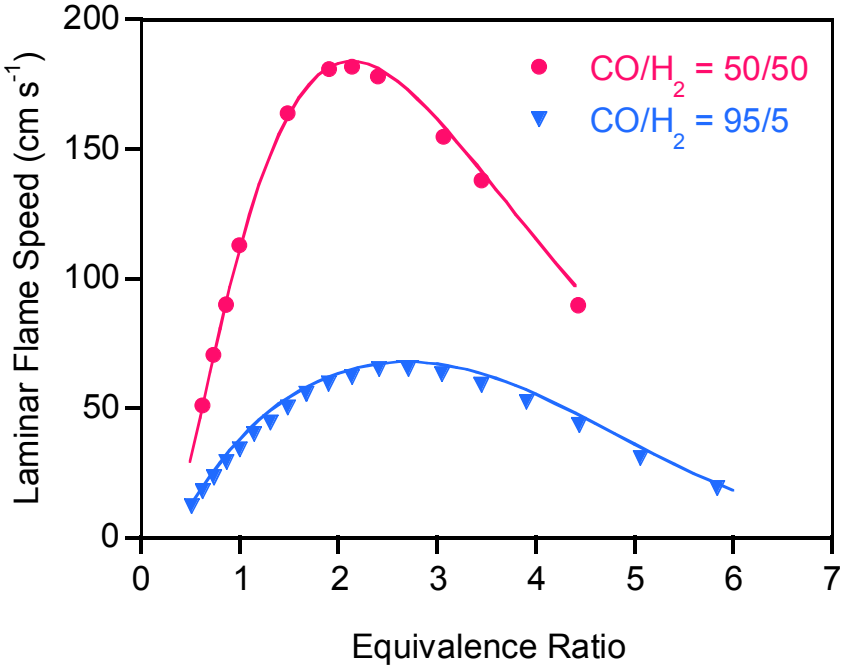
Method	Source	Mixture	T (K)	P (atm)	ϕ
Shock Tube	Gardiner et al. (1971)	$CO/H_2/O_2/Ar$	1400– 2500	0.15– 0.3	0.40
	Dean et al. (1978)	$CO/H_2/O_2/Ar$	2000 – 2850	1.2 – 2.2	1.6– 6.1
Laminar Premixed Flame	McLean et al. (1994)	$CO/H_2/air$	298	1	0.5 – 6.0
	Huang et al. (2003)	$CO/H_2/N_2/air$	298	1	0.7– 1.4
Flow Reactor	Yetter et al. (1991)	$CO/H_2O/O_2/N_2$	1033	1	0.4 – 1.4
	Kim et al. (1994)	$CO/H_2O/O_2/N_2$	960 – 1200	1.0 – 9.6	0.3 – 2.1
	Mueller et al. (1999)	$CO/H_2O/O_2/N_2$	1038	1.0 – 9.6	1.0

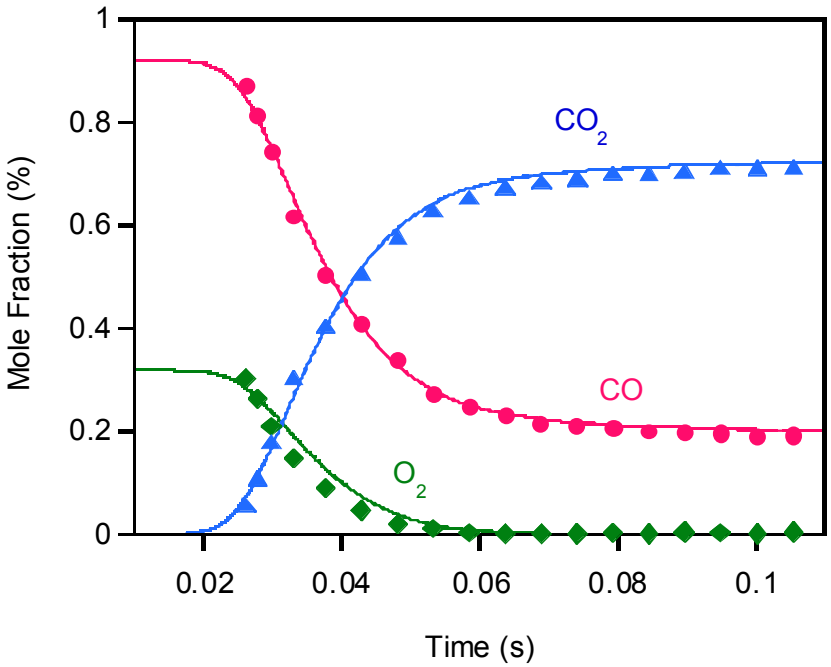
Literature CH_2O Experiments Used for Validation

Method	Source	Mixture	T (K)	P (atm)	ϕ
Shock Tube	Dean et al. (1980)	$CH_2O/O_2/Ar$	1935 – 2150	1.1 – 1.3	pyrolysis – 0.67
	Buxton and Simpson (1986)	CH_2O/Ar	1750 – 2100	0.6 – 3.5	pyrolysis
	Hidaka et al. (1993)	$CH_2O/O_2/Ar$	1240 – 1950	1.5 – 2.9	pyrolysis – 4.0
	Eiteneer et al. (1998)	$CH_2O/O_2/Ar$	1440 – 2120	0.9 – 2.3	pyrolysis – 6.0
	Friedrichs et al. (2002)	CH_2O/Ar	955 – 975	0.3 – 1.8	pyrolysis
Burner-Stabilized Flame	Vandooren et al. (1986)	CH_2O/O_2	300	0.03	0.22
Flow Reactor	Hochgreb and Dryer (1992)	$CH_2O/O_2/N_2$	945 – 1095	1	0.013– 1.74
	Scire (2002)	$CH_2O/H_2O/O_2/N_2$	850 – 950	1.5 – 6.0	~ 0.005

Representative Test Cases

Flame Speeds and 1 Atm Pressure Flow Reactor





Initial Conditions:
298 K, 1 atm, CO/H_2/air mixture

Symbols: laminar flame speed data of McLean et al. (1994)

—— : Present model

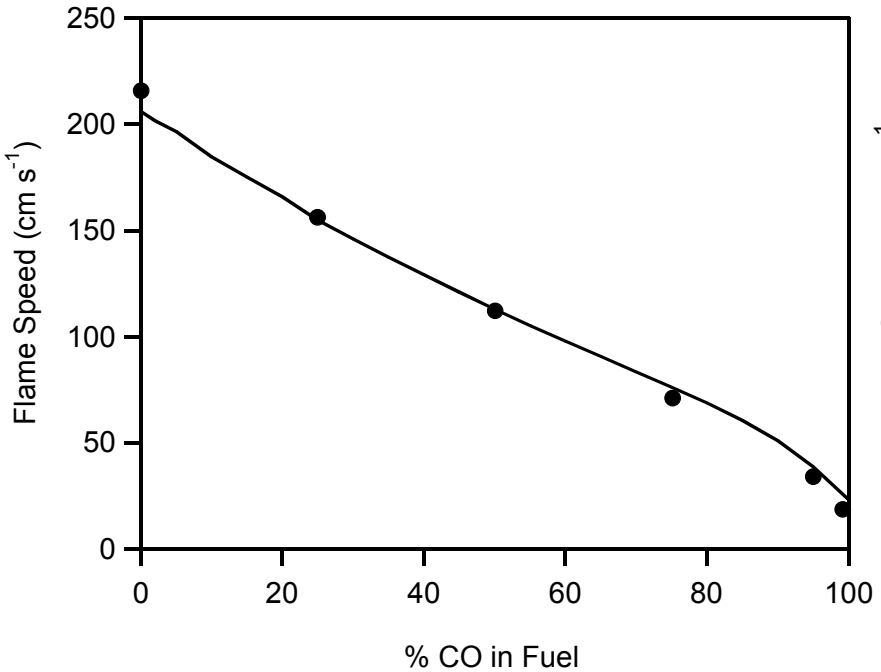
Initial Conditions:
CO = 0.92%, H_2O = 0.59%, O_2 = 0.32% with balance N_2 at 1034 K and 1 atm

Symbols: flow reactor data of Yetter et al. (1991)

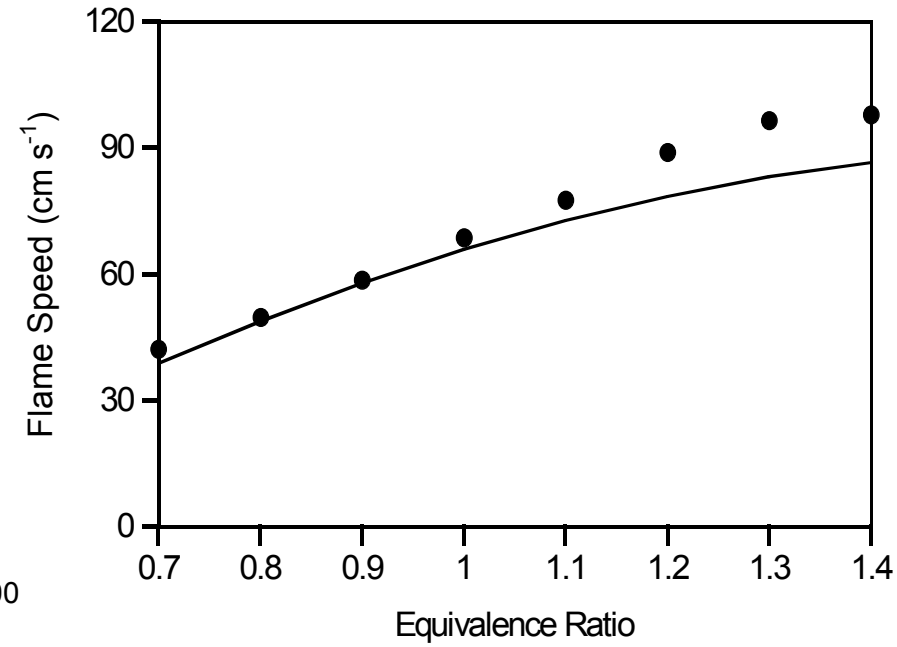
—— : Present model

Representative Test Cases

Flame Speed Comparisons cont'd



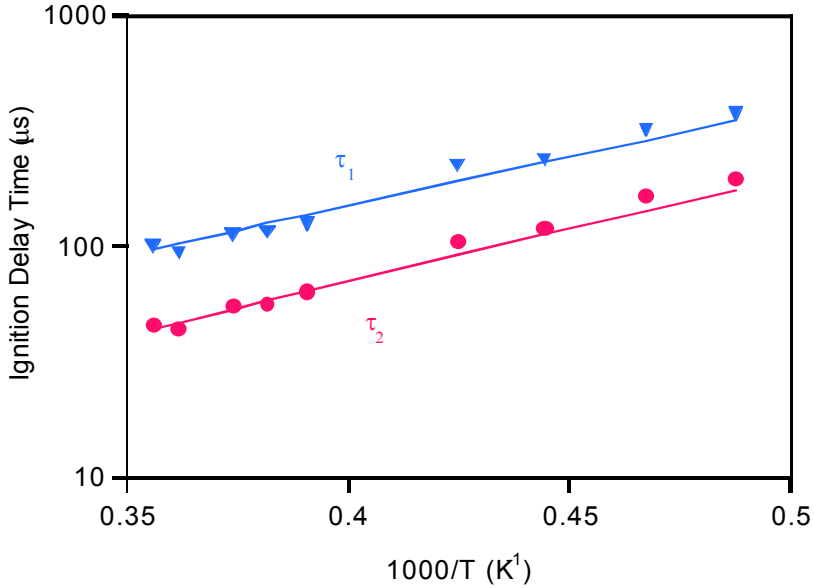
Comparison with stoichiometric CO/H_2/air mixture data at 1atm and 298 K (Mclean et al., 1994)

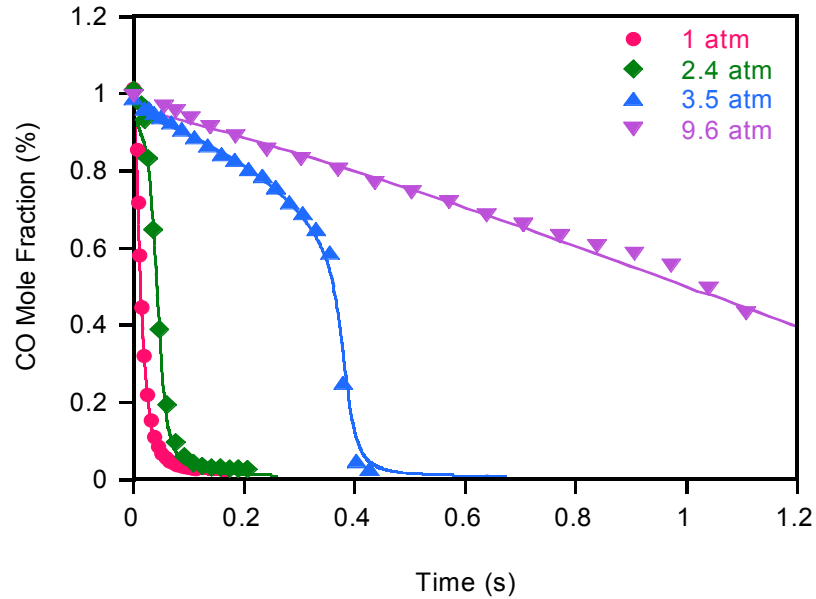


Comparison with reformer gas data (28% H_2, 25% CO, and 47% N_2) at 1atm and 298 K (Huang et al., 2004).

Representative Test Cases

Shock Tube Ignition and VPFR





Initial Conditions:

H_2 = 0.049%, O_2 = 1.01%, CO = 3.28% with balance Ar

τ_1 and τ_2 are defined as the time when $[CO_2]$ reaches 2.4×10^{16} and 8×10^{15} molecule/cm^3, respectively.

Symbols: shock tube data of Dean et al. (1978)

—— : Present model

Initial Conditions:

CO = 1.01%, H_2O = 0.65%, O_2 = 0.52% with balance N_2 at 1038 K and 1.0 atm; CO = 1.01%, H_2O = 0.65%, O_2 = 0.50% with balance N_2 at 1038 K and 2.4 atm; CO = 0.99%, H_2O = 0.65%, O_2 = 0.49% with balance N_2 at 1038 K and 3.5 atm; CO = 0.99%, H_2O = 0.65%, O_2 = 0.49% with balance N_2 at 1040 K and 9.6 atm

Symbols: VPFR data of Mueller et al. (1999)

_____ : Present model

Computational Singular Perturbation (CSP)

(Lam, 1993)

Chemical kinetic ODE system: $\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z})$

where $\mathbf{z} = \left(\tilde{T} \quad y_1 \quad y_2 \quad \ldots \quad y_n\right)^T$ – state variable vector

$\mathbf{g}$ – vector of rates defined by reaction mechanism

y_i – species mass fractions (*n* total)

$\tilde{T}$ - normalized temperature

At any given time, t, the rate vector can be "perturbed" with respect to time, i.e.

$\frac{d\mathbf{g}(z)}{dt} = \mathbf{J} \bullet \mathbf{g}(\mathbf{z})$, to define a local Jacobian matrix, $\mathbf{J} = \frac{d\mathbf{g}(\mathbf{z})}{d\mathbf{z}}$, and $\mathbf{J}$

can be decomposed , $\mathbf{J} = \mathbf{V}\Lambda\mathbf{V}^{-1}$ where $\mathbf{V} = \left(\mathbf{v}_1 \mathbf{v}_2 \ldots \mathbf{v}_{n+1}\right)$ - matrix of eigenvectors

Λ - diagonal matrix containing eigenvalues

$$\therefore \mathbf{g}(t + \Delta t) \approx \sum_{i=1}^{n+1} f_i \mathbf{v}_i \exp\left(\lambda_i \Delta t\right)$$

mode amplitude (importance)

mode timescale
may be complex
(complex conjugate pairs)

CSP (Cont'd)

Mode classification:

Re(λ_i) < 0 – stable (decaying) mode
Re(λ_i) > 0 – unstable (explosive) mode – **associated with ignition**
Im(λ_i) ≠ 0 – oscillatory mode; complex conjugate modes are transformed in the analysis into two real modes with the same damping coefficient Re(λ_i) and oscillatory frequency |Im(λ_i)| and a phase shift of π (Liu et al. 2001).

Mode makeup (Participation Index):

$$\mathbf{g} = \sum_{j=1}^{J} r_j \mathbf{S}_j$$

r_j - *j*th reaction rate

$$\mathbf{S}_j = \frac{\partial \mathbf{g}}{\partial r_j}$$ - vector of effective stoichiometric coefficients

$$\mathbf{P}_j = r_j \mathbf{V}^{-1} \bullet \mathbf{S}_j \big/ \mathrm{norm}$$ - Normalized vector of contributions of *j*th reaction for individual modes

Participation Index values present the importance of reactions promoting (positive) and inhibiting (negative) the thermal evolution (ignition) of the system.

CSP (Cont'd)

CSP advantages:

- More "direct" analysis of kinetic ODE system as opposed to typical sensitivity analysis
- Identifying and following the explosive modes allows determination of the factors controlling ignition *unambiguously*
- In conjunction with flux analysis, *more complete* interpretation can be derived

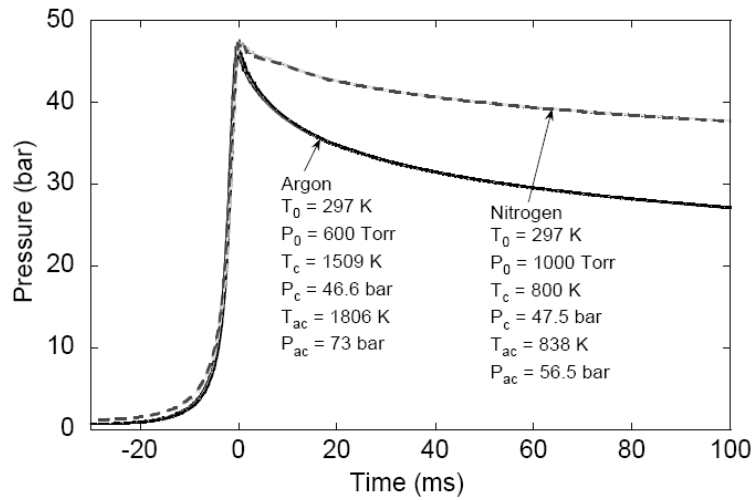
Implementation:

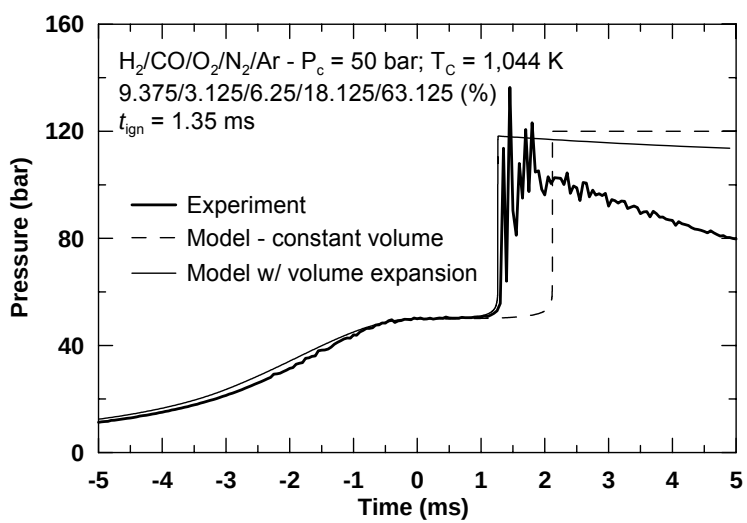
- An in-house software package coupled with CHEMKIN library for post-processing of SENKIN outputs
- Unlike most prior implementations, temperature is included in the variable vector (important for thermal feedback)
- Eigenvalue analysis is performed using LAPACK's facilities

CSP – Different Experimental Systems

Rapid Compression Machine (RCM) Analyses

RCM's can generate high pressure ignition information~ 20 to 40 atm



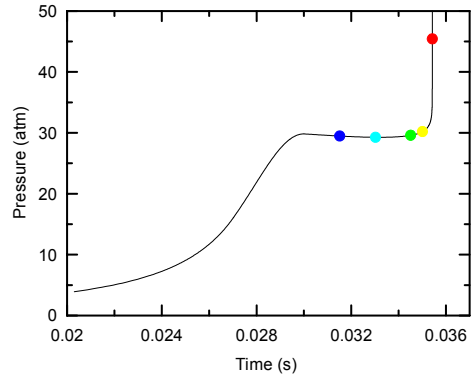


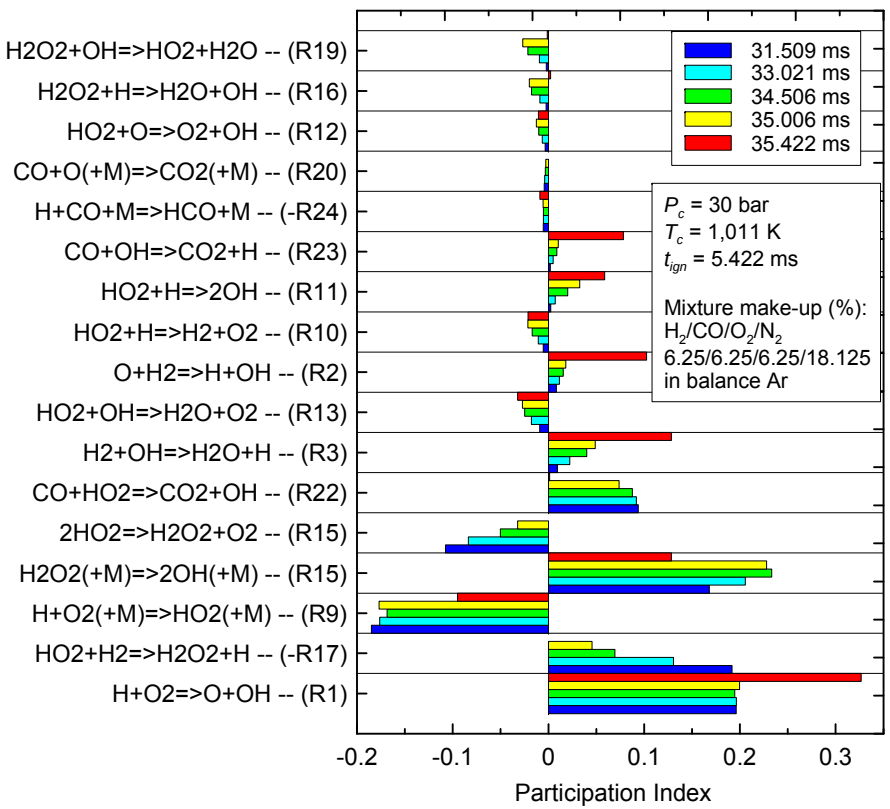
- As originally developed (Kazakov et al. 2006), the CSP analysis only treated constant volume systems (e.g. shock tubes)
- High pressure data obtained in Rapid Compression Machines (RCM) (e.g., Mittal and Sung, 2006) show heat losses need to be included in modeling these systems
- Sung and co-workers correct for heat losses by introducing a time-dependent volume expansion term after the piston reaches TDC
- This type of treatment effectively changes the rate vector **g** from its constant-volume counterpart
- A newly developed version of the CSP code can now implement these volume-changing systems

Results - Rapid Compression Machine Ignition

Mixture Composition:

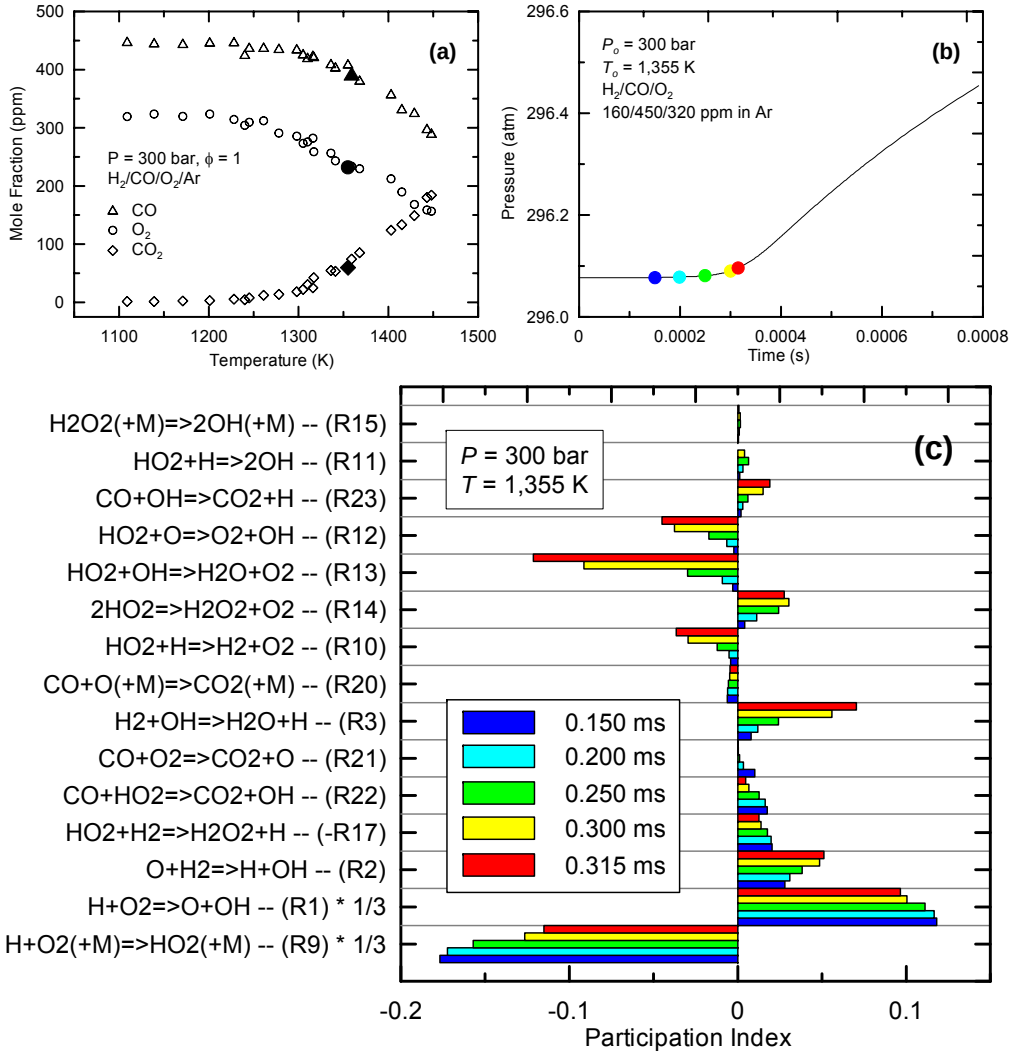
$H_2/CO/O_2/N_2/Ar$ = 6.25/6.25/6.25/18.125/63.125





- Analysis of typical conditions (above) studied by Mittal et al. (2006) in an RCM
- Mittal et al. identify that $CO+HO_2=CO+OH$ (R22) is primarily responsible for disagreement of C_1 model with experiment
- (R22) is only contributory during chemical induction phase (initial radical pool growth)
- Variation of ignition properties with CO/H_2 ratio comes primarily from competition of (R22) and $H_2+HO_2=H_2O_2+H$ (R17)
- The following reactions contribute to describing heat release:
  - $HO_2 + OH = H_2O + O_2$ (R13)
  - $HO_2 + H = OH + OH$ (R11)
  - $H + O_2 + M = HO_2 + M$ (R9)
  - $H_2 + OH = H_2O + H$ (R3)
  - $H_2 + O = H + OH$ (R2)
  - $H_2O_2 + M = OH + OH + M$ (R15)
  - $CO + OH = CO_2 + H$ (R23)
- (R22) is likely much slower that previously estimated.

Results – High Pressure Shock tube ignition



- High pressure shock tube data of and analysis for Sivaramakrishnan et al.(2005)
- Present C_1 model compares favorably with these high pressure shock tube experiments
- Dilute character of these studies emphasizes the importance of $HO_2 + OH = H_2O + O_2$ (R13)
- Analysis at the above conditions and mixture composition shows no importance of (R22)
- Analysis for these P and T conditions with mole fractions of prior RCM experiments identifies same relative importance of reactions shown in RCM experiments at lower P and T.
- Under all conditions the importance of collision efficiencies in $H + O_2 + M = HO_2 + M$ (R9) is important to both ignition and heat release events

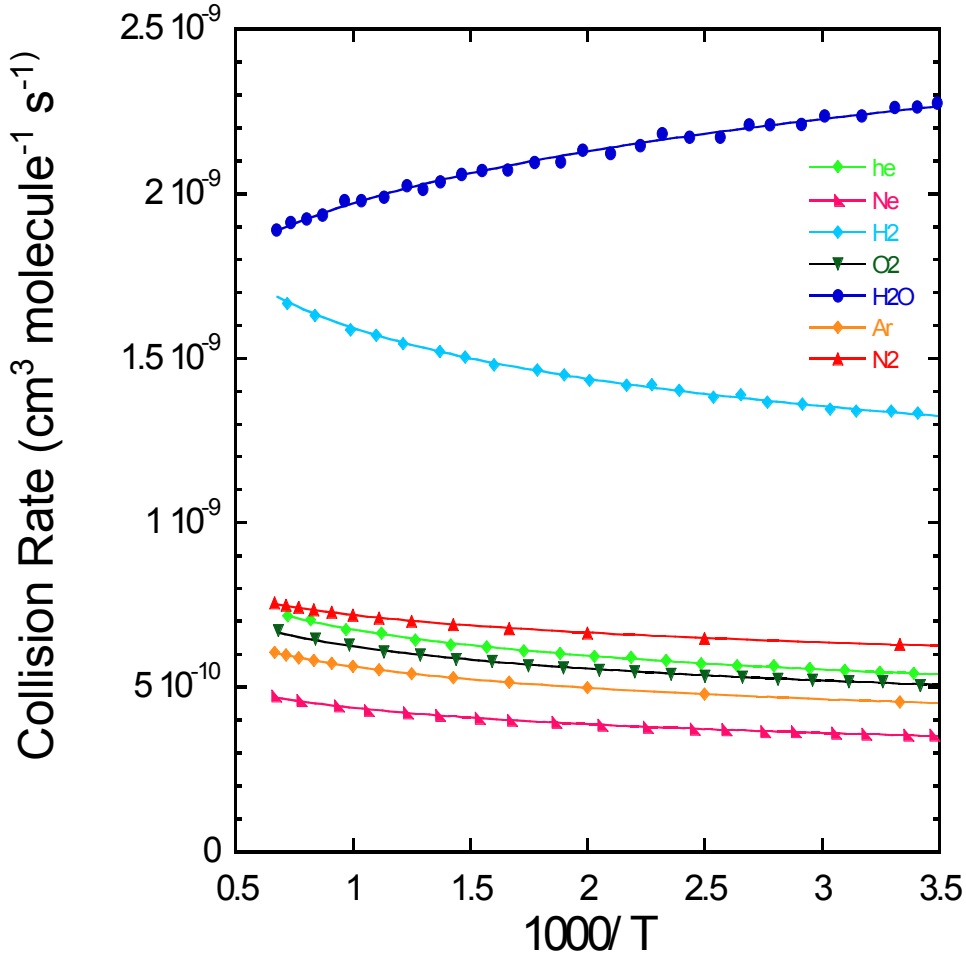
Collision Efficiencies

Michael et al (2002) measured chemical rates and estimated collisional rates of various species for $H+O_2+M=HO_2+M$

Water is a much more effective collider than other combustion species

Are the collisional characteristics of strong and weak colliders interactive in mixtures?

	CR (cm^3/mol/s) = $A\ T^n$ *From Michael et al.. (2002)*	
Species	***A***	***n***
He	1.9437×10^{-10}	0.18036
Ne	1.3121×10^{-10}	0.17441
H_2	5.7633×10^{-10}	0.14711
O_2	1.9923×10^{-10}	0.16539
H_2O	4.2451×10^{-9}	-0.11109
Ar	1.6733×10^{-10}	0.17565
N_2	3.3311×10^{-10}	0.11154



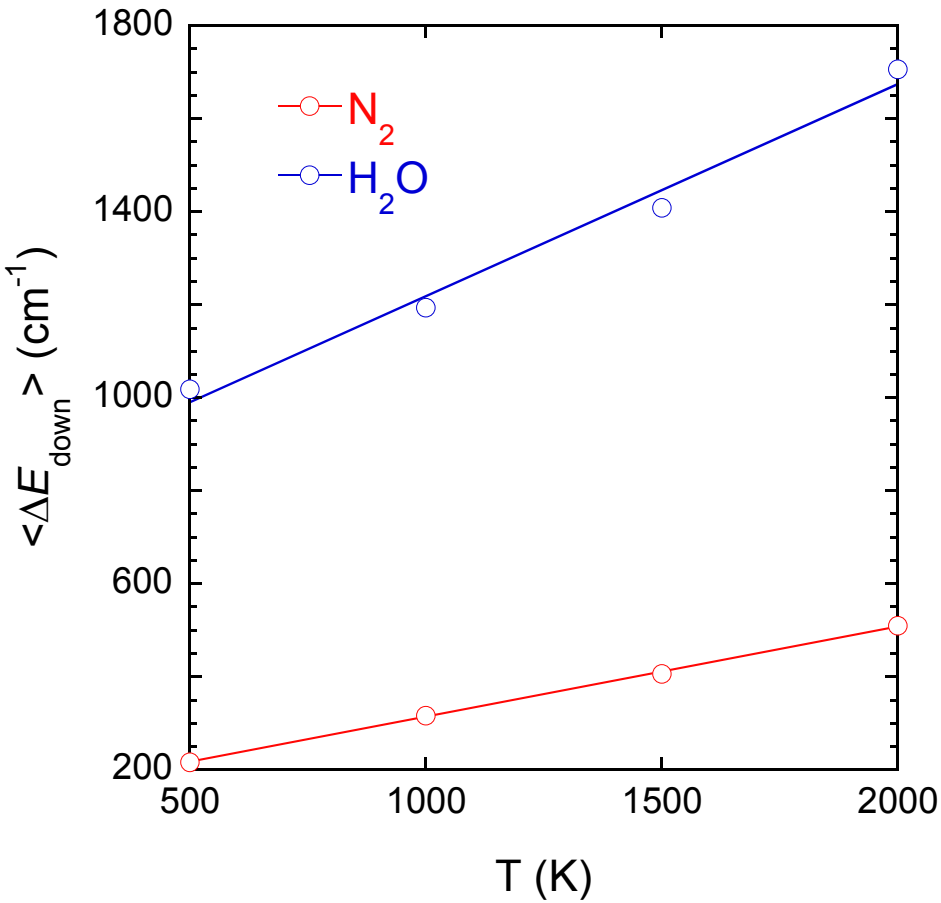
Assessment Method

❖Assess impact of possible interactions rather than develop a rigorous theory

- Use an in house RRKM/Master code modified to accommodate mixtures of bath gases to estimate interactions
- Apply a simple one-dimensional Master Equation
- Assign loose transition state using properties of resulting dissociation (H & O_2).
- Evaluate the high pressure limit using the rate of recombination (R-1) and the equilibrium constant.
- Use Michael et al. (2002) collision rate estimates (fitted with power curves) to input collision rates into the modified RRKM/Master code.

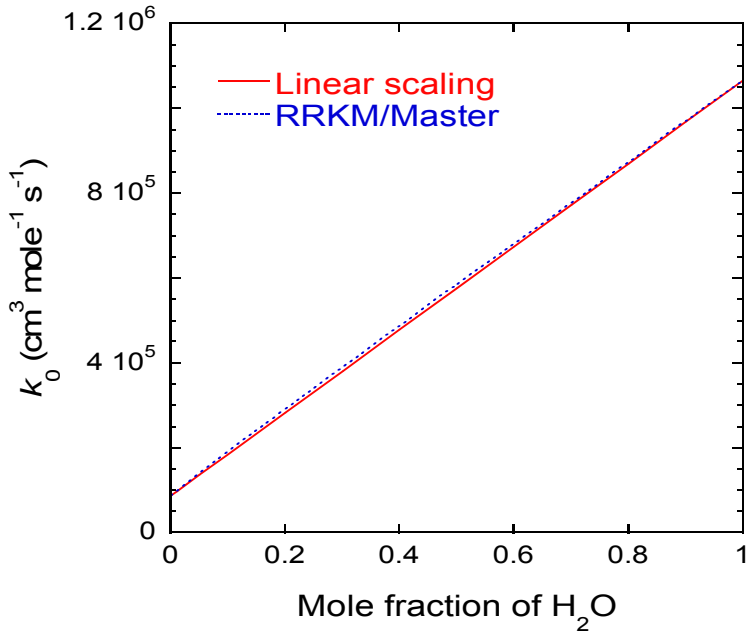
Collision Energy Transfer

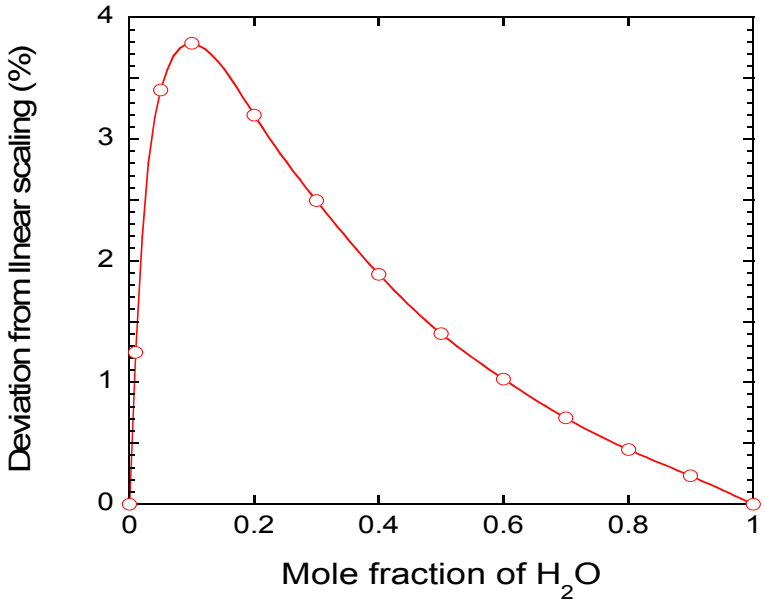
- Use conventional "exponential down" model for collisional energy transfer.
- Choose $<\Delta E_{\text{down}}>$ for water and nitrogen to fit corresponding low-pressure limiting collision rate expressions for pure bath gases.
- Fit expressions for $<\Delta E_{\text{down}}>$ as linear functions of temperature for final RRKM/master calculations for mixtures.



Low Pressure limits for Mixtures at 1000 K

- The low pressure limit of mixtures of water and nitrogen based upon linear interpolation vary less than 4% from the RRKM Master result at about 10% water in the mixture.
- For purposes of syngas combustion, the collisional efficiencies of mixtures even at high concentrations of water and/or carbon dioxide can be reasonably predicted based linearly on relative molar fractions.





$H_2/O_2/NO_X$ Kinetic Interactions

NO_X promotes oxidation via:

$$H+O_2(+M) = HO_2(+M)$$

$$NO+HO_2 = NO_2+OH$$

$$NO_2+H = NO+OH$$

$$H_2+OH = H_2O+H$$

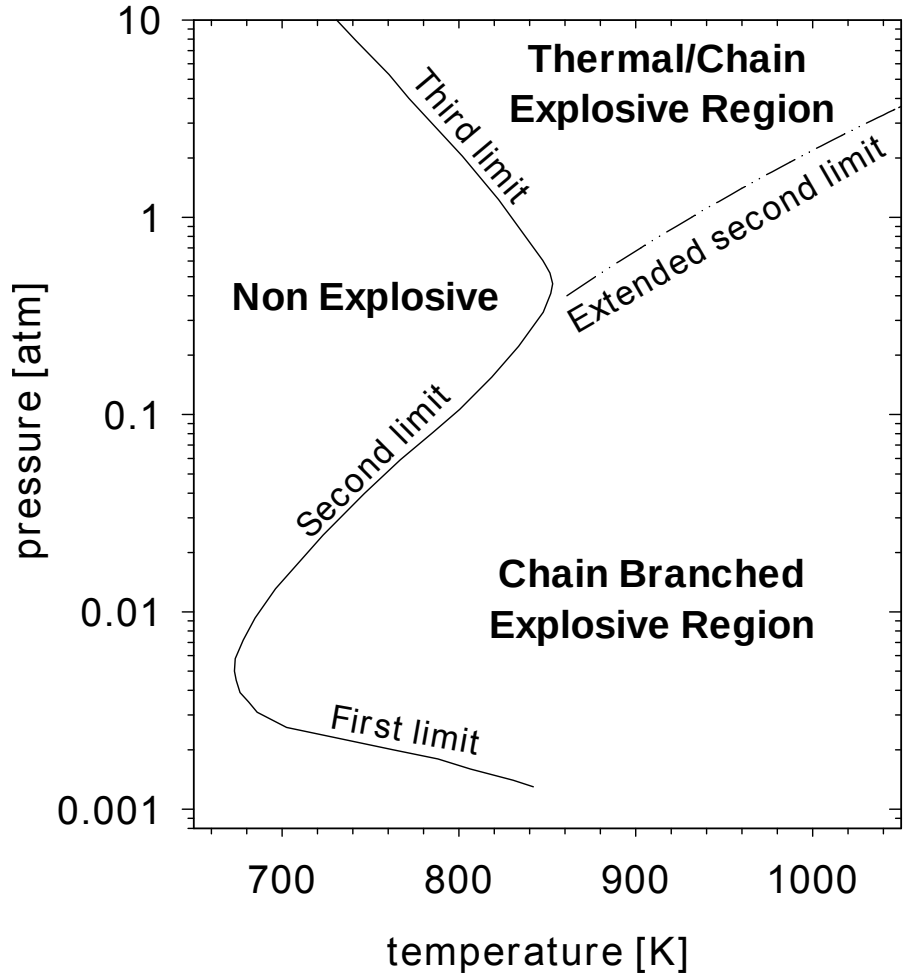
and inhibits oxidation via:

$$NO+X(+M) = XNO(+M)$$

$$XNO+Y = XY+NO$$

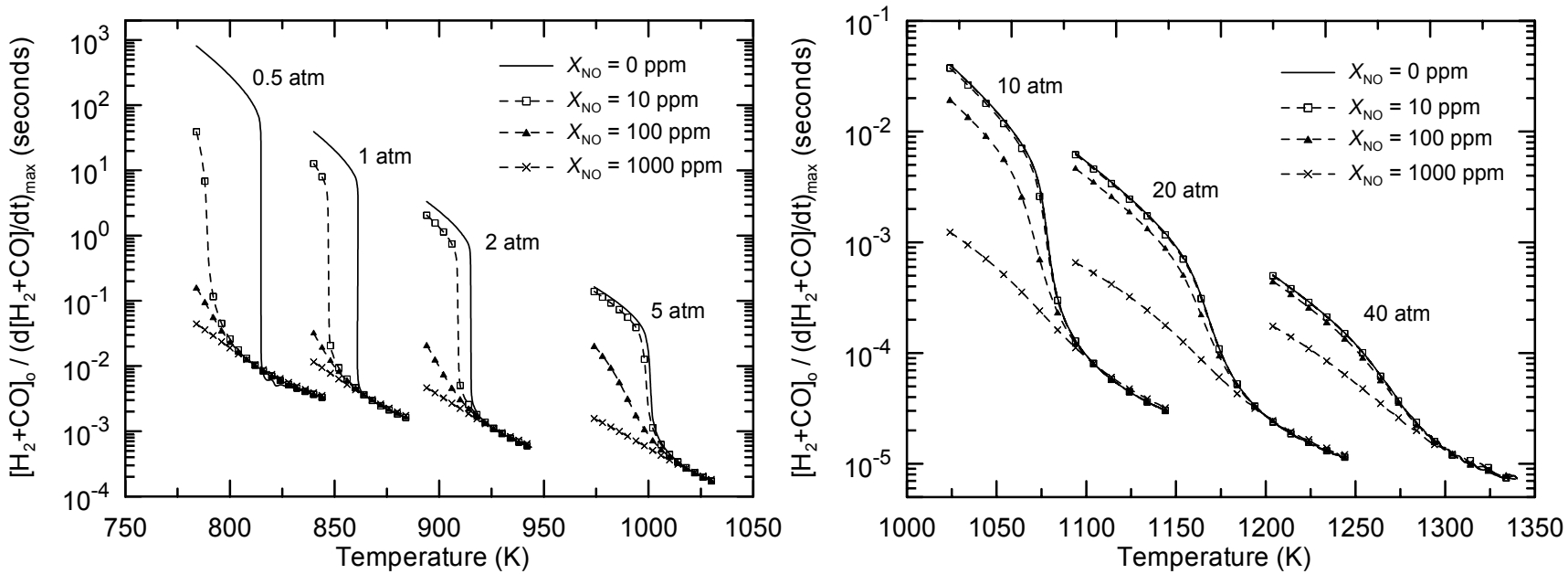
$$X+Y = XY$$

where X,Y = H, O, or OH



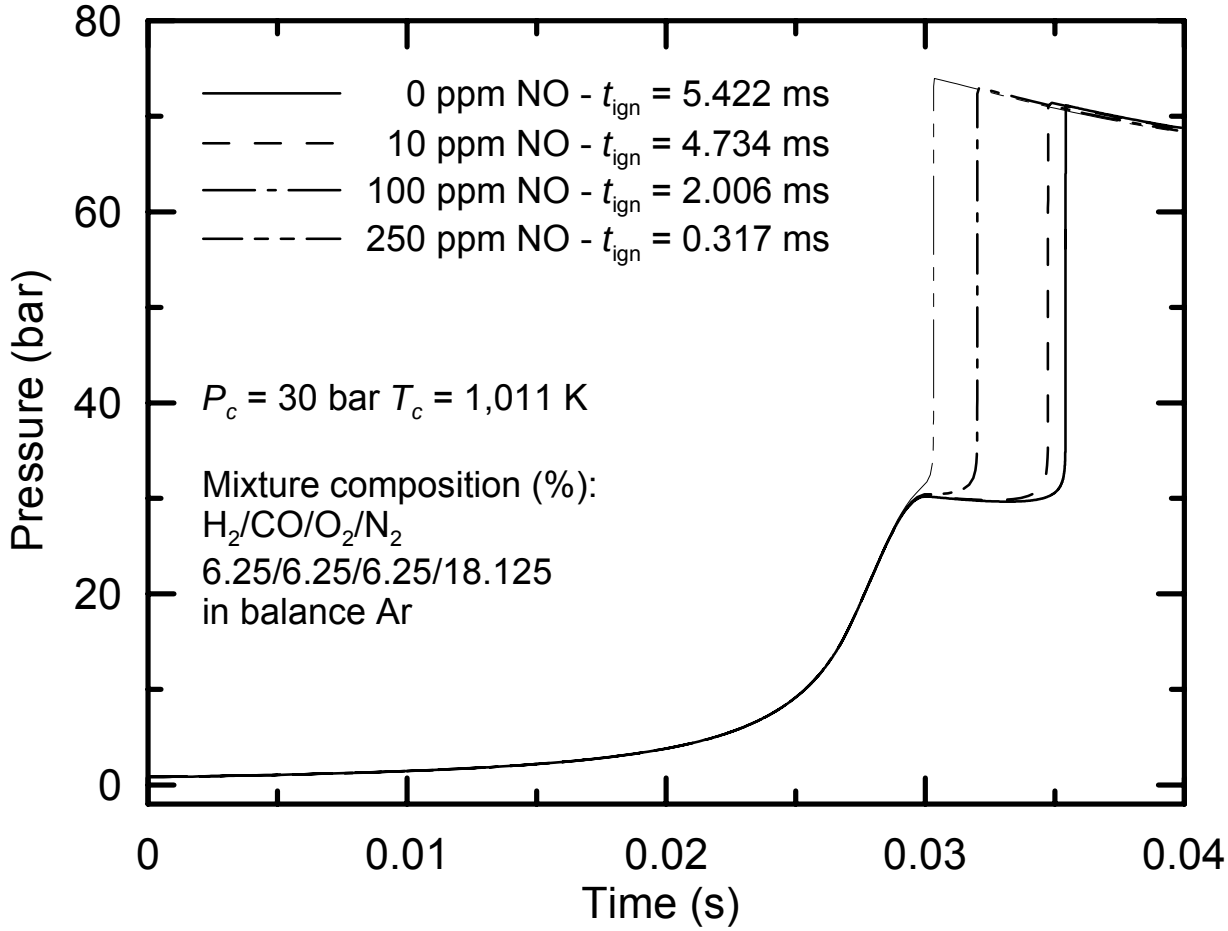
Overall Reaction Rate Variations with P

Conditions - $H_2/CO/O_2/N_2/Ar$ = 6.25/6.25/6.25/18.125/63.125



- "Explosion limit" moves to significantly higher temperatures at increased operating pressures.
- Change in maximum reaction rate decreases dramatically at higher pressures.
- Small amounts of NO/NO_2 can have dramatic effects on the maximum rate of reaction.
- Effect is even more dramatic at higher hydrogen content.
- Most conservative control of reaction rate is *Temperature*.

RCM Ignition Delay Variations with NO Present
(prediction)



- Small amounts of NO/NO_2 can have dramatic effects on the ignition delay at inlet temperatures relevant to gas turbine combustion.
- What other contaminants may be present in Syngas compositions?

Determining Collisional Efficiencies

- The determination of rate data for H+ O_2 (+M) = HO_2 (+M) at temperatures of interest for combustion chemistry is complicated by competition with H + O_2 = OH + O.
- At pressures where HO_2 formation dominates the branching reaction, H_2/O_2 kinetics are influenced by HO_2-H_2O_2 reactions which are not well-characterized.
- The addition of NO simplifies the high-pressure kinetics by providing an alternate consumption route for HO_2 via HO_2+NO=NO_2+OH.
- NO_2 reacts with H atoms via NO_2 + H = NO + OH to form a catalytic cycle which results in steady-state NO_2 concentrations.

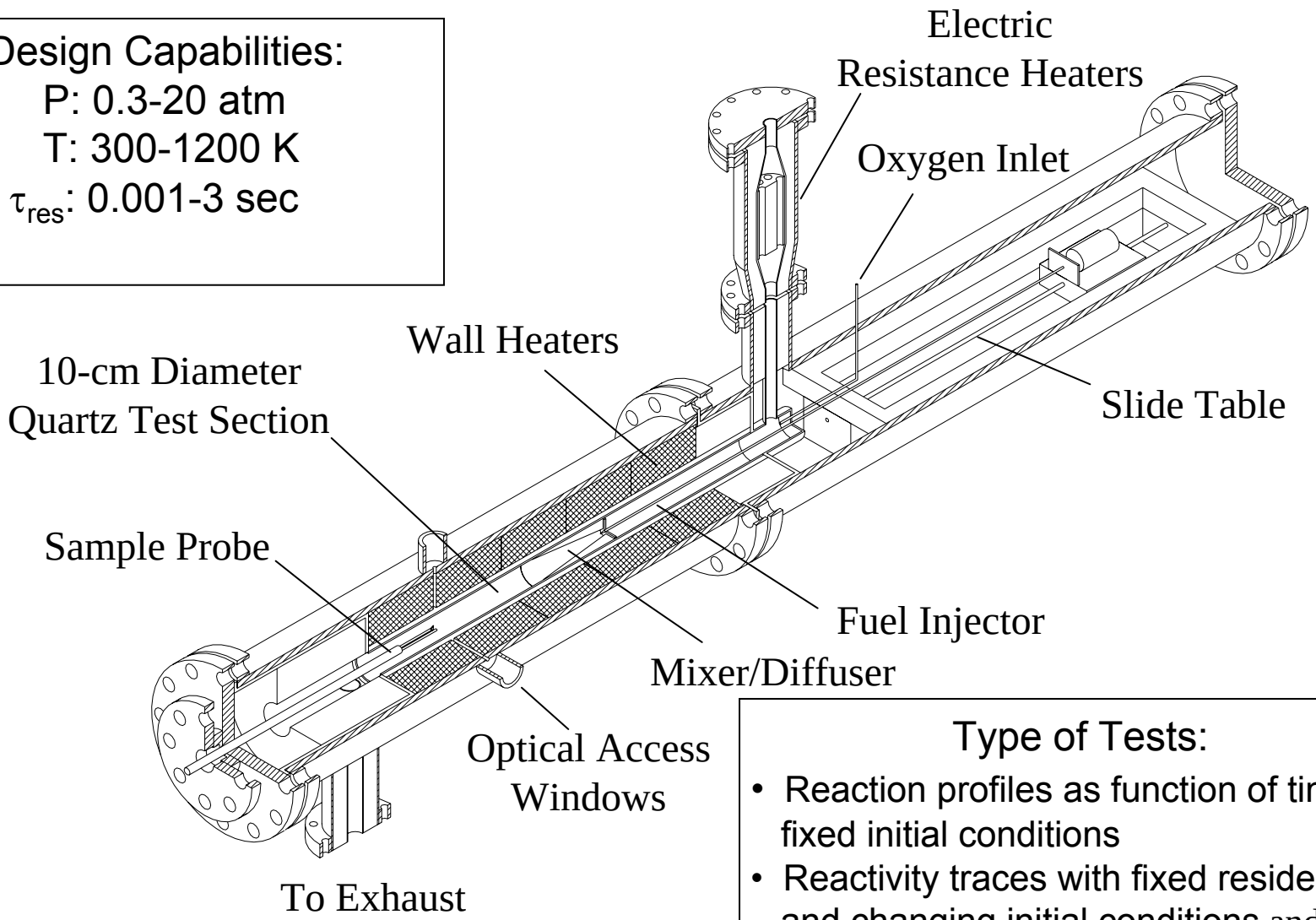
$$[NO_2]_{ss} = \frac{k_{H + O2(+M) = HO2(+M)}[O_2]}{k_{NO2 + H = NO + OH}}$$

Determining Collisional Efficiencies

- High flow rates and dilute mixtures (typically 1% fuel) minimize spatial gradients within the VPFR and permit neglect of the diffusion terms in the governing equations.
- The experiment can thus be model as a zero-dimensional system using SENKIN with isobaric and adiabatic assumptions.
- Experimental data for $H_2/NO/O_2/N_2$ seeded with amounts of water vapor or CO_2 are shifted in time to agree with model predictions at point of 50% fuel consumption.
- To determine $k_{2,0}$, reaction profiles are modeled with the baseline C1/NOx reaction mechanism in which $k_{2,0}$ is treated as an adjustable parameter.
- The Troe formulation with $k_{2,\infty}=4.52\text{x}10^{13}(T/300)^{0.6}$ cm^3 $mole^{-1}$ sec^{-1} and $Fc^{N2(Ar)}=0.5$ (0.45) is used to model fall-off behavior.

Variable-Pressure Flow Reactor

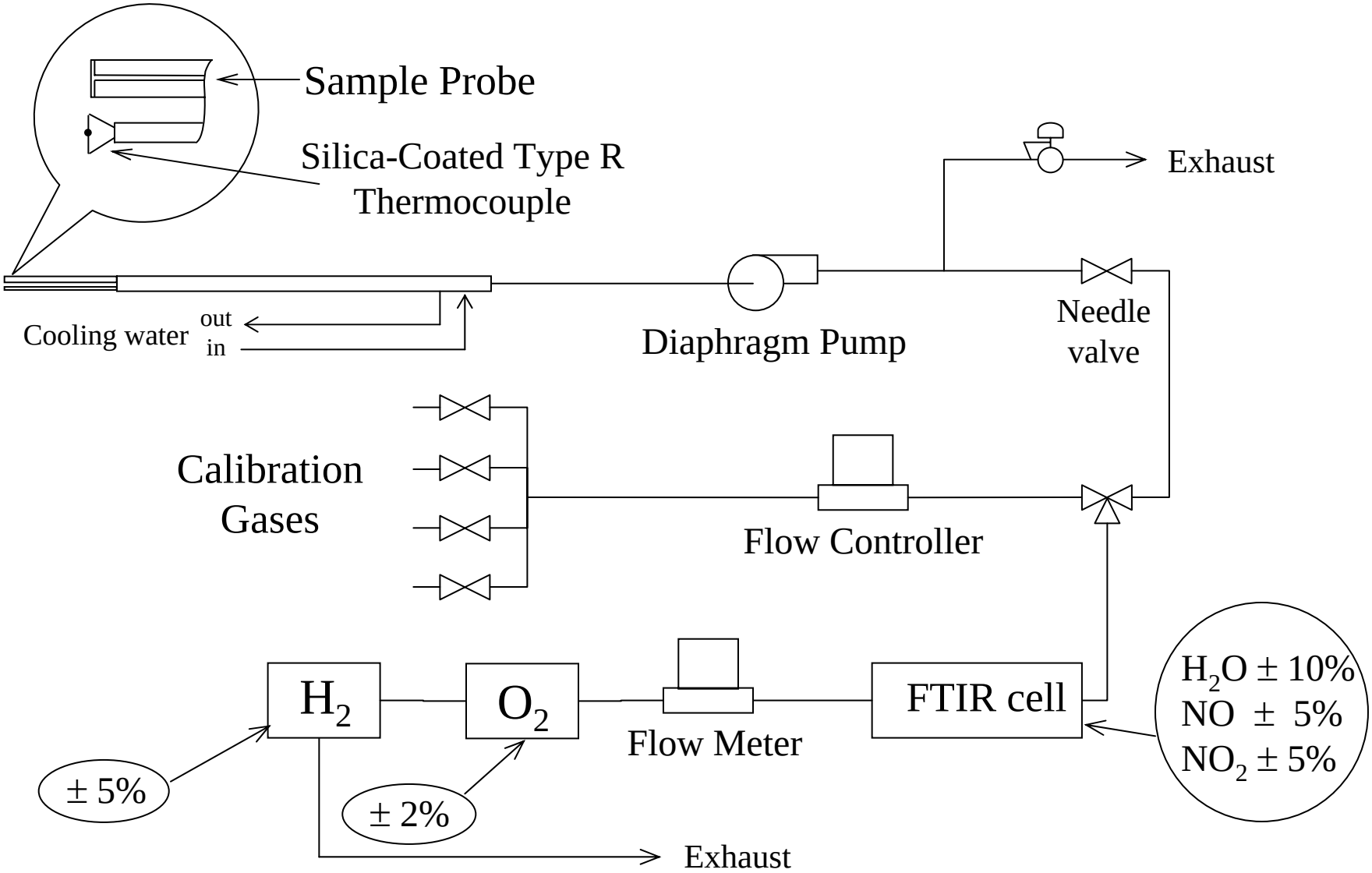
Design Capabilities:
P: 0.3-20 atm
T: 300-1200 K
τ_{res}: 0.001-3 sec



Type of Tests:

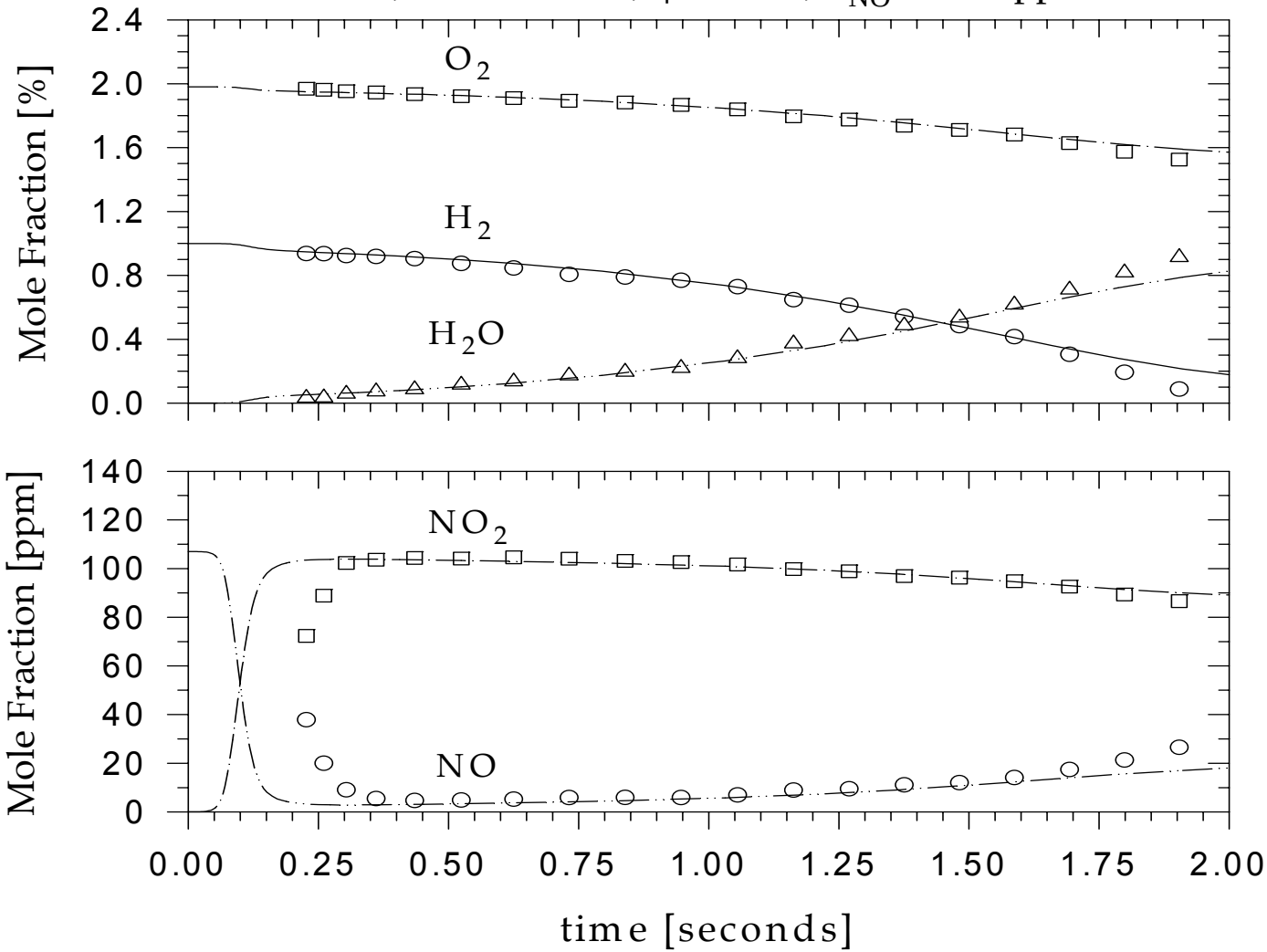
- Reaction profiles as function of time with fixed initial conditions
- Reactivity traces with fixed residence time and changing initial conditions and/or initial reactant mole fractions

Analytical Equipment



Reaction Profiles ($M=N_2$)

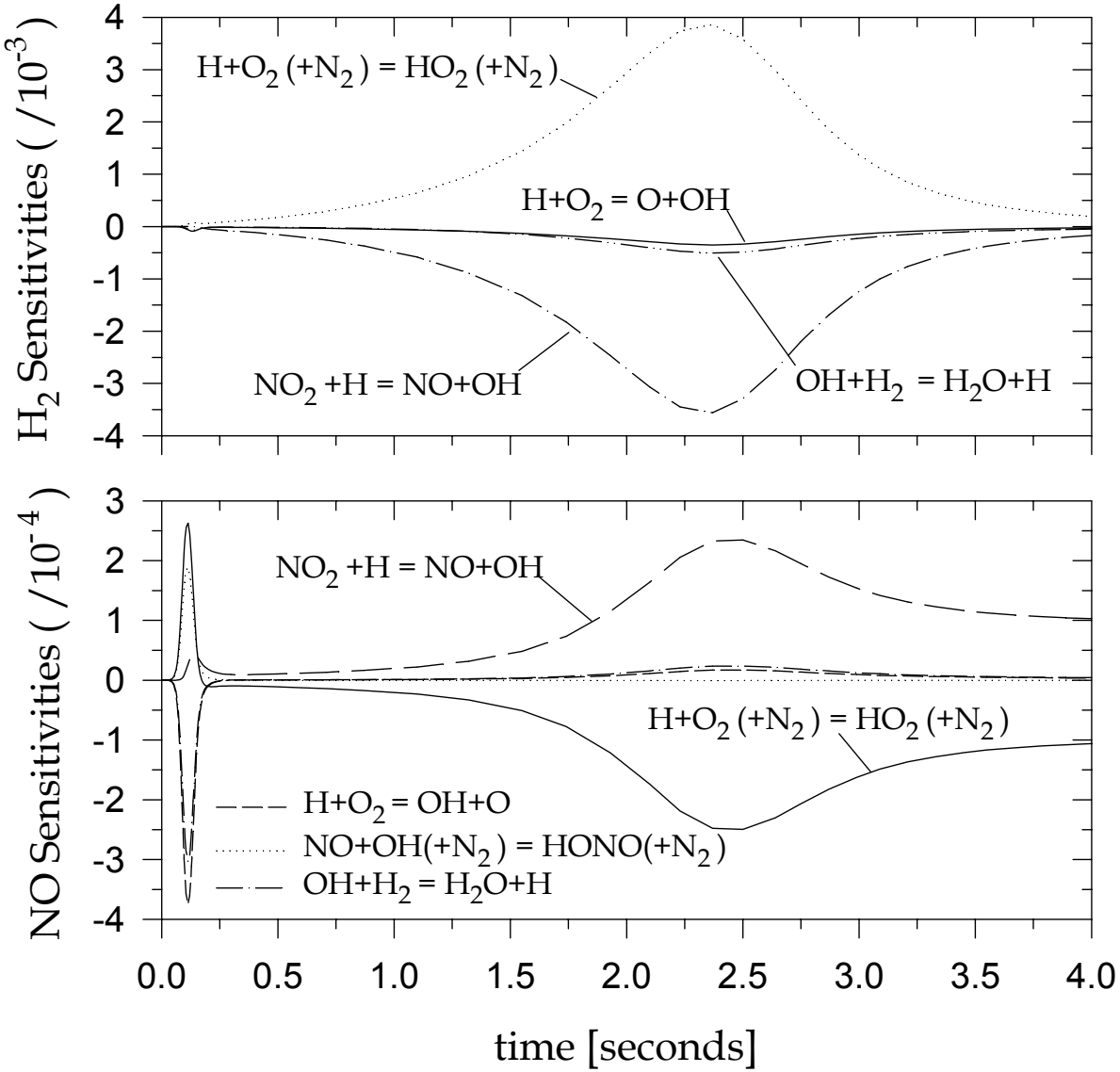
P = 12.5 atm; Tin = 808 K; φ = 0.25; x_{NO} = 107 ppm



Symbols represent experimental data; lines are model predictions with $k_{2,0}^{N2} = 4.03\text{x}10^{15}$ cm^3 $mole^{-1}$ sec^{-1}.

Sensitivity Analysis Results ($M=N_2$)

Sensitivity coefficients ($S_{ij} = \partial \ln x_i / \partial \ln A_j$) for the H_2 and NO profiles in previous figure.



Summary

- Further analyses of a C_1 reaction mechanism we have developed show the mechanism can be utilized to predict phenomena over a wide range of parameter space that encompasses chemical system behavior under syngas gas turbine combustion conditions.
- The reactions $CO+O+M = CO_2+M$ (R22) and $CO + HO_2 = CO_2 + OH$ (R20) primarily affect chemical induction time in *pure* carbon-monoxide-hydrogen-oxygen mixtures diluted by nitrogen, water, and/or carbon dioxide, and are not important to predicting energy release rate.
- CSP based analyses of recent RCM experiments show variation of ignition properties with CO/H_2 ratio comes primarily from competition of (R22) and $H_2+HO_2=H_2O_2+H$ (R17) during chemical induction (initial radical pool growth). Similar analyses of recent high pressure shock tube data are disparate with this result because of mole fraction differences in reactants and not the pressure/temperature range studied.
- The collisional efficiencies of mixtures even at high concentrations of water and/or carbon dioxide can be reasonably predicted based linearly on relative molar fractions.

Summary (cont'd)

- Similar analyses show that the following reactions are important to heat release at high pressure conditions:

$HO_2 + OH = H_2O + O_2$	(R13)
$HO_2 + H = OH + H$	(R11)
$H + O_2 + M = HO_2 + M$	(R9)
$H_2 + OH = H_2O + H$	(R3)
$H_2 + O = H + OH$	(R2)
$H_2O_2 + M = OH + OH + M$	(R15)
$CO + OH = CO_2 + H$	(R23)

- The change in overall reaction rate before and after crossing the extended second explosion decreases and temperature remains the principal parameter affecting overall rate as reaction pressure increases from 0.5 to 40 atm.
- The presence of small amounts of NO has the potential to essentially remove the importance of the above HO_2-H_2O_2 reactions altogether.
- Contaminants in syngas are important to defining initial reaction behavior.
- Experimental assessment of collisional efficiency issues for water and carbon dioxide in (R15) at high dilutions remain to be fully investigated experimentally and are the principal issues in the remaining work under this effort.

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  - G. Mittal, C.J. Sung, R. A. Yetter (2006) "Autoignition of H_2/CO at Elevated Pressures in a Rapid Compression Machine", *Int. J. Chem. Kin.* (In Press).
  - Initial conditions and heat loss volume corrections for experiments
  - Other technical discussions