

# New Paradigm in Modeling and Simulation of Complex Oxidation Chemistry



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Kevin McNesby and Ralph Anthenien

# Outline

- Background
- Concept
- Results
- Summary and conclusions
- Future work

# Background

- Necessity to reduce the computational cost of chemistry in simulations of turbulent combustion
- Some existing chemistry reduction schemes:
  - reduction of detailed mechanisms to a few reactions and species
  - reduction of detailed mechanisms to ‘representative’ reactions past C<sub>4</sub> hydrocarbons using species lumping
  - piecewise implementation of solution mapping (PRISM)
  - *in-situ* adaptive tabulation (ISAT)
  - intrinsic low-dimensional manifold (ILDm)
  - computational singular perturbation (CSP)
  - directed relation graph (DRG) reduction

# Making chemistry modeling framework consistent with turbulence modeling

## Turbulence modeling

1. Exact solution computable: Direct Numerical Simulation (DNS), but it is too costly for practical computations



2. Reduced modeling: solve differential equations only for energetically important scales and model the other scales (Large Eddy Simulation (LES))

- find models

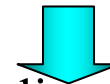
- test to see how they fit the neglected scales (*a priori* analysis)



3. Conduct LES using the model(s) for the neglected scales and see how well one recovers the exact solution (*a posteriori* analysis)

## Our chemistry modeling

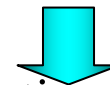
1. Start with exact set of elementary reactions, e.g. LLNL database, which is too costly for practical computations



2. Reduced modeling: solve differential equations only for energetically important (and pollutant, if of concern) species and model other species

- find models

- test to see how they fit the modeled species (*a priori* analysis)



3. Conduct simulations using the model(s) for the approximated species and see how well one recovers the set of elementary reactions (*a posteriori* analysis)

# Our Concept

## Facts

1. Plots of the heats of combustion for alkanes and for alkenes having a C double bond at the molecular chain end have a linear variation with the C number,  $n$ .
2. At fixed  $T$ , the species  $C_p$  vary linearly with  $n$ .

## Implications

- ➡ Heats of combustion and  $C_p$ 's may be considered obtainable by summing those of constituent radicals  $CH_2$ ,  $CH_3$  and  $C_2H_3$  that form these hydrocarbons.
- ➡ For  $n \geq 3$ , species may be decomposed into constituent radicals. This is consistent with group additivity theory.

# Group additivity and constituents

- Starting point akin to, but different from, typical chemical group additivity

## Group additivity

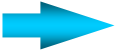
- interactions with adjacent groups
- interactions with non-adjacent groups
- accounts for steric effects

## Constituents

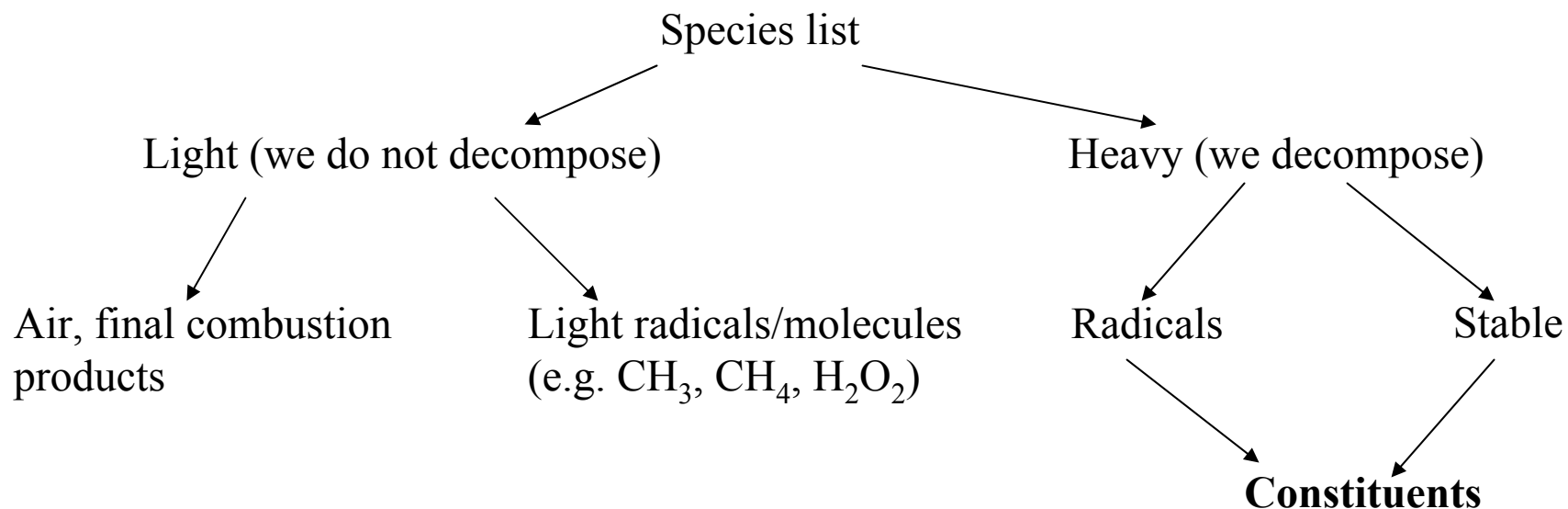
- only interactions with adjacent groups
- only first order (compositional) effects

- Focus is on
  - comprehensiveness
  - accuracy
  - relative simplicity
- Our process is different from lumping
  - we are decomposing ALL heavy species
  - a constituent may span the entire species set of heavy species
  - we can recover the individual constituent molar fraction in the ensemble of constituents

# Requirements for the set of reactions for the base

- Preserve the heat release 
  - Heat capacities
  - Heats of combustionmust be appropriately modeled.
- More detailed requirements could be added in the future.
- Reported in the past on energetics modeling using the LLNL kinetics.
- Present report is on modeling chemical kinetic rates.

# The base , 1 of 2



**For general alkane or alkene with air:**

**The base = Light species + Constituents**  
(26) (13)

Remove NO<sub>x</sub>, C, C<sub>2</sub>, N<sub>2</sub> and N at this preliminary stage, and then,

**The base = Light species + Constituents**  
(20) (13)

# The base, 2 of 2

1. Inspection of the LLNL kinetics shows that a subset of the light species is quasi-steady (i.e. gain and loss balance within 5% or less). These species are radicals: O, CH, CH<sub>2</sub>, CH<sub>3</sub>, HO, HCO, HO<sub>2</sub>, HC<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>
2. Examination of the global constituent mole fraction,  $N_c$ , shows that, appropriately multiplied/divided by other variables/parameters and plotted against a non-dimensionalized temperature, it has a self-similar behavior (will show).
3. Conclusion: the final base is
  - $N_c$ ,
  - mole fractions of unsteady light species: H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, H, CO, H<sub>2</sub>,  
CH<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>,  
C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>O

# Base behavior in stirred reactor heptane combustion: framework

1. Examined data from LLNL: 160 species and 1540 reaction rates with the goal of forming non-dimensional groups of variables.
2. Systematic tests performed for  $p_0$  from 1 to 60 bar and for molar equivalence ratios  $\phi \in [1/8, 8]$ . Very time-consuming iterative process.
3. Try to reduce the problem to its essence by defining

$$N_c \equiv \sum_{k=1}^{13} N_k \quad K_c \equiv -\frac{d(\ln N_c)}{dt}$$

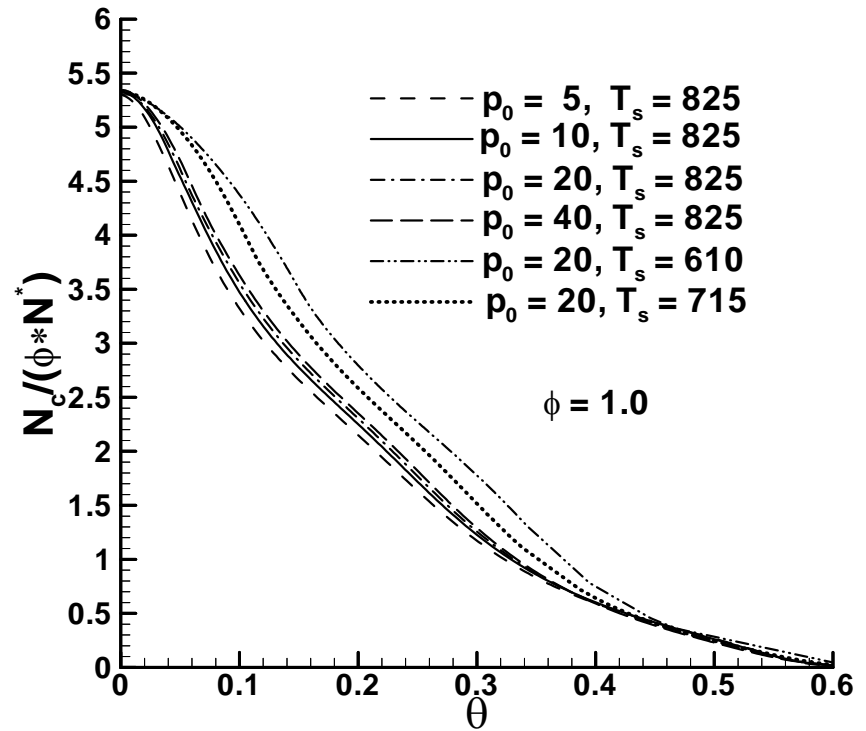
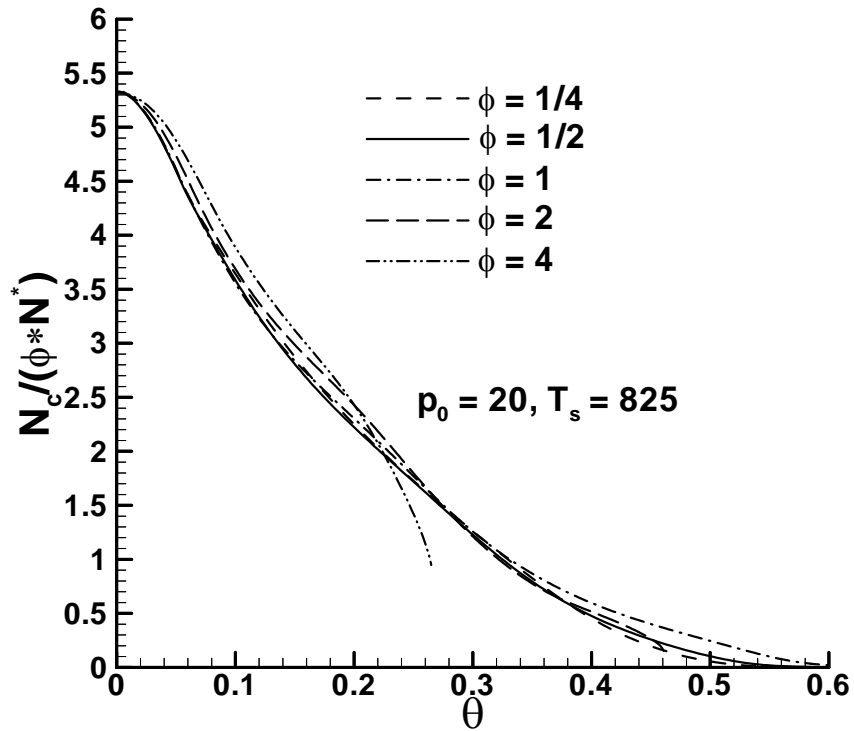
The LLNL database shows that the  $K_c$  variation is quasi-steady.

4. Non-dimensional groups of variables

$$N^* \equiv N_{N_2}/N_{ref} \quad N_{ref} = 31.5 \text{ mol/m}^3$$

$$\theta \equiv \frac{T - T_s}{T_r(\phi, N^*)}, \quad T_r \equiv 2065(N^*)^{0.06} w(\phi), \quad w(\phi) = \phi \frac{1.5 + 1.31\phi}{1 + 0.71\phi + 1.1\phi^2}$$

# Identification of self-similar behavior



$N_c / (\phi \times N^*)$  in mol/(m<sup>3</sup>),  $p_0$  in bar,  $T_s$  in K

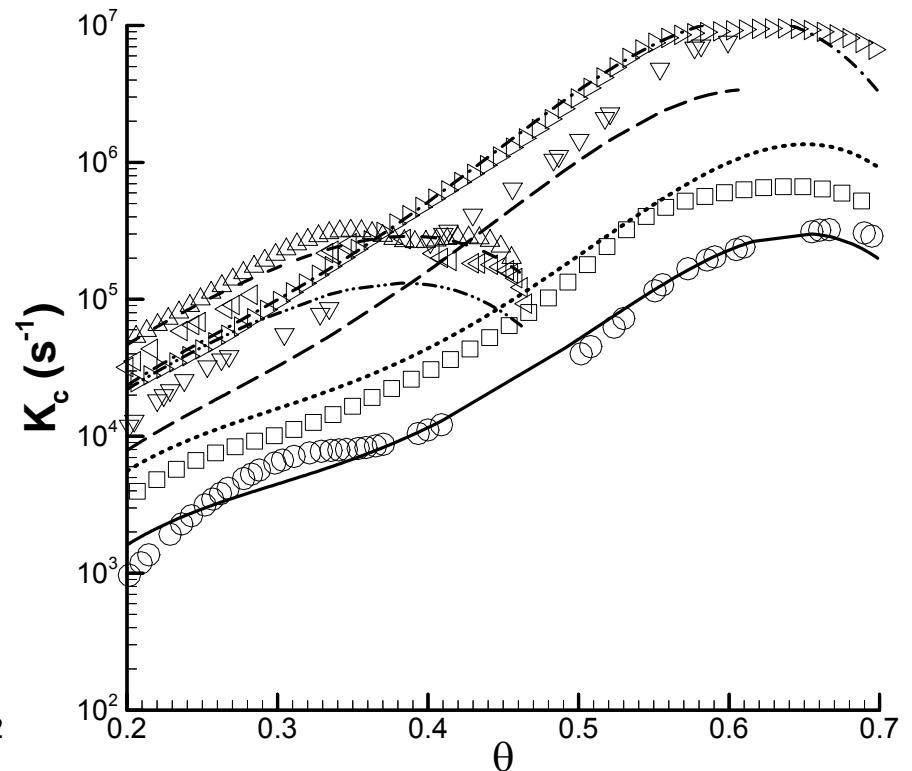
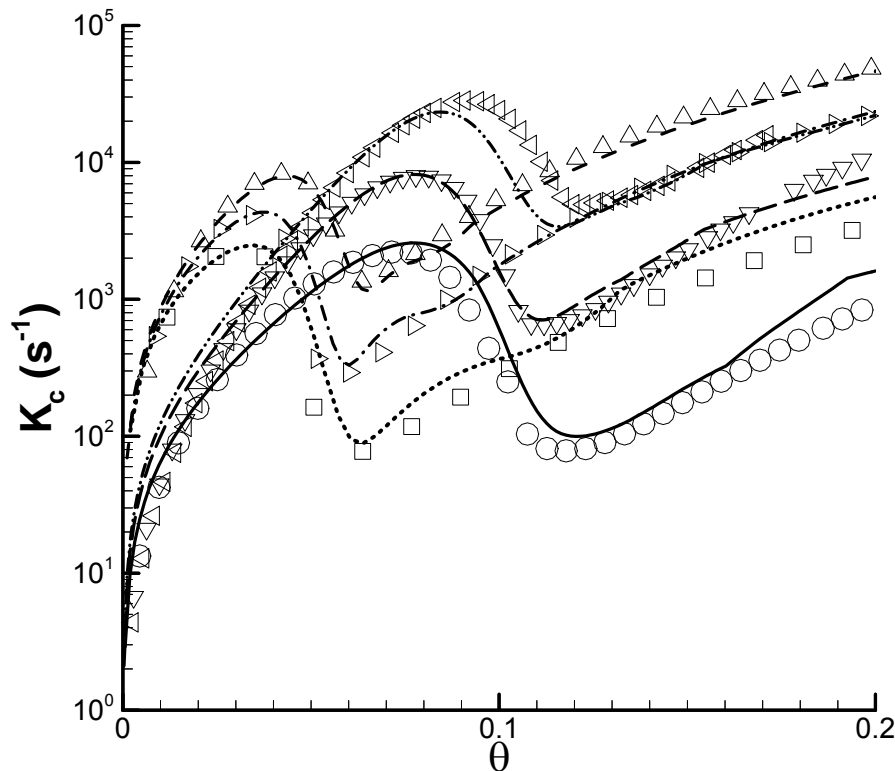
# Modeling of $K_c$ : fixed $p_0$

$p_0 = 20$  bar, T in K

$\square, \triangleright, \Delta, \circ, \nabla, \triangleleft$  represent selected data from LLNL runs

$\bullet\bullet\bullet \phi = 0.5, T_s = 825$ ;  $\text{---} \phi = 0.5, T_s = 715$ ,  $\text{-}\bullet\text{-}\bullet\text{-} \phi = 1.0, T_s = 825$

$\text{---} \phi = 1.0, T_s = 715$ ;  $\text{-}\bullet\text{-}\bullet\text{-} \phi = 2.0, T_s = 825$ ,  $\text{-}\bullet\bullet\text{-}\bullet\bullet\text{-} \phi = 2.0, T_s = 715$



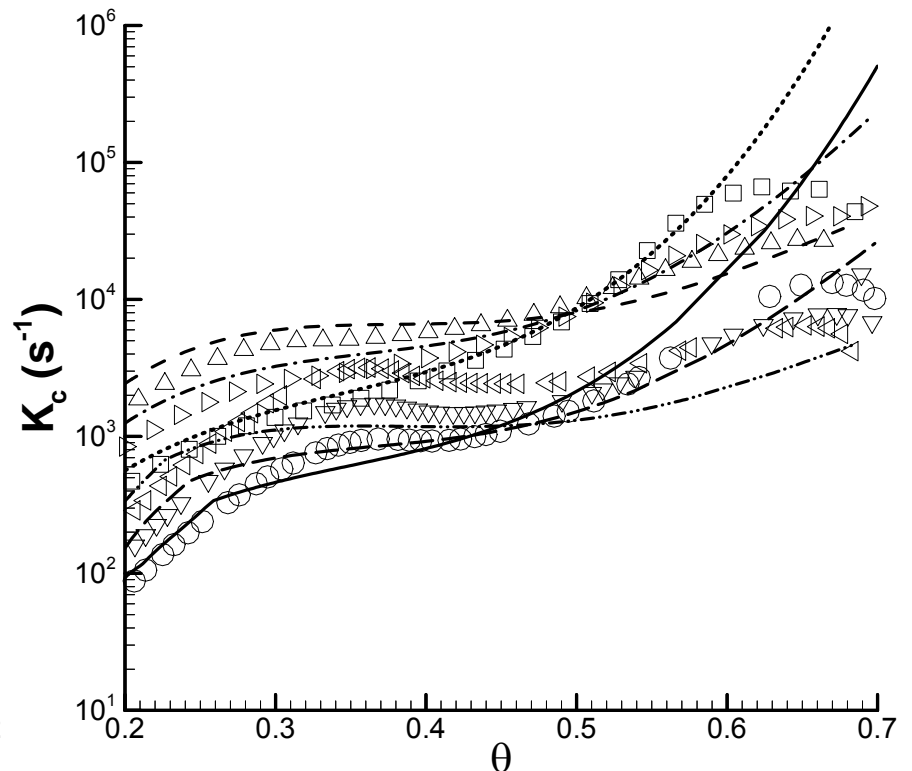
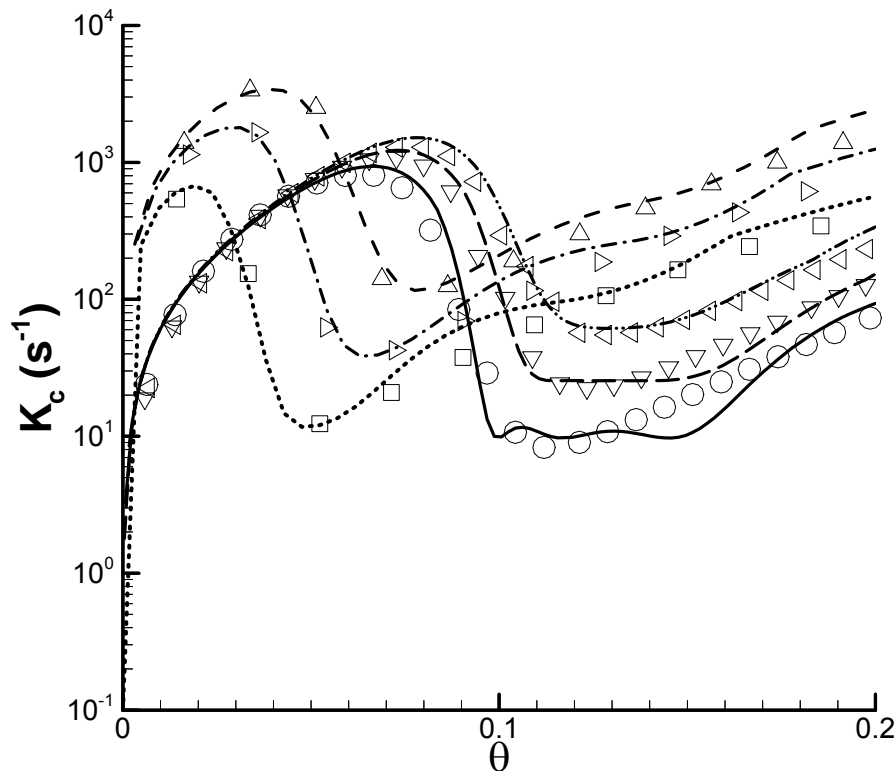
# Modeling of $K_c$ : fixed $\phi$ lean

$\phi=1/3$ ,  $p_0$  in bar, T in K

$\square, \triangleright, \triangle, \circ, \nabla, \triangleleft$  represent selected data from LLNL runs

$\bullet\bullet\bullet p_0 = 10, T_s = 825$ ;  $\text{---} p_0 = 10, T_s = 715$ ,  $-\bullet-\bullet-\bullet p_0 = 20, T_s = 825$

$\text{---} p_0 = 20, T_s = 715$ ;  $\text{---} p_0 = 40, T_s = 825$ ;  $-\bullet-\bullet-\bullet p_0 = 40, T_s = 715$



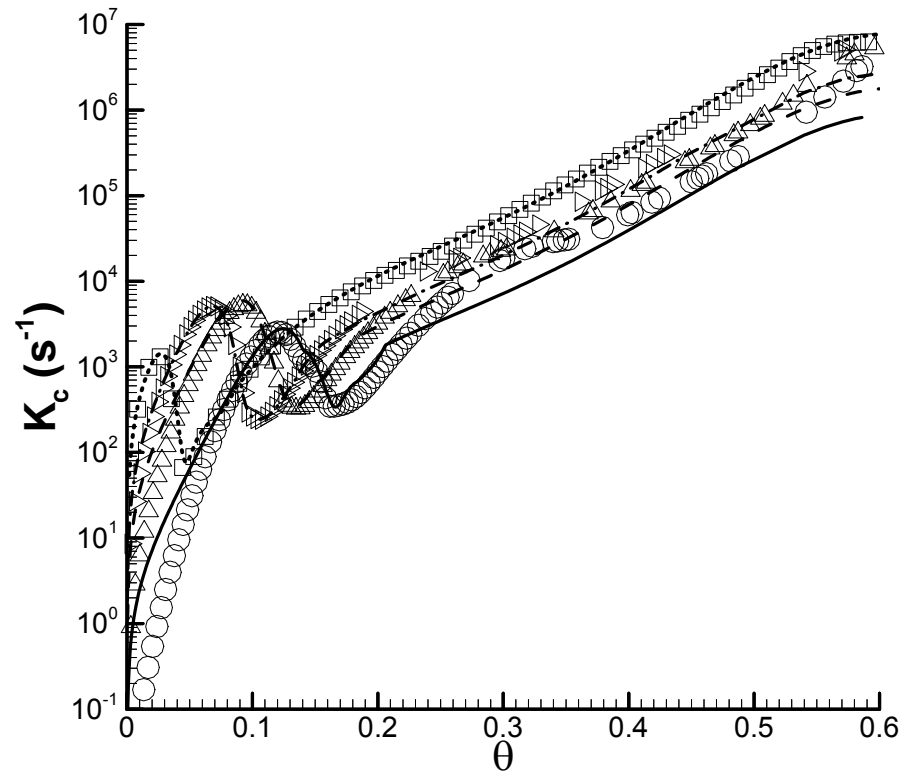
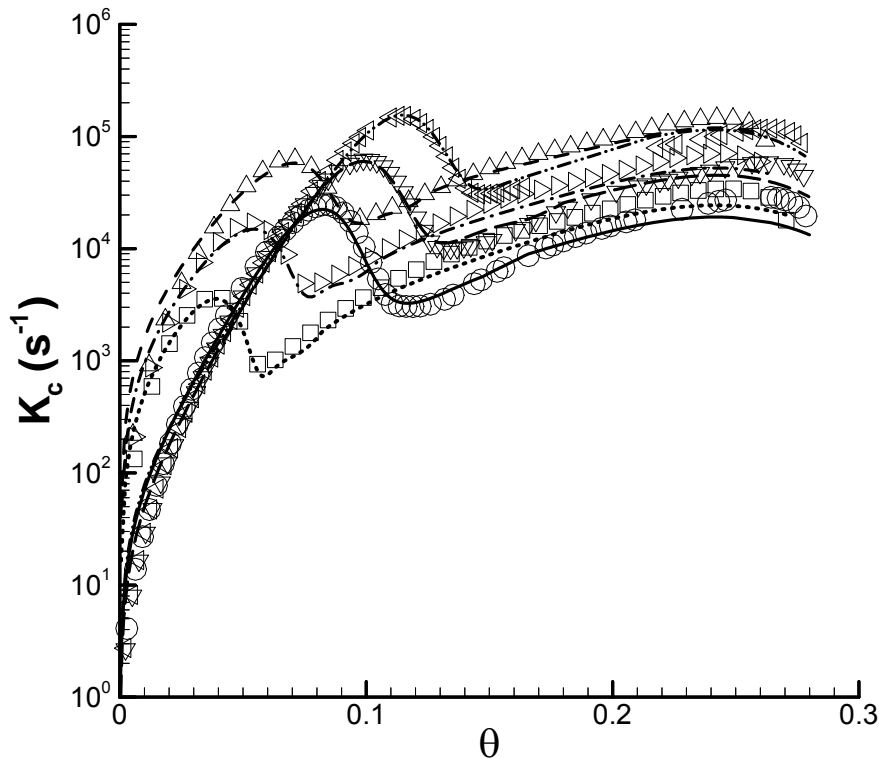
# Modeling of $K_c$ : fixed $\phi$ rich and $T_s$ variation

$\phi=4$ ,  $p_0$  in bar,  $T$  in K

- $p_0 = 10$ ,  $T_s = 825$ ; —  $p_0 = 10$ ,  $T_s = 715$
- $p_0 = 20$ ,  $T_s = 825$ ; - - -  $p_0 = 20$ ,  $T_s = 715$
- - -  $p_0 = 40$ ,  $T_s = 825$ ; -••-••-  $p_0 = 40$ ,  $T_s = 715$

$p_0 = 10$  bar,  $\phi=1$ ,  $T$  in K

- $T_s = 825$ ; —  $T_s = 715$  ( $\square$ ;  $\circ$ )
- $T_s = 655$ ; - - -  $T_s = 560$  ( $\triangleright$ ;  $\triangle$ )



# The energetics

Energy equation:

$$\left( N_c C_{p,h} + \sum_{i \in \text{lights}} C_{p,i} N_i \right) \frac{dT}{dt} = - \sum_{i \in \text{lights}} h_i \mathcal{R}_i + N_c (R_u T_{ref}) K_h$$

where  $N_i$  is the light species mole fraction and

$$\mathcal{R}_i \equiv (dN_i/dt)_{\text{reac}}$$

$$C_{p,h} \equiv \left( \sum_{l \in \text{heavies}} C_{p,l} N_l \right) / N_c$$

$$K_h \equiv - \left( \sum_{l \in \text{heavies}} h_l \mathcal{R}_l \right) \frac{1}{R_u T_{ref} N_c}$$

$$\left( \frac{dN_i}{dt} \right)_{\text{reac}} = \left. \frac{dN_i}{dt} \right|_{\text{lights}} + \left. \frac{dN_i}{dt} \right|_{\text{heavies}}$$

$$\left. \frac{dN_i}{dt} \right|_{\text{heavies}} = N_c (K G_i - X_i K L_i)$$

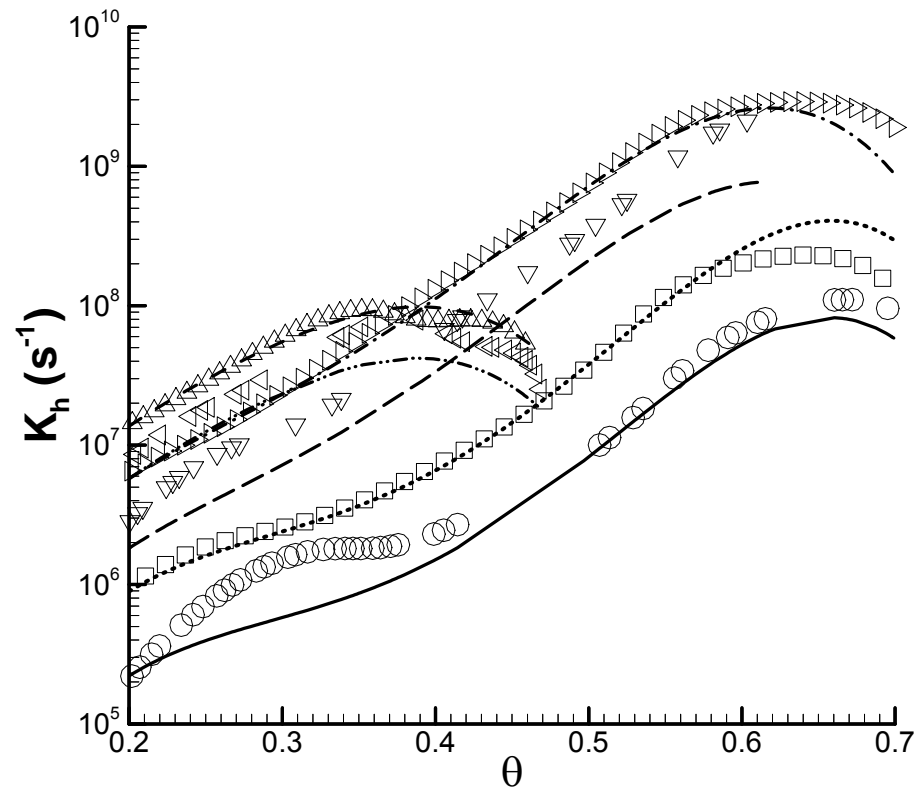
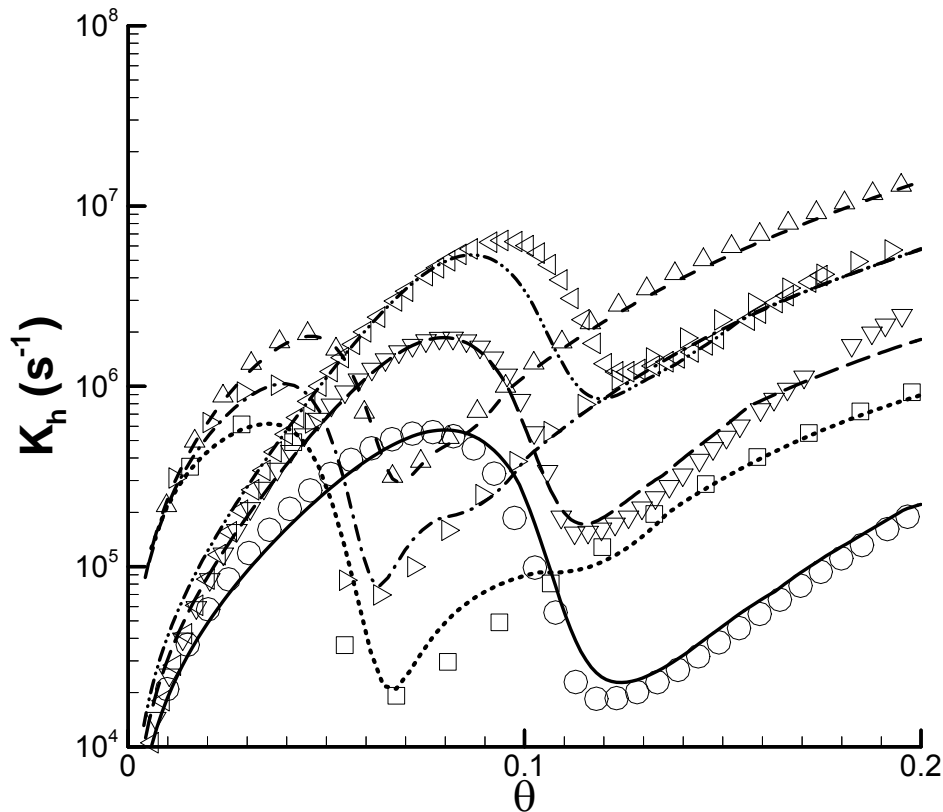
# Recovery of the heavy species energetics, 1 of 2

$p_0 = 20$  bar,  $T$  in K

$\square, \triangleright, \Delta, \bigcirc, \nabla, \triangleleft$  represent selected data from LLNL runs

$\bullet\bullet\bullet \phi = 0.5, T_s = 825$ ;  $\text{---} \phi = 0.5, T_s = 715$ ,  $\text{-}\bullet\text{-}\bullet\text{-}\phi = 1.0, T_s = 825$

$\text{---}\text{---}\phi = 1.0, T_s = 715$ ;  $\text{-}\text{---}\phi = 2.0, T_s = 825$ ;  $\text{-}\bullet\text{-}\bullet\text{-}\phi = 2.0, T_s = 715$



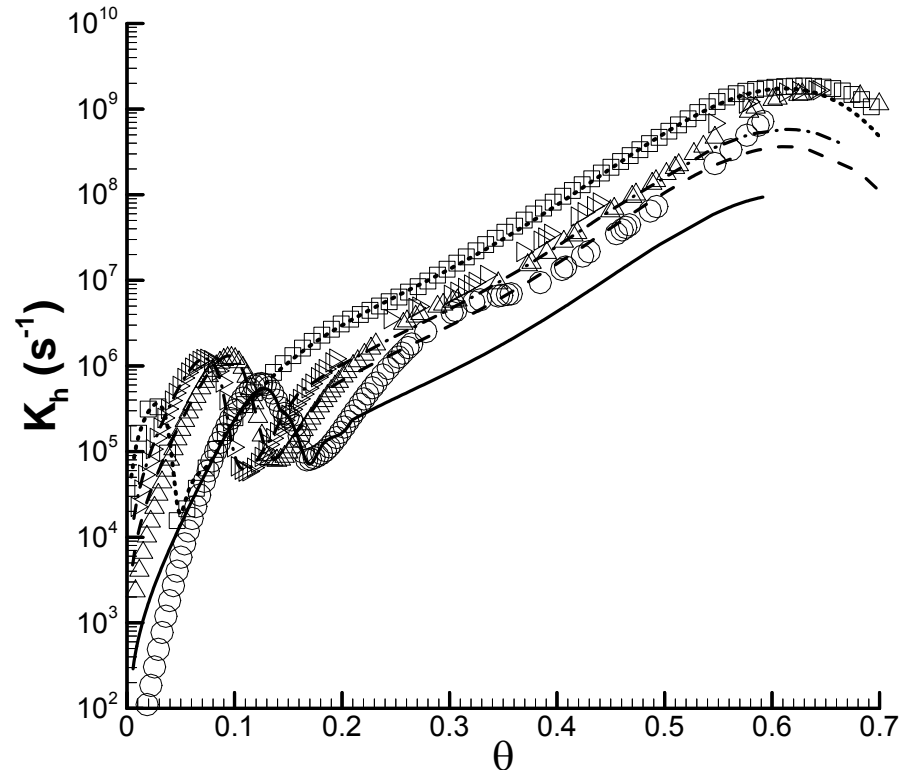
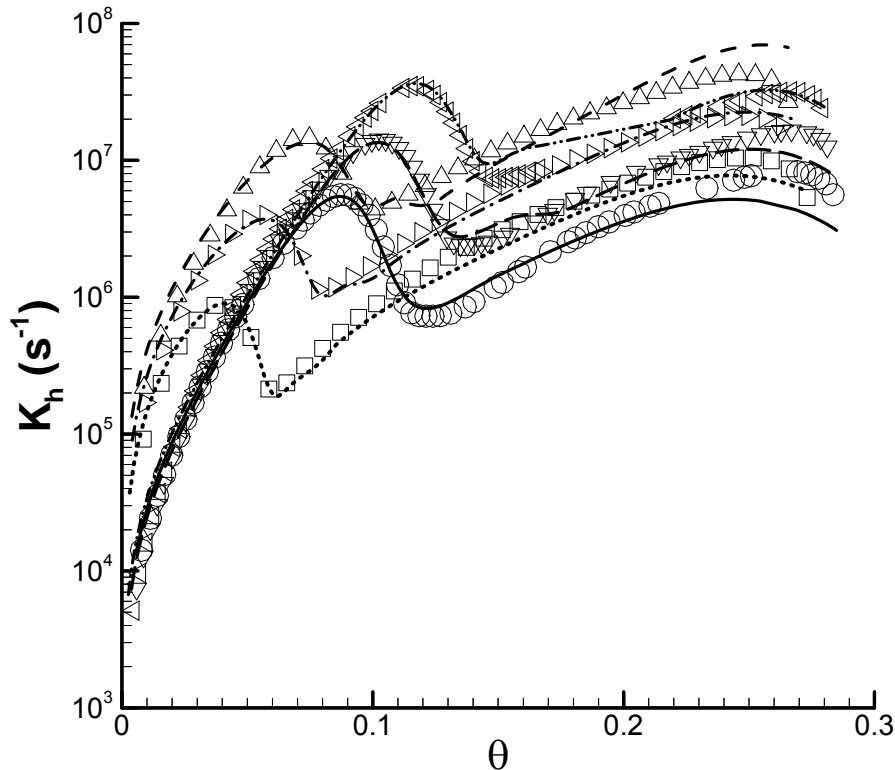
# Recovery of the heavy species energetics, 2 of 2

$\phi=4$ ,  $p_0$  in bar,  $T$  in K

- $p_0 = 10$ ,  $T_s = 825$ ; —  $p_0 = 10$ ,  $T_s = 715$
- $p_0 = 20$ ,  $T_s = 825$ ; - - -  $p_0 = 20$ ,  $T_s = 715$
- - -  $p_0 = 40$ ,  $T_s = 825$ ; -••-••-  $p_0 = 40$ ,  $T_s = 715$

$p_0 = 10$  bar,  $\phi=1$ ,  $T$  in K

- $T_s = 825$ ; —  $T_s = 715$  ( $\square$ ;  $\circ$ )
- $T_s = 655$ ; - - -  $T_s = 560$  ( $\triangleright$ ;  $\Delta$ )



# The light species

Ensemble partitioned into two categories:

1. Species that require rate equations and are part of the base set:

H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, H, CO, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>O (all require modeling of  $KG_i$  and only H<sub>2</sub>O, O<sub>2</sub>, H and H<sub>2</sub> require modeling of  $KL_i$ )

➡ 11 species (10 for a PSR, as H is quasi-steady)

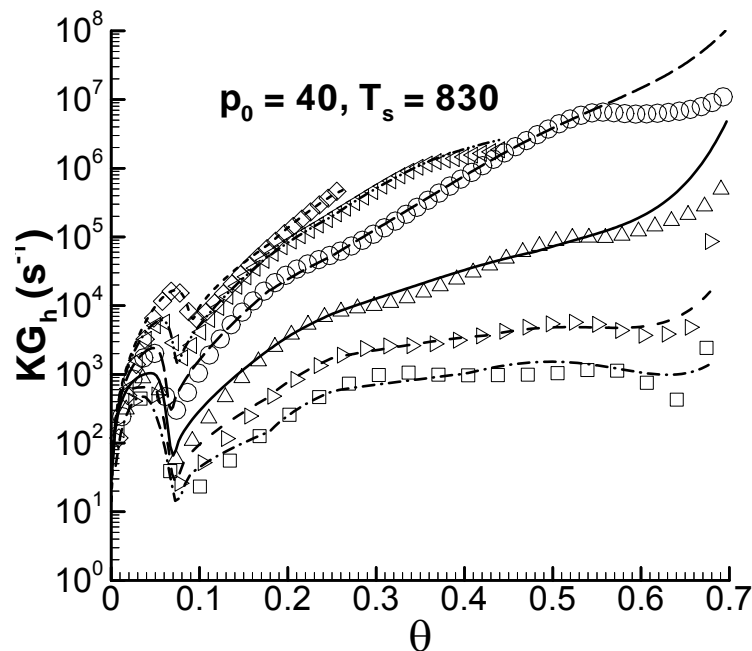
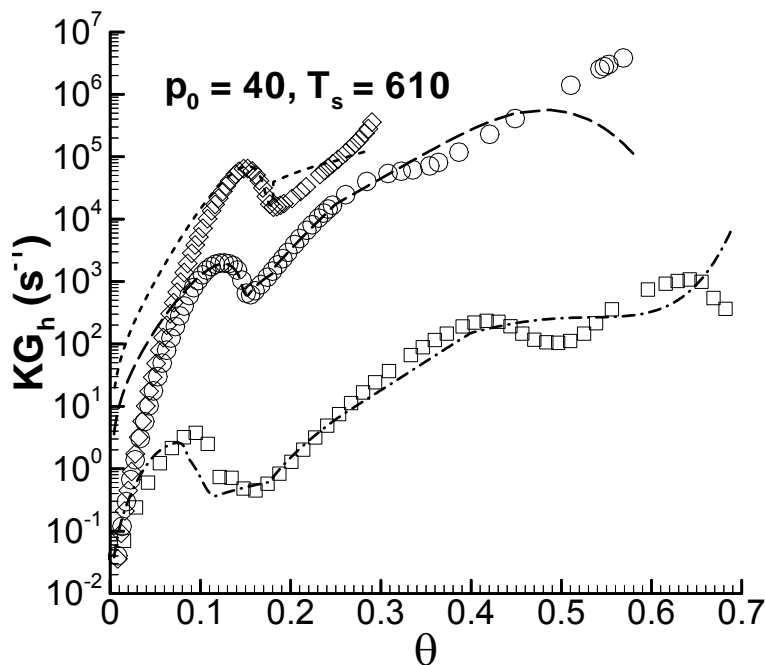
$$\left( \frac{dN_i}{dt} \right)_{\text{reac}} = \frac{dN_i}{dt} \Big|_{\text{lights}} + \frac{dN_i}{dt} \Big|_{\text{heavies}}$$

2. Species having a quasi-steady behavior that will be reproduced with curve fits: O, CH, CH<sub>2</sub>, CH<sub>3</sub>, HO, HCO, HO<sub>2</sub>, HC<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>

➡ 9 species

# Contribution of the heavy species to the light species H

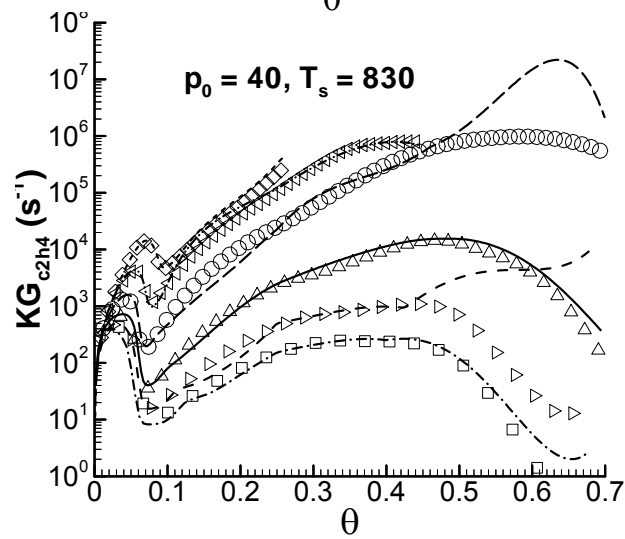
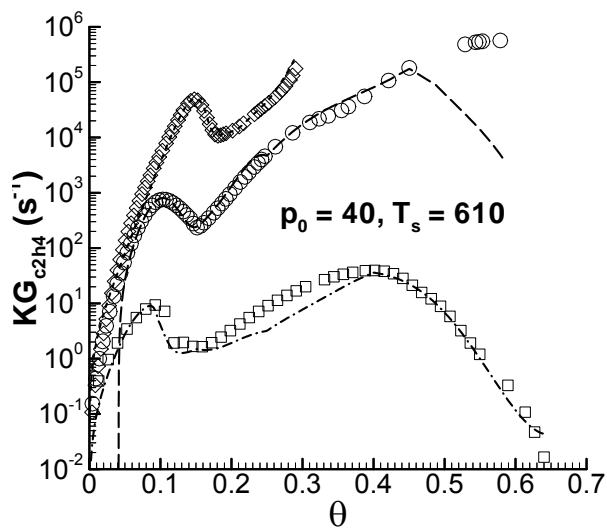
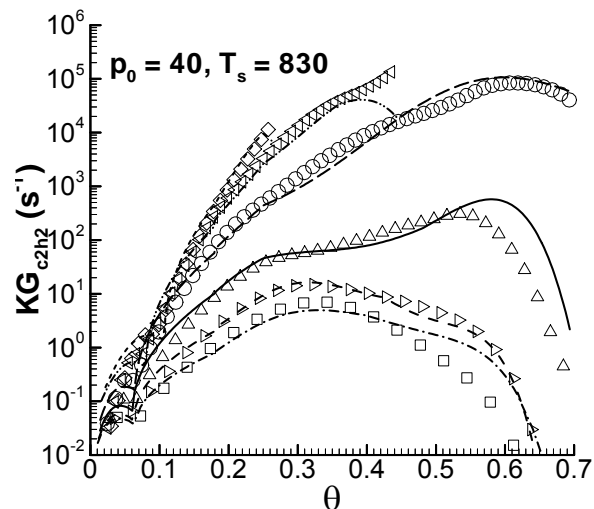
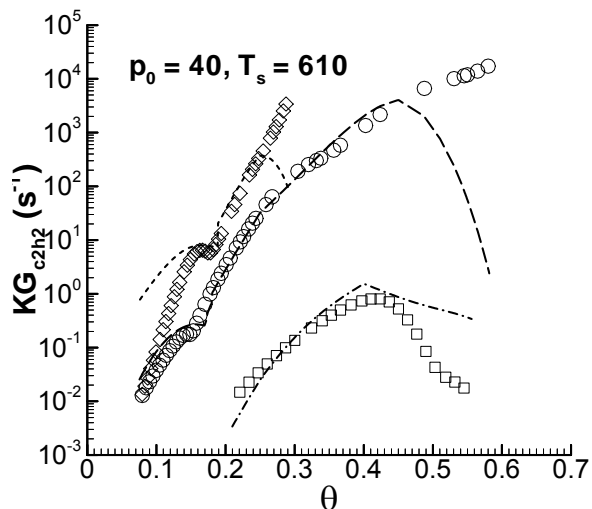
$$\left. \frac{dN_i}{dt} \right|_{\text{heavies}} = N_c (KG_i - X_i KLi)$$



$p_0$  in bar,  $T_s$  in K

$\phi=1/4$ , --- · --- □;  $1/3$ , ---- ▷;  $1/2$ , ----- Δ;  $1$ , ---- ○;  $2$ , -- · -- ◁;  $4$ , ---- □

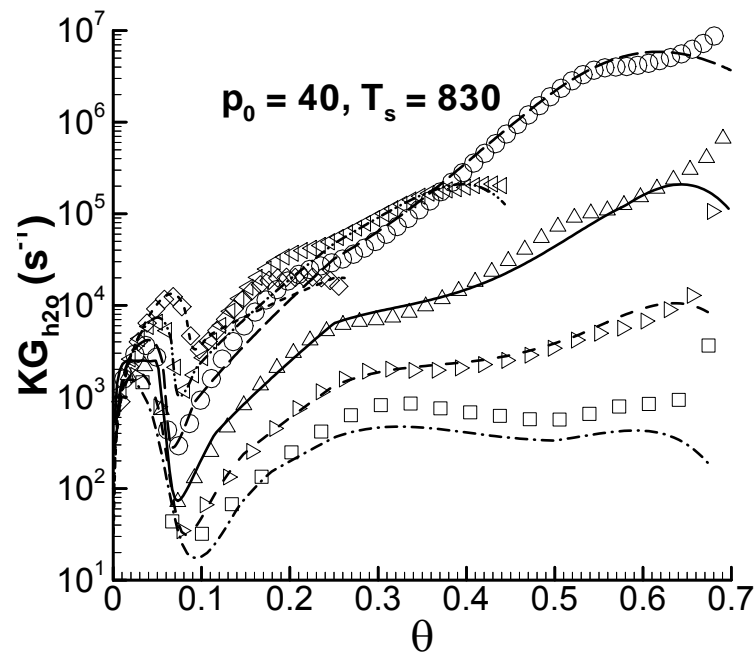
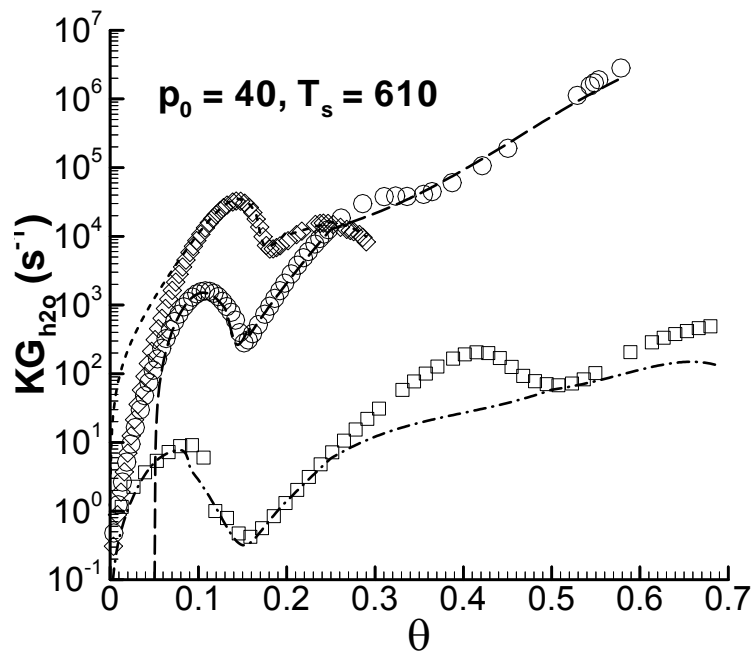
# Contribution of the heavy species to the light species $C_2H_2$ and $C_2H_4$



$p_0$  in bar,  $T_s$  in K

$\phi=1/4$ , --- · --- □;  $1/3$ , --- ▽;  $1/2$ , ----- Δ;  $1$ , --- ○;  $2$ , --- ◁;  $4$ , --- □

# Contribution of the heavy species to the light species H<sub>2</sub>O



$p_0$  in bar,  $T_s$  in K

$\phi=1/4$ , --- · --- □;  $1/3$ , - - - - ▷;  $1/2$ , ----- Δ; 1, --- ○; 2, -- · · - ◁; 4, - - - - □

# Summary and conclusions, 1 of 2

1. Species ensemble partitioned into light and heavy (i.e.  $n \geq 3$ ) species.
2. Combined all constituents into a global one,  $N_c$ , which decays in a quasi-steady way.
3. Analyzed the LLNL data and found a temperature-like parameter,  $\theta$ , for which  $N_c/(\phi \times N^*)$  shows a self-similar behavior with  $p_0$ ,  $\phi$  and a modeling parameter  $T_s$  where  $N^*$  is a non-dimensional surrogate  $p$ .
4. Fitted the kinetic rate of  $N_c$  and the heat release from the heavy species over a very wide regime of  $p_0$ ,  $\phi$ ,  $T_s$  and  $T$ .
5. Only 12 process variables remain after reduction.
6. The model is very compact and enlargement to higher C alkanes is conceptually straightforward if the quasi-steady aspect is preserved.

# Summary and conclusions, 2 of 2

7. The final model has

- 12 ultimate progress variables (1 for the constituents and 11 for light molecules or free radicals),
- 17 quasi-steady rate functions ( $K_c$ ,  $K_h$ ,  $KG_i$  for the 11 light species of the base and  $KL_i$  for  $H_2O$ ,  $O_2$ ,  $H_2$  and  $H$ )
- 9 curve fits for light species quasi-steady mole fractions
- 1 curve fit for  $C_{p,h}$

8. Model advantages

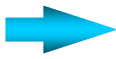
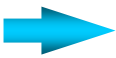
- very compact
- enlargement to higher C alkanes is conceptually straightforward if the quasi-steady aspect is preserved because additional species do not lead to additional progress variables due to the  $N_c$  grouping

9. Remains to be seen if the present curve fits are valid for higher C alkanes or must be modified

# Future work

1. Fits for  $KL_i$  following the described methodology
2. Fits for the mole fractions of the light quasi-steady species
3. Extend the model to iso-octane
4. Perform computations with our model and compare to the LLNL data
5. Extend to mixtures of n-heptane/iso-octane
6. Extend to laminar flames

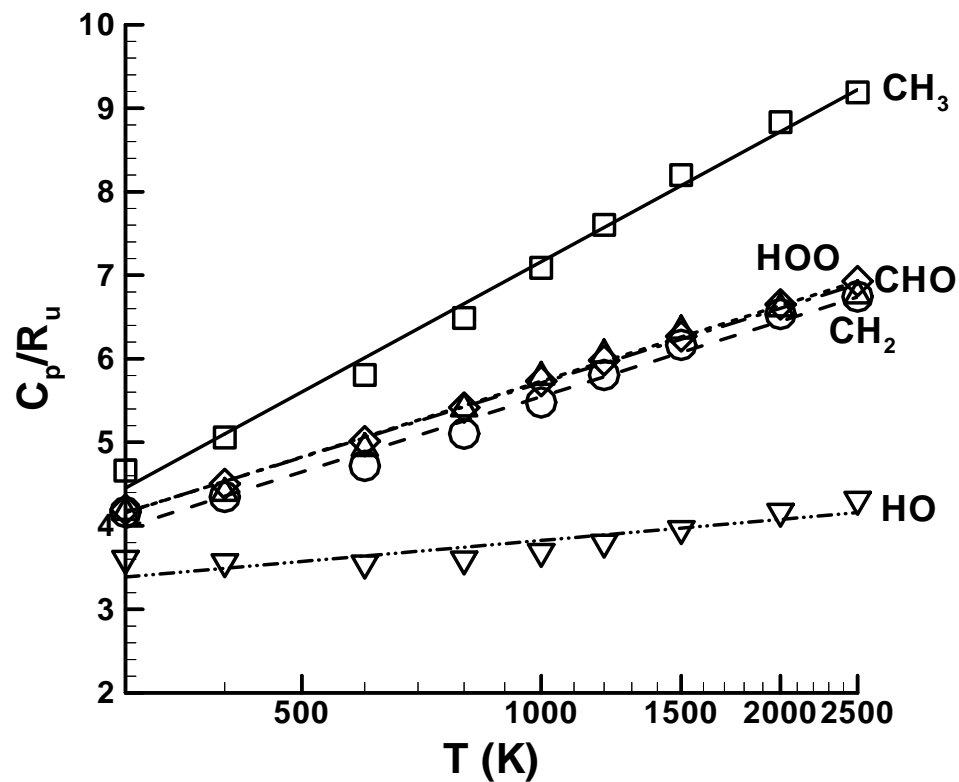
# $K_c$ quasi-steadiness

1.  $K_c$  represents only a small difference between production and loss rates which are nearly equal and are much larger than  $K_c$ . The  $K_c$  value is typically about 1.5% to 5% of either production or loss rate.
2. The maximum difference between production and loss rates is about 5% for  $N^* \lesssim 1$ , then decreases to about 3% at larger  $N^*$ .
3. These maximum differences tend to occur during very large values of  $dT/dt$ .
4. Suggests that  $K_c$  could be treated as a rate of a nearly quasi-steady process.  Develop fits for  $K_c$ .
5. Do not try to find  $K_c$  from slopes of  $N_c$   one would miss the important incubation region.

# Species with double bonds not at the end of the chain or oxidized species

- The linearity of the constituents as building blocks no longer rigorously, but only approximately, holds.
- How does one calculate combustion energies once either breakup of a hydrocarbon into free radicals or oxidation reactions occur? Assume:
  - One can associate a constant partial enthalpy with each constituent, independent of the species to which they belong.
  - The contribution of the combustion enthalpy in forming a free radical is determined by adding to the constituent contributions a correction (for a given radical) using a set of empirical rules that we have determined.
- Assumptions are not entirely correct (when subtracting contributions from  $\text{CH}_2$ ,  $\text{CH}_3$ , etc.)
  - the variation across species is not that substantial
  - an average over species is taken.

# Correlations for the heat capacity



Some free radicals

# List of constituents

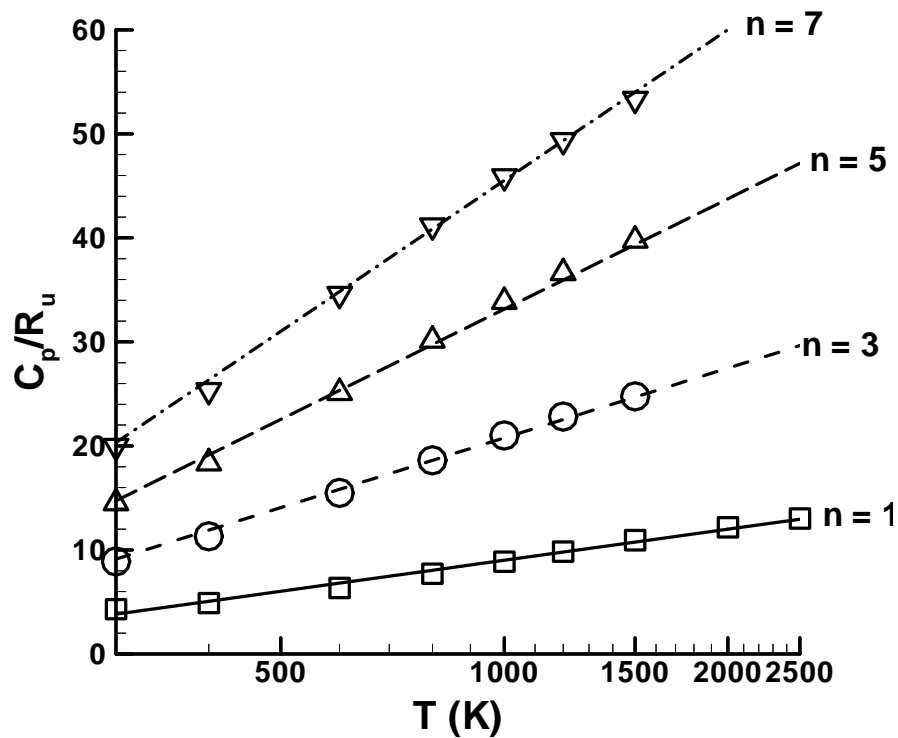
- Linearity of thermal properties of heavy species with C number: 13 constituents

Constituent	$\delta h^o$	$\delta h^c$	$\delta h^f$	$a^h$	$b^h$
CH <sub>3</sub> (methyl)	-42.0	714	188	3.137	3.433
CH <sub>2</sub> (methylene)	-20.8	614.3	411	2.784	2.812
CH (methyldiyne)	$\cong -7$	$\cong 507$	$\cong 603$	2.068	3.038
C <sub>2</sub> H <sub>3</sub> (vinyl)	62.5	1212	237	4.432	4.468
C <sub>2</sub> H <sub>2</sub> (CH=CH) <sup>◊</sup>	73±2	1102±2	not relevant	3.82	3.72
C <sub>2</sub> (C≡C, dicarbon)	230	1017	608	2.919	1.796
HC <sub>2</sub> (HC≡C, ethynyl)	227	1135	339 **	3.937	2.2515
CO (keto)	-133±2	260.5	23	2.892	1.531
HCO (formyl)	-124±3	390.3	167	3.5	2.1
HO (hydroxyl)	-166±6***	-45	204	2.084	1.0945
HOO (hydro-peroxy) <sup>*⊕</sup>	-205+116/n <sub>a</sub>	-84+116/n <sub>a</sub>	215-116/n <sub>a</sub>	4.194	1.908
OO (peroxy) <sup>*</sup>	-16-13n <sub>a</sub>	-16-13n <sub>a</sub>	not relevant	3.65	2.135
O (ethers) <sup>*#</sup>	-74-13n <sub>a</sub>	-74-13n <sub>a</sub>	323+13n <sub>a</sub>	-1.46	2.44

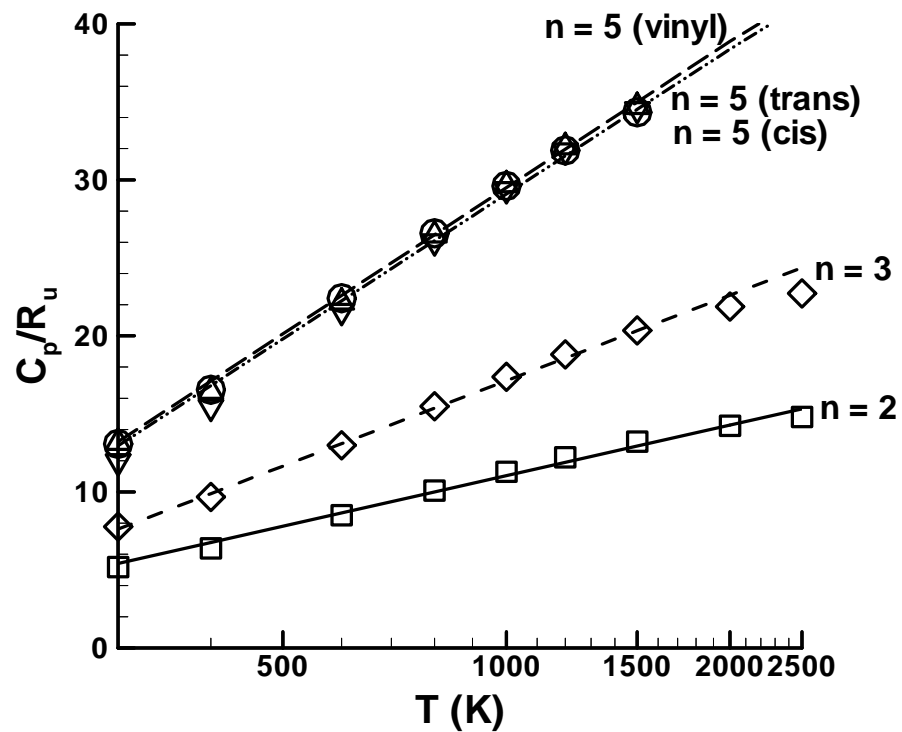
$\delta h^o$ ,  $\delta h^c$ ,  $\delta h^f$  heats of formation, combustion, and constituent-to-free transition, respectively, in kJ/mol; constants  $a^h$  and  $b^h$  for partial molar heat capacity in the form

$$\delta C_p/R_u = a^h + b^h \ln(T/T_{ref}); T_{ref} = 25 \text{ C} = 298.15 \text{ K}$$

# Heat capacity correlations, 1 of 2

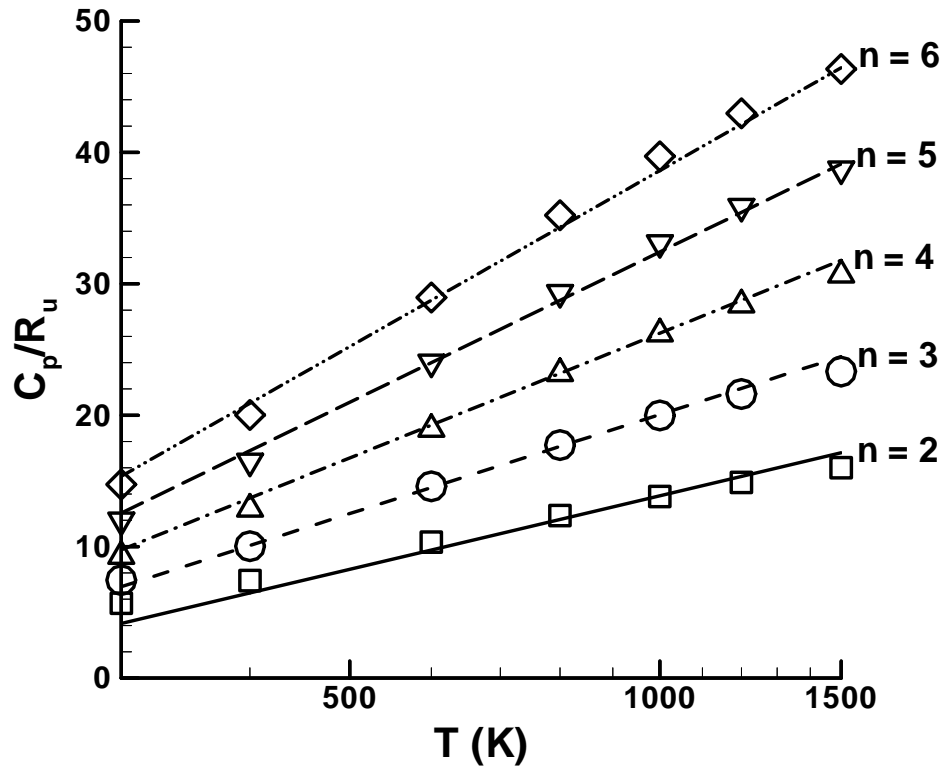


alkanes



alkenes

# Heat capacity correlations, 2 of 2



Ring ethers  $(CH_2)_nO$