Second International Workshop on CHEMKIN in Combustion

Edinburgh, Scotland
July 30, 2000

Sponsored by:
Department of Energy
Sandia National
Laboratories/CA
and Reaction Design

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Reaction Design's CHEMKIN COLLECTION

Fundamentals In Chemistry Modeling

Applications

Introduction

The Second International Workshop on CHEMKIN in Combustion was held at the University of Edinburgh, Scotland on July 30, 2000. This was immediately prior to the 28th International Symposium on Combustion in the same location.

In the first 20 years of its existence, CHEMKIN has enabled significant advances in combustion modeling. Over two hundred people attended the daylong Workshop to further the use of CHEMKIN. Their purpose was to exchange ideas related not only to combustion modeling but also to modeling chemical systems in general. It is hoped the Workshop helped participants expand the application of CHEMKIN-related modeling approaches in their own research and educational activities. Coming as it did just before the Symposium, the Workshop was also a time to greet old acquaintances and make new friends.

The Workshop featured ten invited talks, several contributed presentations, and much lively discussion. These Proceedings record only the invited presentations; they divide into three groups. The two presentations in the first group report the status and plans for the commercial version of CHEMKIN. This is the software distributed by Reaction Design under its exclusive license from Sandia National Laboratories. The second group of talks addresses fundamental issues in modeling reaction mechanisms. These range from thermodynamic databases and from rate expressions for pressure-dependence, to algorithms for constructing mechanisms and to algorithms for tracing the behavior of reacting systems. The four talks in the final group illustrate various applications of CHEMKIN. Of particular interest to many readers will be Prof. Turns' discussion of educational uses. No doubt many Workshop participants have used CHEMKIN in their classrooms; this may be the first recorded discussion of the pedagogic issues involved.

The use of CHEMKIN has given the combustion community some edge over other disciplines that require models of chemical reaction systems. The final presentations discuss three fields closely related to combustion science that are benefiting from the use of general-purpose software for treating chemical mechanisms. These are flame synthesis of materials, computational fluid dynamics, and catalytic combustion.

The members of the organizing committee, Dr. Robert Gallagher, Prof. Peter Glarborg, Dr. Joseph Grcar, Prof. Robert Kee, and Dr. Ellen Meeks, offer heartfelt thanks to all the speakers, who are listed in the table of contents, for the stimulating presentations that made the Workshop a success and to the session chairs, Profs. Robert Kee and Peter Glarborg, and Dr. Charles Westbrook who admirably discharged their assignments..

The University of Edinburgh was a gracious and helpful host; particular thanks are due Anne Hall. The Combustion Institute and the organizers of the 28th Combustion Symposium shared their resources and lent valuable advice; thanks are due especially to Sue Terpack and to Profs. Chris Lawn and David Smith. The considerable preparation required for such a meeting would not have been possible without the dedicated assistance of the Workshop secretary, Kimberly Whitaker.

The Workshop was sponsored by the United States Department of Energy's Office of Industrial Technology, by Sandia National Laboratories' Combustion Research Facility, and by Reaction Design.

It is anticipated a third Workshop will be held in conjunction with the 29th International Symposium on Combustion in Sapporo, Japan in 2002.

Robert Gallagher
Joseph Grcar
Combustion Research Facility
Sandia National Laboratories

Dear Friends,

As the Program Manager for combustion activities in the US Department of Energy's Office of Industrial Technologies, I was pleased to provide support for the Second International Symposium on CHEMKIN in Combustion in Edinburgh, Scotland.

As I stated at the Symposium, I have believed for some time that there is a need for the appropriate application of computational tools to the development of advanced combustion systems. The increasing competitive and regulatory pressures that industry faces require the rapid and cost-effective development of burners and related equipment with performance that could only have been imagined only a decade ago. Tools such as CHEMKIN have been central in moving combustion technologies into the 21st century.

But to continue to successfully apply tools like CHEMKIN, we must continually assess where we are and where we want to go. This is the reason behind Symposia like this. It was a *working* meeting, where all participants were encouraged to share their perspective. Only through the open exchange of views and the free exploration of possible new directions can we hope to continue to get the most from the application of our understanding.

I trust that you found the Symposium worthwhile and hope to see you in the future as we continue to look for new ways to meet the challenges facing the combustion community.

Robert Gemmer
Combustion Program Manager
Office of Industrial Technologies
US Department of Energy

Current Status of CHEMKIN

DAVID KLIPSTEIN

REACTION DESIGN

2nd International Workshop on CHEMKIN in Combustion
July 30, 2000
Edinburgh, Scotland

Structure of the Talk

- 1998/2000 Then and Now
- 1998 Needs for Broader Use
  & Progress Made
- Current Hot Topics

Following Bob Kee

- A Habit but a good one
- The CHEMKIN "Movement"
- Kee's CHEMKIN, A foundation to build on
  - Modular generalized architecture
  - Kinetics plus transport
  - Libraries of properties
- Surface CHEMKIN, A hugely important addition

REACTION DESIGN

* * *

1998/2000 Then and Now

- This Meeting
- Growing the User Base
- Enriching Functionality
- Strengthening Staff

REACTION DESIGN

This Meeting

- This year's meeting 2x'98, 200 Vs 100
- Broadly representative
  - By Geography
  - By type of application
- A unique and meaningful event
  - Highly focused
  - Leading practitioners
  - Direct input to future development

Growing the User Base

- Number of users 2.7x'98, now close to 300
- Geographically diverse: Europe, Asia, US, each1/3
- Combustion still dominates (65% of total)

Some Current Users

Leading Companies

Combustion

ABB/Alstom (4)
Mitsubishi Heavy (2)
Catalytica
Corning
Electricity de France

NKK
Nippon Steel
Nissan
Honda
Solar Turbines

Microelectronics

Applied Materials (2)
Hitachi (2)
LSI Logic.
Infineon
Toshiba
Motorola (3)

Chemicals

BASF
Lubrizol
Conoco
Dow
Praxair

Leading Universities and Research Laboratories

US

Los Alamos(3)
Oak Ridge
Wright Patterson
MIT
Stanford
U of Minnesota

Europe

Def. Res. Agency(UK)
Gas. Warm. Inst.(Ger)
Royal Inst of Tech (Swe)
Tech U of Delft (Neth)
Cambridge U. (UK)
U of Stuttgart (Ger)

Asia

MITI(Japan)
Def.Sci & Tech(Aus)
Inst. Of Energy Res. (Kor)
U of Tokyo(Japan)
Gnarl Chi-Tug U (Taiw)
Seoul National U (Kor)

Enriching Functionality, CHEMKIN III

- New releases in 1998 (3.03) and 1999 (3.5)
- Key features and benefits
  - Added PC to SGI, HP, SUN and Compaq Alpha
  - Dynamic memory allocation
  - On-line documentation & sample problems
  - Integral post-processing graphics
  - Windows application manager interface
  - Oppdif (Opposed diffusion flame) application
  - Improved quality, fewer bugs

Enriching Functionality, CK II Vs CK III

- Handles global and reduced mechanisms
- Accepts chemically activated reactions
- Handles gas, gas-surface& surface reaction systems
- Allows partitioning of reactive surfaces; surface coverage modified rates

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Strengthening Staff

- Doubled in size, 5 to 11
- Important additions
  - **Fran Rupley** brings 20 CHEMKIN years to programming & support
  - **Dr.Cheng Wang** brings database design & application coupling skills
  - **Ola Adigun** brings systems support & quality control skills
  - **Dr Dan Coronell** brings process engineering & interface design skills

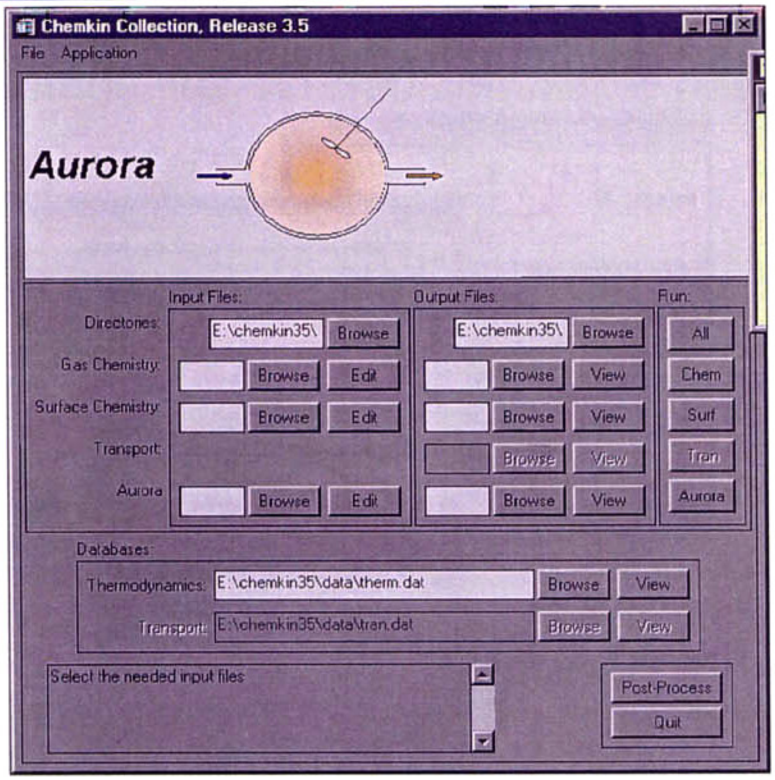
1998 - Areas to Improve

- Ease of use
- Availability of input data
- Post processing tools
- Customer support
- User customization capability

Ease of Use

- Added Windows application manager interface
- On line documentation
- Getting Started Manual
- On line samples for every application
- Improved, more robust software quality

Application Manager Interface



Directories: E:\chemkin35\ (Input Files); E:\chemkin35\ (Output Files)

Thermodynamics: E:\chemkin35\data\therm.dat

Transport: E:\chemkin35\data\tran.dat

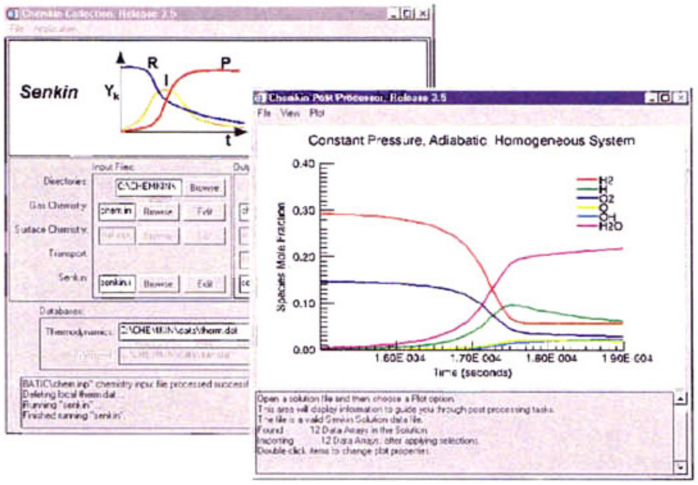
Select the needed input files

Availability of Input Data

- Links to external input databases (e.g.Westbrook, NIST, NASA, Burcat, Exgas)
- Website for user data exchange
- Broader adoption of CHEMKIN mechanism format in scientific journals

Post Processing Tools

- Integrated graphing capabilities



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BATIC\chem.inp" chemistry input file processed successf
Deleting local therm.dat ...
Running "senkin"...
Finished running "senkin"
```

```
Open a solution file and then choose a Plot option.
This area will display information to guide you through post processing tasks.
The file is a valid Senkin Solution data file.
Found        12 Data Arrays in the Solution.
Importing        12 Data Arrays, after applying selections.
Double click items to change plot properties.
```

- Easy export to Excel etc.

Customer Support

- Rapid response hot line
- Increased number (5) & specialization of support staff
- FAQ databank
- User website for problem solving dialogue with other users

User Customization Capability

- Command line user-customizable post processing
- Reaction Design Cooperative Development Agreement (RDCDP)
  - Applications source code available for approved enhancement projects
  - Ten projects currently under way

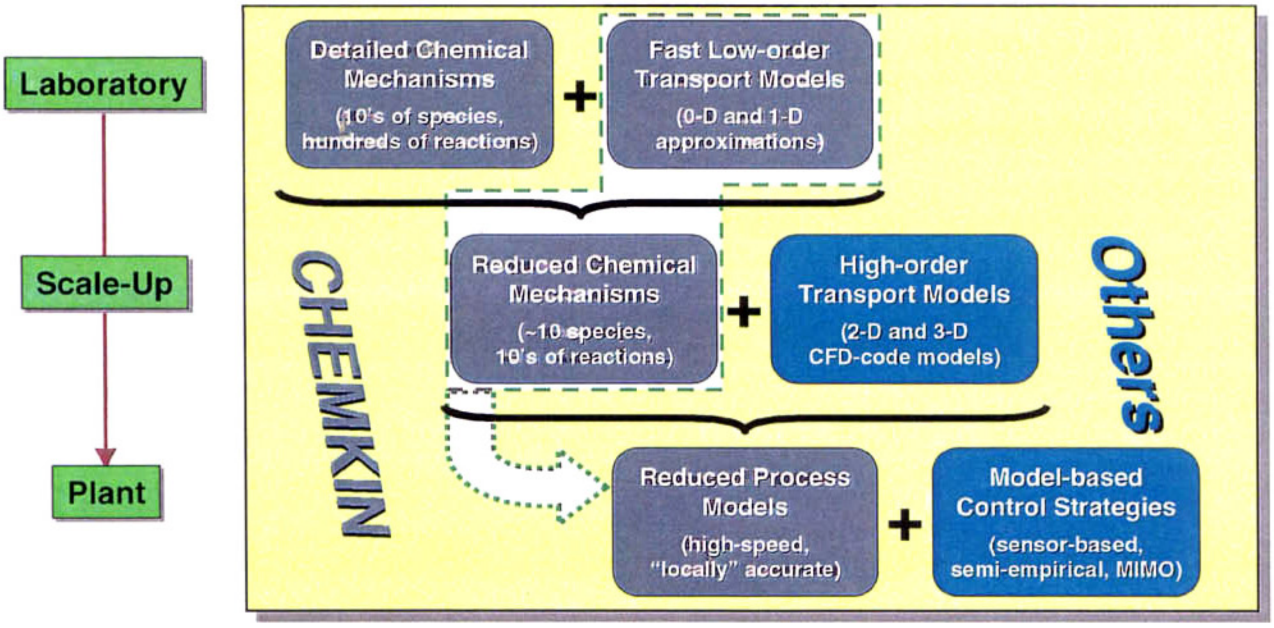
Hot Topics

- IC Engines
- Turbulence
- Catalytic Combustion

Solution-focused Tools for "Hot Topics"

- Modified SENKIN facilitates application to IC engines (Meeks)
- CHEMKIN linked with CFD for Turbulence (Deur)
  - Hierarchical combination speeds convergence

Hierarchical Modeling



Laboratory

Scale-Up

Plant

Detailed Chemical Mechanisms
(10's of species, hundreds of reactions)

\+

Fast Low-order Transport Models
(0-D and 1-D approximations)

Reduced Chemical Mechanisms
(~10 species, 10's of reactions)

\+

High-order Transport Models
(2-D and 3-D CFD-code models)

Reduced Process Models
(high-speed, "locally" accurate)

\+

Model-based Control Strategies
(sensor-based, semi-empirical, MIMO)

CHEMKIN

Others

Solution-focused Tools for "Hot Topics"

- Modified SENKIN facilitates application to IC engines (Meeks)
- CHEMKIN linked with CFD for Turbulence (Deur)
  - Hierarchical combination speeds convergence
- CRESLAF boundary layer module provides improved simulation for
  - Catalytic Combustion (Deutschmann)
  - Exhaust catalyst
  - Selective Oxidation (materials & chemicals mfr.)

REACTION DESIGN

This is Just a Beginning

- There's lots we can do; the opportunities for further enhancements are endless.
- The question is in what gets priority
- Ellen Meeks, who manages RD's CHEMKIN development, will next tell you what we think

→ THEN….. It will be your turn ←

REACTION DESIGN

Near-term and Future Development of CHEMKIN

Ellen Meeks

REACTION DESIGN

2nd International Workshop on CHEMKIN in Combustion
July 30, 2000
Edinburgh, Scotland

Outline

- Long-term development plan
  - Market drivers
  - Partnerships and collaborations
- What's in the next release of the CHEMKIN Collection
- Customer interactions
  - Cooperative Development
  - Technical Support
  - Training / Short-courses
- Request for your continued suggestions

Our long-term efforts are driven towards increasing our market presence

- Software integration
  - Database management
  - Links to quantum chemistry and estimation methods
  - Links to analysis/comparison/optimization tools
- Hierarchical modeling
  - Links to multidimensional Computational Fluid Dynamics (CFD)
  - Links to process simulators (e.g. Aspen)
- Expansion of physical models
  - Dynamic (transient) capability
  - Build engineering models from ideal reactor components
  - Liquid and solution chemistry & transport

We seek to aid communication between chemist and engineer from process design to scale-up

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Reaction Design has important long-term alliances and partnerships

SANDIA National Laboratories

- Development partner for the continuing enhancement of CHEMKIN
- Funded R & D into new applications areas e.g. corrosion & batteries

Computational Fluid Dynamics

- Sales agreement with CFD/RC, ADAPCO; negotiations with others
- Provides entree to > 600 additional customers

National Institute of Standards and Technology (NIST)

- Collaborative agreement on reaction mechanism development

American Institute of Chemical Engineers (AIChE)

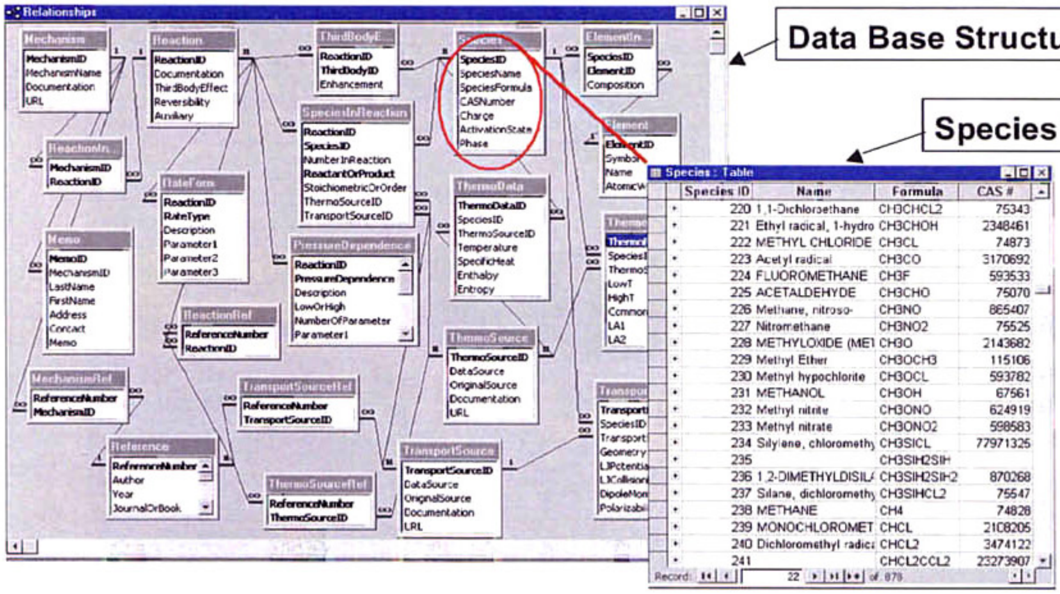
- Klipstein heading industry roadmap project on Reaction Engineering

U.S. Department of Energy (DoE)

- Cooperative Research and Development Agreements (2)

Managing reaction mechanism data is an essential part of problem-solving

- Funded by a phase 1 SBIR with NIST, we have developed a prototype database manager
- Relational database tracks data sources and history



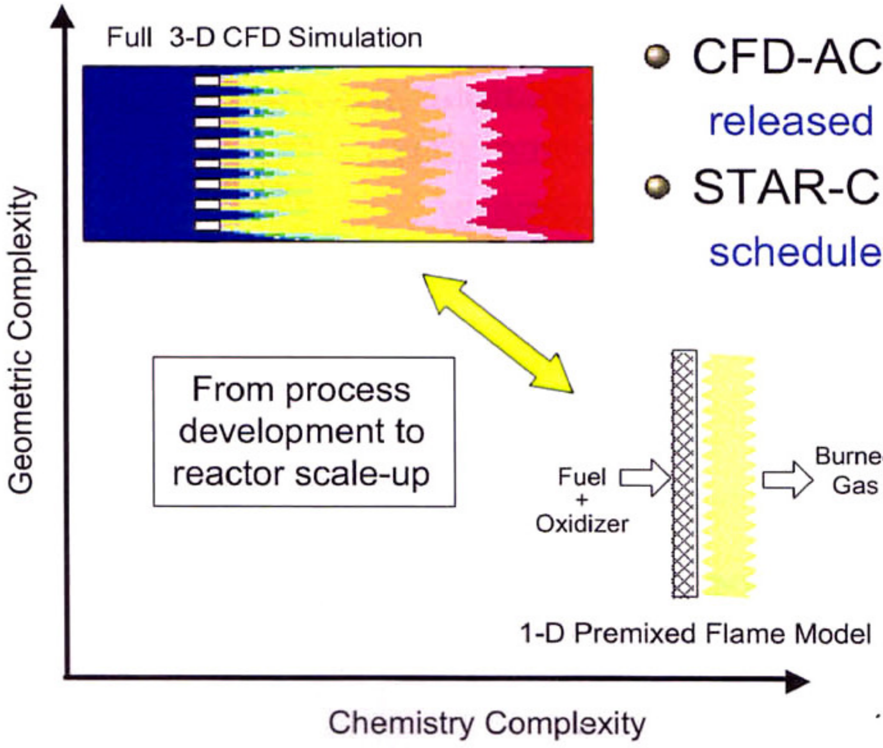
Data Base Structure

Species Table

Species ID	Name	Formula	CAS #
220	1,1-Dichloroethane	CH3CHCL2	75343
221	Ethyl radical, 1-hydro	CH3CHOH	2348461
222	METHYL CHLORIDE	CH3CL	74873
223	Acetyl radical	CH3CO	3170692
224	FLUOROMETHANE	CH3F	593533
225	ACETALDEHYDE	CH3CHO	75070
226	Methane, nitroso-	CH3NO	865407
227	Nitromethane	CH3NO2	75525
228	METHYLOXIDE (MET	CH3O	2143682
229	Methyl Ether	CH3OCH3	115106
230	Methyl hypochlorite	CH3OCL	593782
231	METHANOL	CH3OH	67561
232	Methyl nitrite	CH3ONO	624919
233	Methyl nitrate	CH3ONO2	598583
234	Silylene, chloromethy	CH3SICL	77971325
235		CH3SIH2SIH	
236	1,2-DIMETHYLDISIL/	CH3SIH2SIH2	870268
237	Silane, dichloromethy	CH3SIHCL2	75547
238	METHANE	CH4	74828
239	MONOCHLOROMET	CHCL	2108205
240	Dichloromethyl radica	CHCL2	3474122
241		CHCL2CCL2	23273907

Our partnerships with CFD Companies enable a hierarchical modeling approach

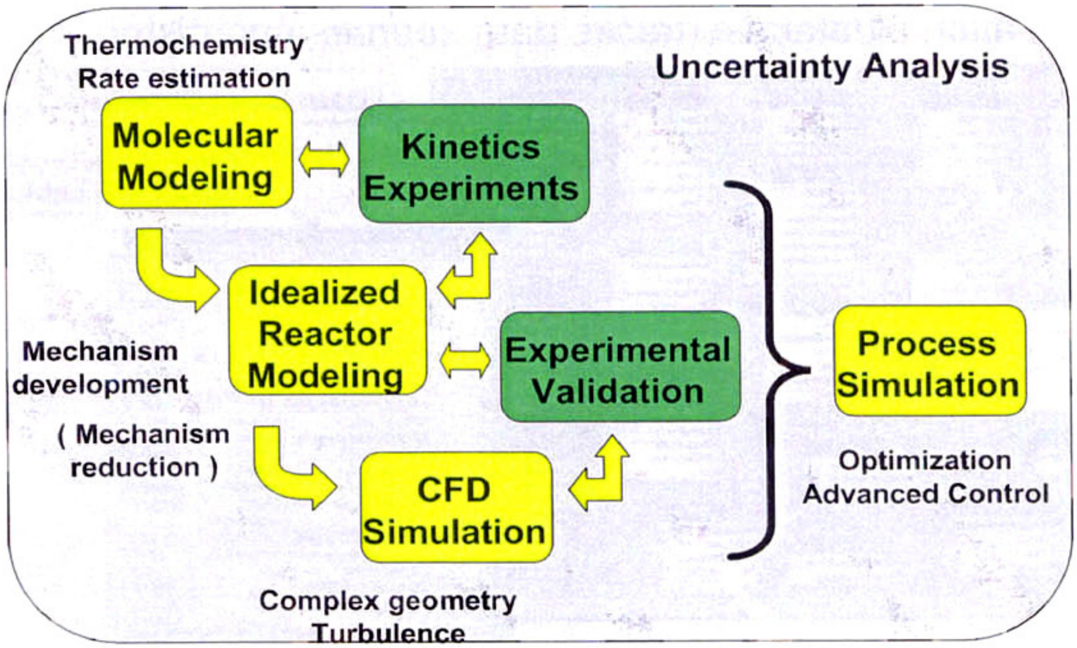
- CFD-ACE$^{+\text{CHEMKIN}}$
  released 9-1998
- STAR-CD+CHEMKIN
  scheduled release in 2000



From process development to reactor scale-up

Links to quantum chemistry are also critical to a problem-solving environment

- We are involved in a DOE-funded CRADA to build the Chemical Engineer's Workbench



Thermochemistry
Rate estimation

Uncertainty Analysis

Molecular Modeling

Kinetics Experiments

Idealized Reactor Modeling

Mechanism development

(Mechanism reduction)

Experimental Validation

Process Simulation

Optimization
Advanced Control

CFD Simulation

Complex geometry
Turbulence

Architectural improvements to CHEMKIN software facilitate long-term goals

- Enable linking of applications
  - License of GRI-mech Calculator capability
  - Establish common data format (XML)
- Improve robustness / reliability
  - Improve modularity and code reuse
  - Better error checking
  - Automated testing and defect tracking
- Design of flexible user interface
  - Customize for different applications

We invest continuously in architectural improvements

Our short-term projects target the Internal Combustion (IC) Engine market

- Dynamic simulation of engine cycle
  - Input data are engine parameters
- Integration of CHEMKIN with STAR-CD for geometrically realistic engine simulations
  - 3-D, complex geometry
  - Transient, turbulent flow
  - Prediction of NO_x
- Highlight of catalytic combustion and conversion through sample problems

Regulation of emissions continues to drive need for better engine simulation

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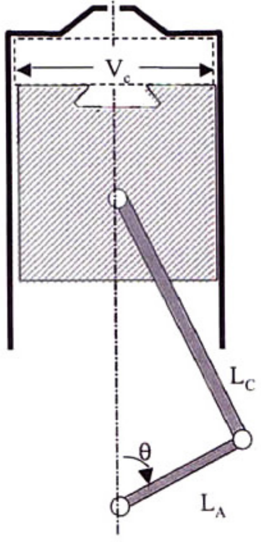
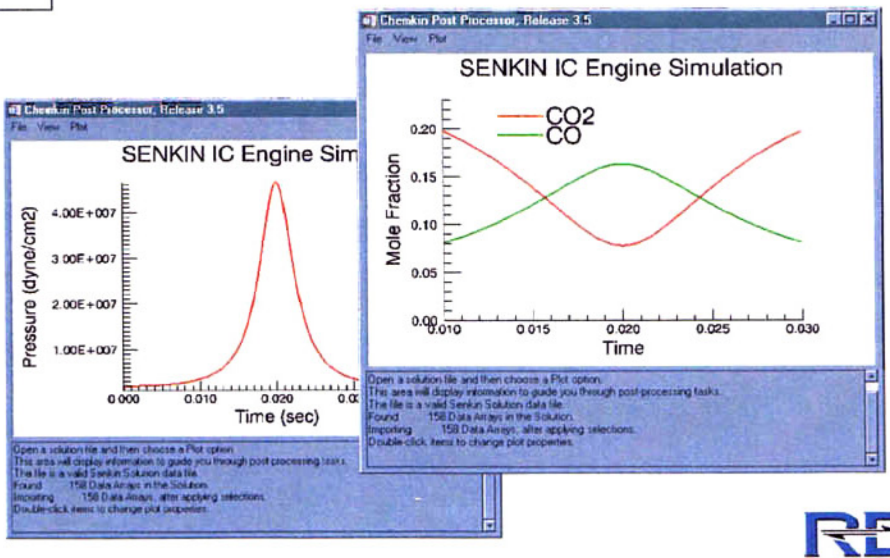
Our IC Engine Model targets pollutant reduction using detailed kinetics

Input:
Compression Ratio
Crank geometry
Fuel / air composition
Angle of injection

Output vs. time:
Temperature
Pressure
Species Fractions





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Found        158 Data Arrays in the Solution.
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Double-click items to change plot properties.
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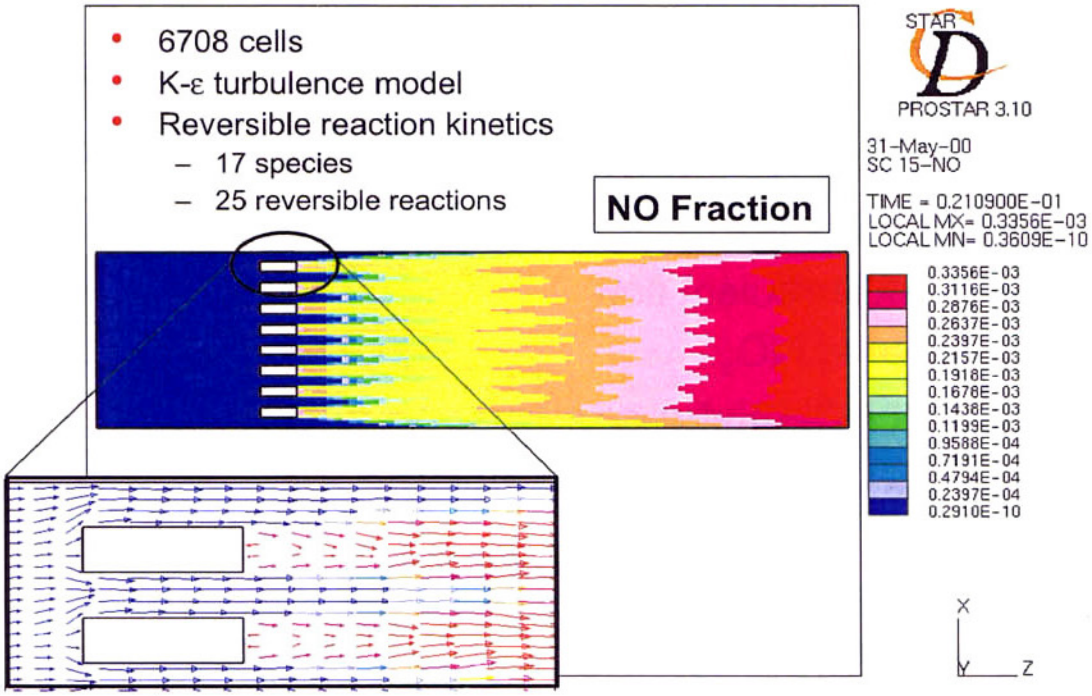
The integration of CHEMKIN with STAR-CD allows more realistic combustor simulation

Lean Premixed Pre-vaporized (LPP) Flame Tube

- 6708 cells
- K-ε turbulence model
- Reversible reaction kinetics
  - 17 species
  - 25 reversible reactions



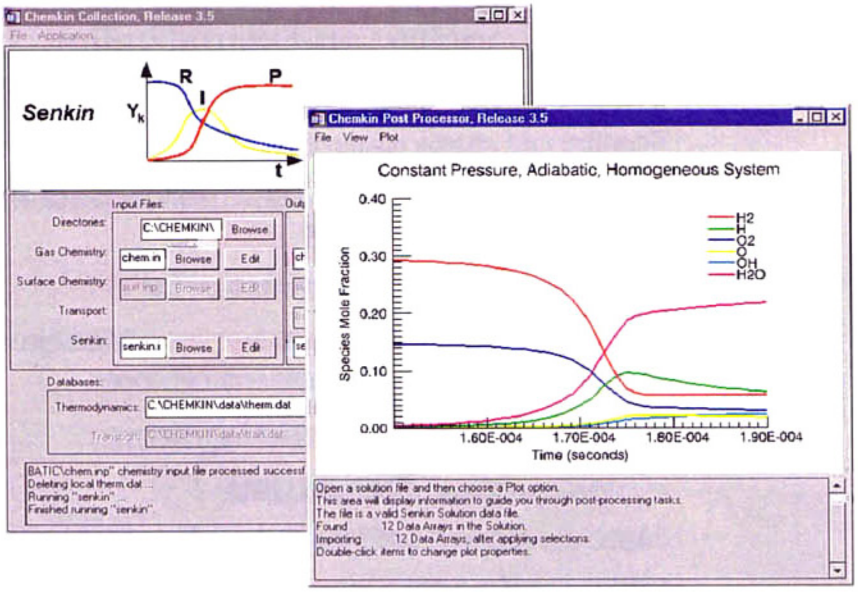
REACTION DESIGN

Additional short-term projects respond directly to customer demand

- Improved ease-of-use
  - Simplified licensing
  - User Interface and Post-processor
  - Speed enhancements
  - Better documentation
- Enhanced functionality & flexibility
  - Transient simulations
  - Expanded heat-transfer options
  - User-specified profiles
  - Reaction sensitivity and rate analysis options

REACTION DESIGN

The ease-of-use introduced by CHEMKIN 3.5 sparked a large growth in PC users



```
BATIC\chem.inp" chemistry input file processed successf
Deleting local therm.dat ...
Running "senkin" ...
Finished running "senkin".
```

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```

- In two years, we went from 0 to 33% Licenses on PC
- Users no longer need expensive workstations and compilers

CHEMKIN Release 3.6, scheduled for release this year, includes many new capabilities

- New Transient AURORA (PSR)
  - Dynamic systems with surface chemistry
  - IC Engine cycles
  - Pulsed combustion and pulsed plasmas
  - Dynamic sensitivity analysis for gas & surface reactions
  - Dynamic response to system perturbations & control trajectories
- New flexible reactor specifications
  - Variable volume, temperature or pressure vs. time in AURORA
  - Variable geometry, temperature and heat vs. distance in PLUG
  - Variable flame-tube area vs. distance in PREMIX

Dramatic increase in the types of problems that can be solved

CHEMKIN Release 3.6 scheduled for release this year … (cont'd)

- Improved usability and visualization.
  - Improved speed for Graphical Post-Processor
  - Plotting of rates-of-production data from AURORA
  - Ability to plot against experimental data and multiple solutions in the Graphical Post-Processor
  - Generation of initial estimates for SPIN, OPPDIF, and PREMIX
  - Command-line post-processors output comma-separated values that export directly into Excel
- New customer-requested options:
  - > 5 elements in thermo data
  - Material-dependent heat transfer in AURORA
  - Initial crank-angle for IC Engine Model
  - Sensitivity analysis in OPPDIF

And more…

We have established infrastructure required for robust software maintenance

- Central source-code management system
- Defect tracking system
- Internal knowledge-base from 2 years of technical support
- Automated frequent build and test

- In the next year we will make our knowledge base available on the web

Customer interactions are extremely important to us

- We strive to provide high-end Technical Support
  - Quick response: 1-day average
  - Technical depth: Getting Started to Application details
- Web-based user group started this year
  - 123 members
- Citation database on web
- A short-course on CHEMKIN planned for AICHE in November, 2000
- Future training courses

In the next year(s) we have several proposed projects that we are considering

- Links to parameter estimation methods for thermodynamic data and reaction-rates
- Chebychev polynomial description option for pressure & temperature dependence of reaction-rates
- Soot-formation model
- Transient OPPDIF
- Radiation model in flame codes
- Creation of DLLs, callable from Excel and other software
- Utilities to facilitate calling CHEMKIN from C
- Release on Linux Platform (scheduled for 2/2001)

We welcome your comments and suggestions

Conclusions

- We are making steady improvements to the CHEMKIN software
- Our long-term plans include expansion of capabilities to accommodate new markets
- Ease-of-use will continue to be a focus in the next few releases

➡ Your guidance and direction are very important to us

NONLINEAR DYNAMICS IN HOMOGENEOUS AND CATALYTIC COMBUSTION

Dionisios (Dion) G. Vlachos, M. Gummalla, P. K. Young, P. Aghalayam, and R. J. Olsen*

**Department of Chemical Engineering, University of Delaware,
Newark, DE 19716, USA**

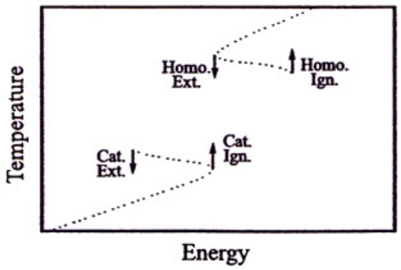
**vlachos@che.udel.edu;
http://www.che.udel.edu/faculty/full/vlachos/**

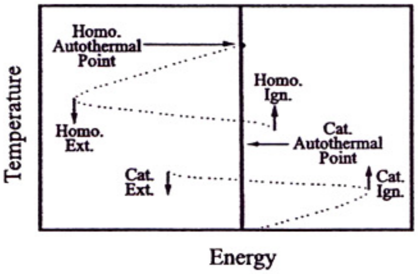
**Research performed at: Department of Chemical Engineering,
University of Massachusetts, Amherst, MA 01003, USA
*Department of Chemistry, Bard College, NY 12504**

Funding: ONR YIA ACS-PRF, NSF Career Award

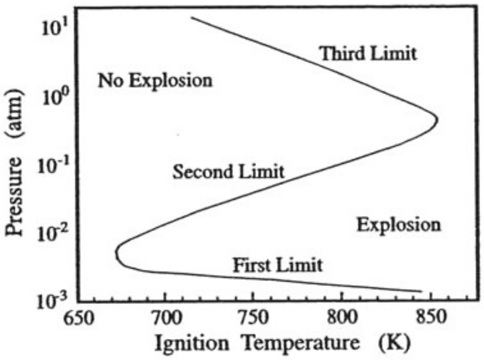
BIFURCATION IS CENTRAL TO OPERATION

- Catalytic ignition is important for startup
- Gas phase ignition can be desirable or not
- Safety is of major concern
- Flammability limit expansion is desirable for combustion of fuel-lean mixtures and NO_x reduction
- Extinction leads to loss of activity



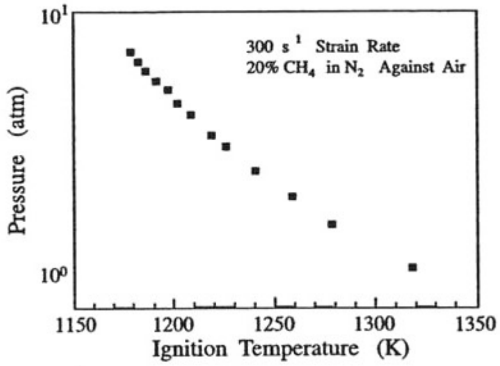


Previous experimental results



Lewis and von Elbe, Combustion Flames, and Explosion of Gases, 1987

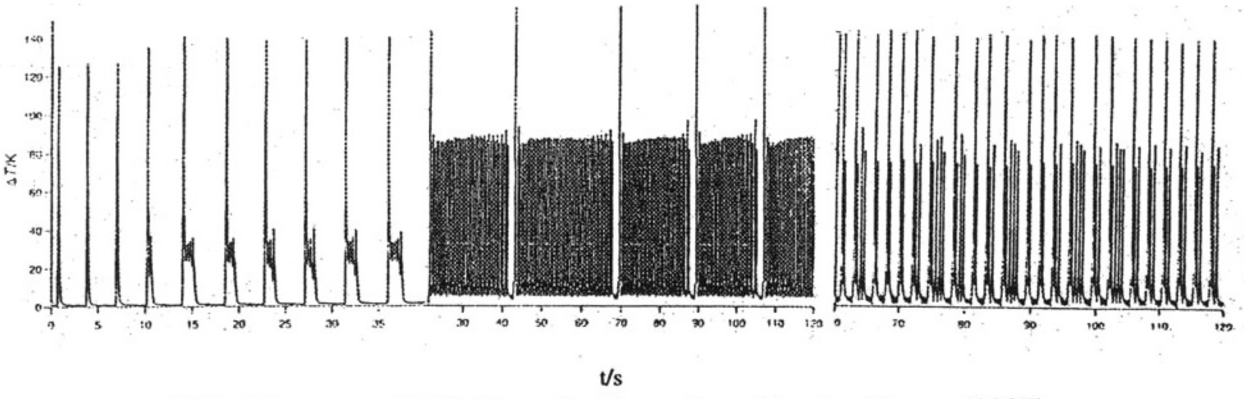
Explosion limit for stoichiometric H_2 and O_2 mixture in a batch reactor



Fotache, Kreutz, and Law, *Combustion and Flame*, 108:442-470, 1997

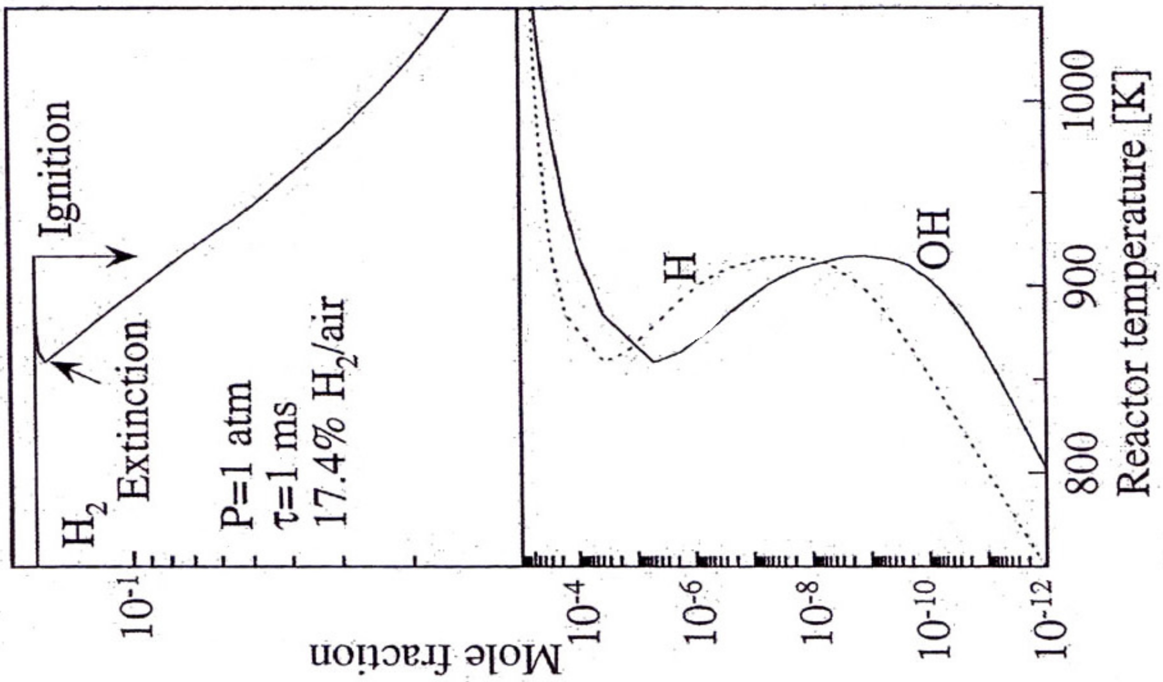
Ignition temperature data for counterflowing non-premixed jet of heated air against CH_4 in N_2

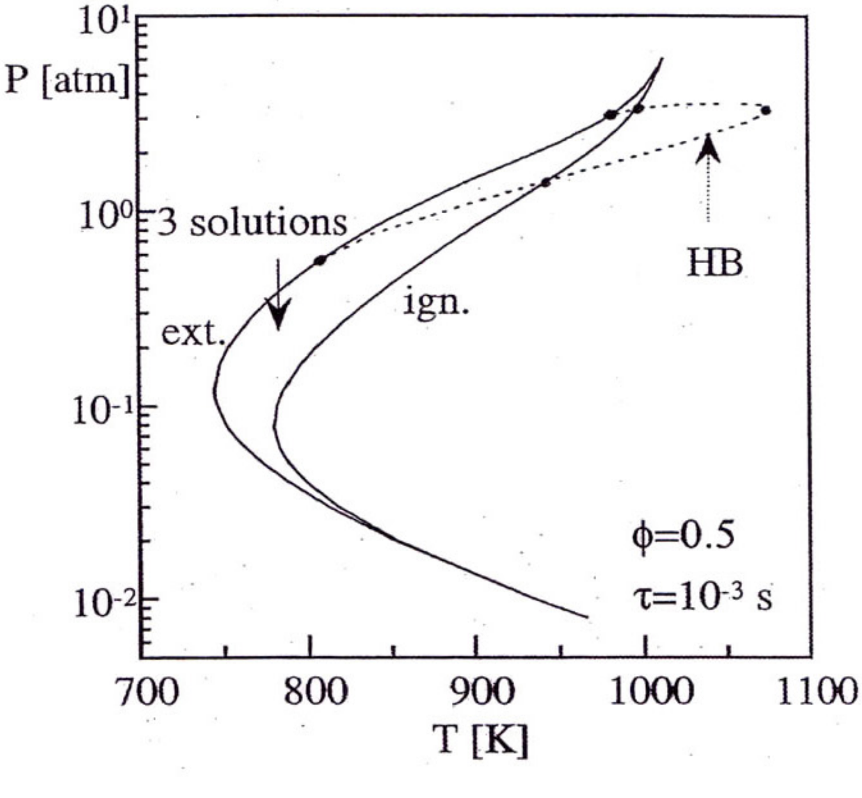
OSCILLATIONS ARE OFTEN SEEN EXPERIMENTALLY

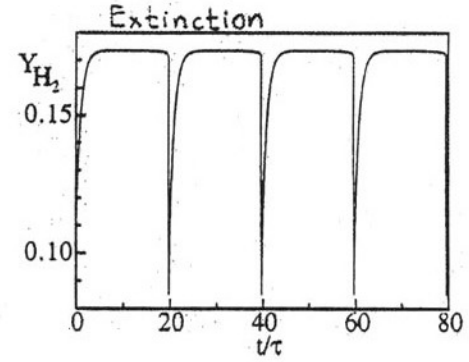


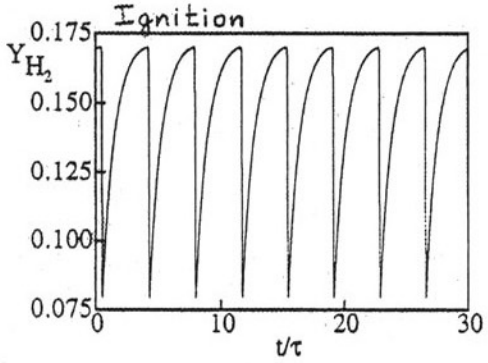
B.R. Johnson and S.K. Scott, J. Chem. Soc., Faraday Trans. (1997)

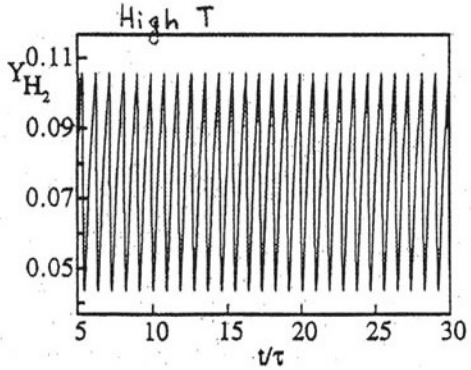
- **Oscillations are usually undesirable (mechanical failure) but can also lead to enhanced combustion**
- **Oscillations are often seen prior to extinction and can render extinction theory of combustion flows complicated**

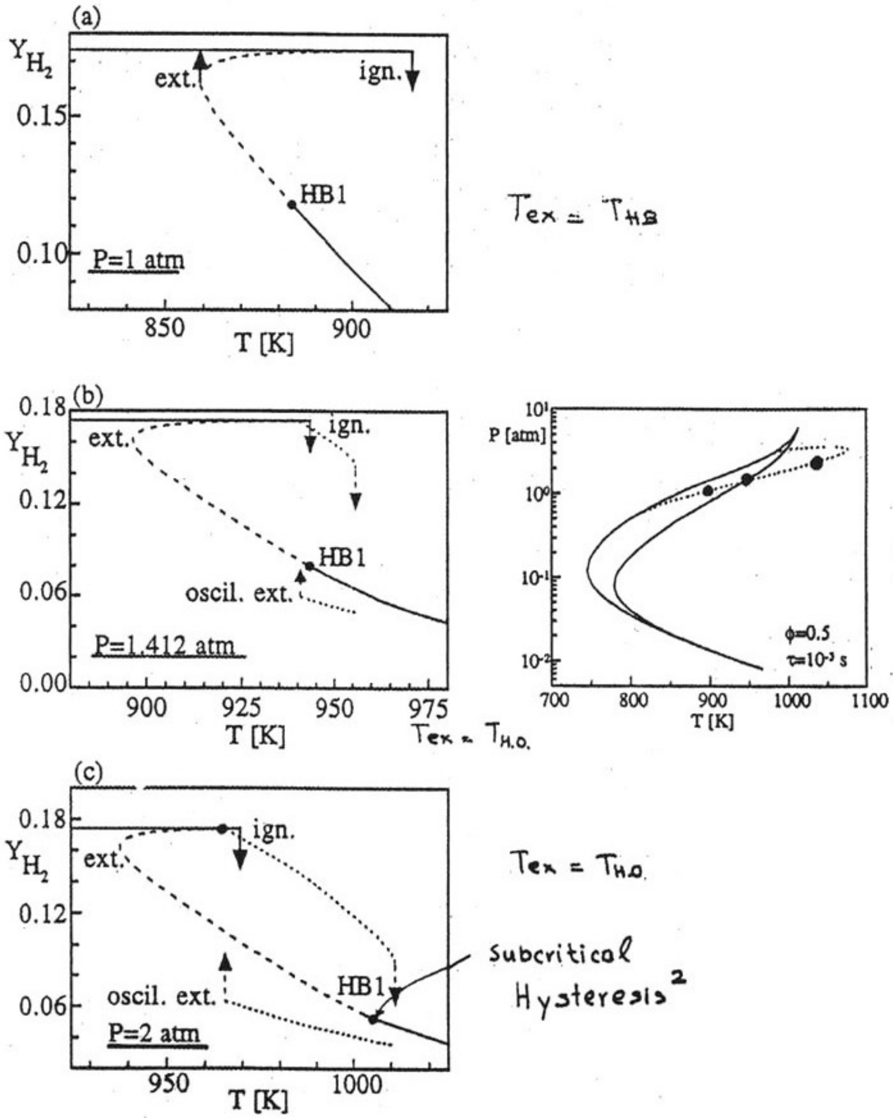

H$_2$
Extinction
Ignition
P=1 atm
τ=1 ms
17.4% H$_2$/air
H
OH
Mole fraction
10^{-1}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
800
900
1000
Reactor temperature [K]


10^1
P [atm]
10^0
10^{-1}
10^{-2}
3 solutions
ext.
ign.
HB
φ=0.5
τ=10^{-3} s
700
800
900
1000
1100
T [K]







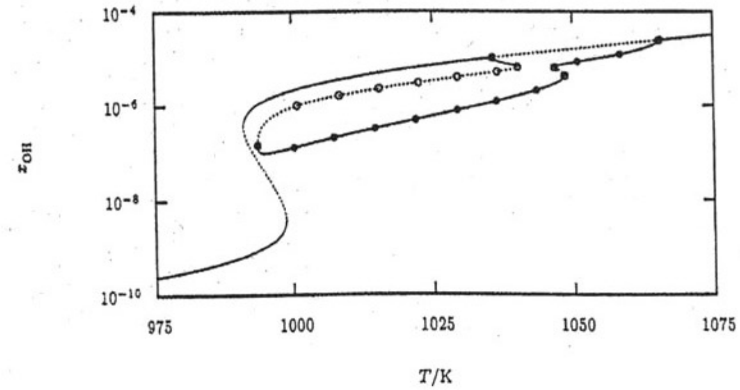


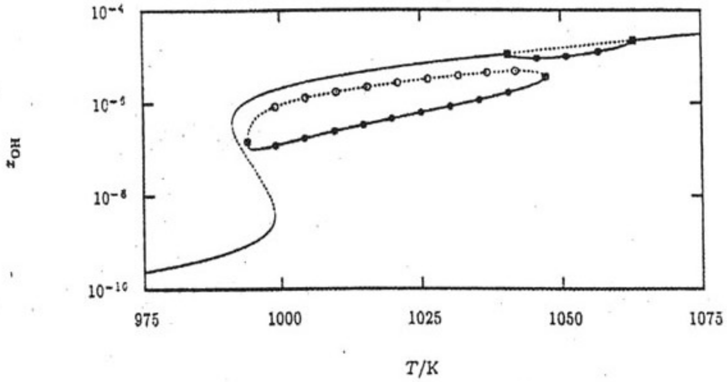
$T_{ex} = T_{HB}$

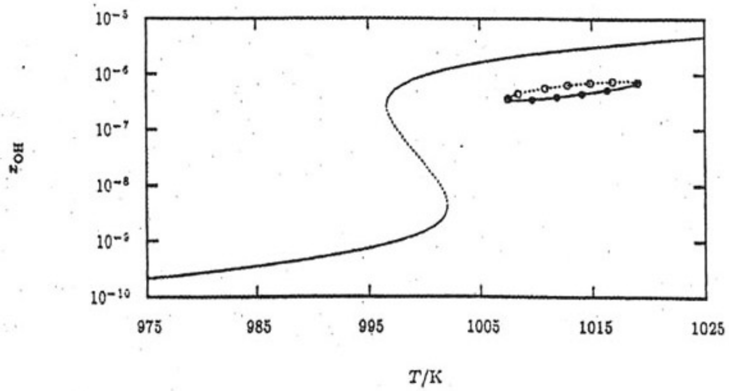
$T_{ex} = T_{H.O.}$

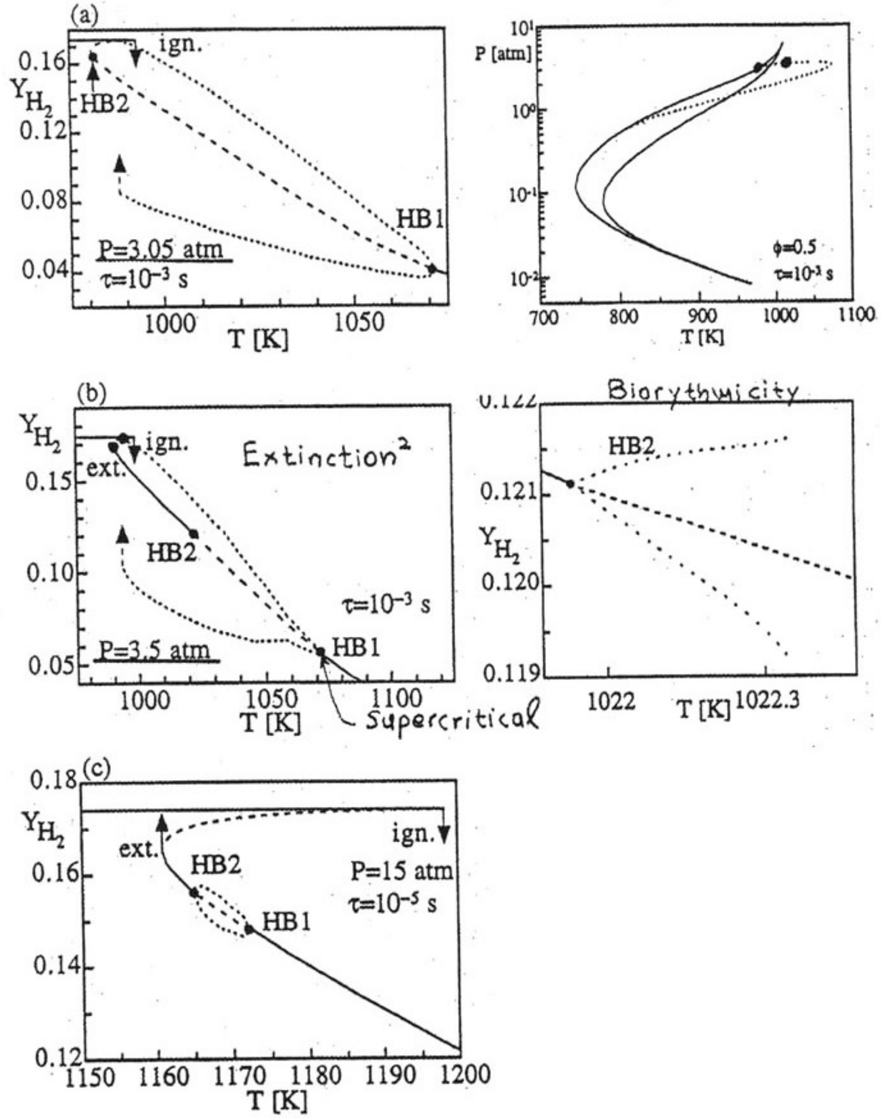
$T_{ex} = T_{H.O}$

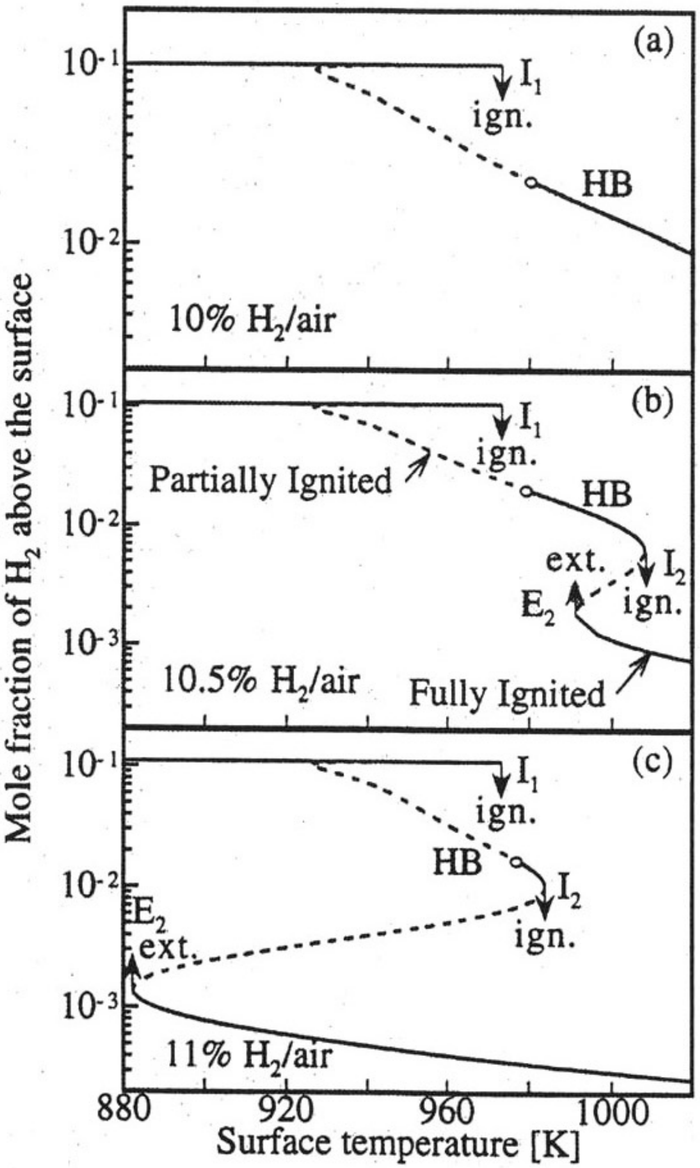
Subcritical Hysteresis [2]


x_{OH}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
975
1000
1025
1050
1075
T/K

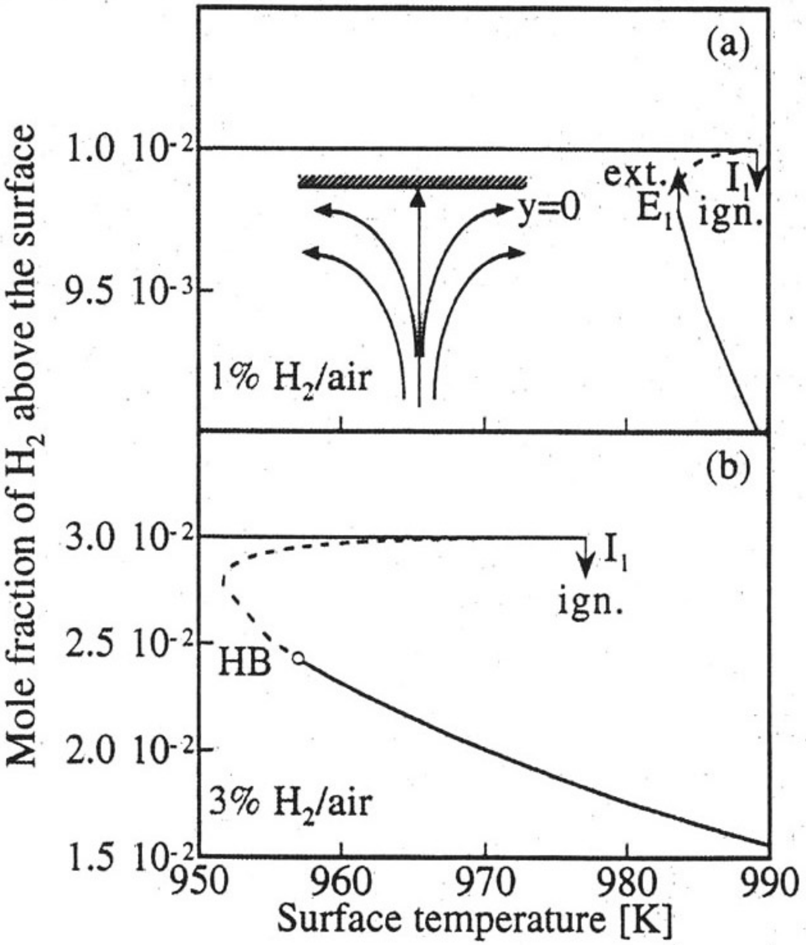

x_{OH}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
975
1000
1025
1050
1075
T/K


x_{OH}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
975
985
995
1005
1015
1025
T/K

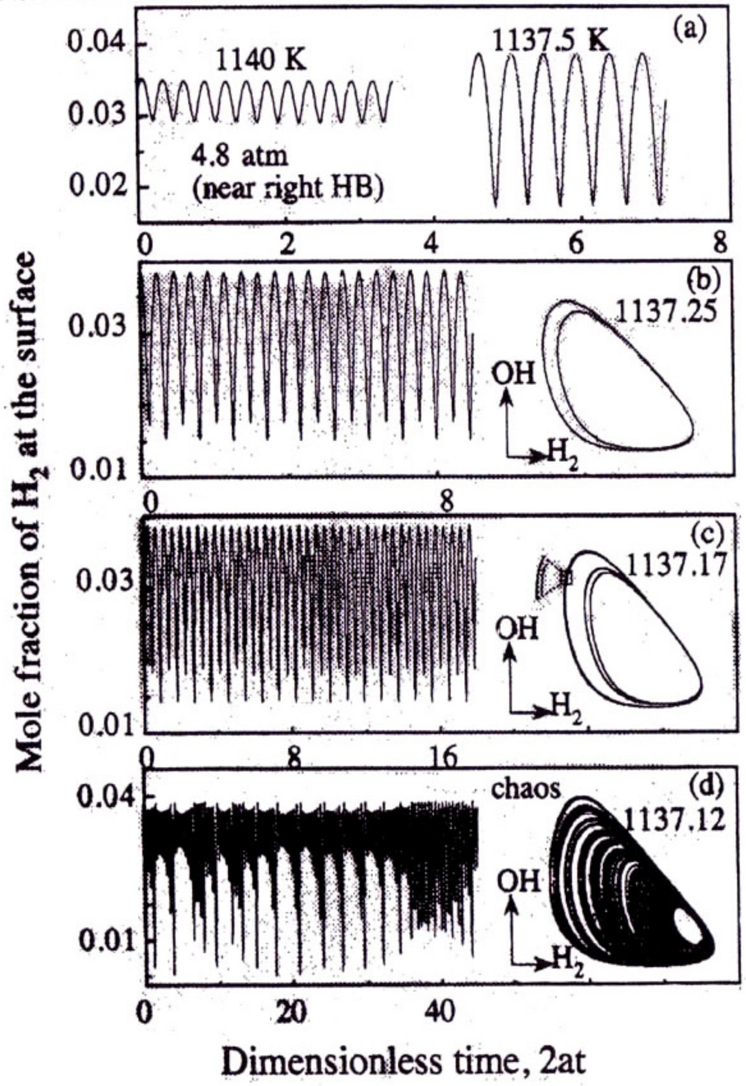

(a)
Y_{H_2}
0.16
0.12
0.08
0.04
ign.
HB2
HB1
P=3.05 atm
τ=10^{-3} s
1000
1050
T [K]
P [atm]
10^{1}
10^{0}
10^{-1}
10^{-2}
φ=0.5
τ=10^{-3} s
700
800
900
1000
1100
T [K]
(b)
Y_{H_2}
0.15
0.10
0.05
ign.
ext.
Extinction²
HB2
τ=10^{-3} s
HB1
P=3.5 atm
1000
1050
1100
T [K]
Supercritical
Biorythmicity
0.122
0.121
0.120
0.119
Y_{H_2}
HB2
1022
T [K]
1022.3
(c)
Y_{H_2}
0.18
0.16
0.14
0.12
ext.
ign.
HB2
HB1
P=15 atm
τ=10^{-5} s
1150
1160
1170
1180
1190
1200
T [K]



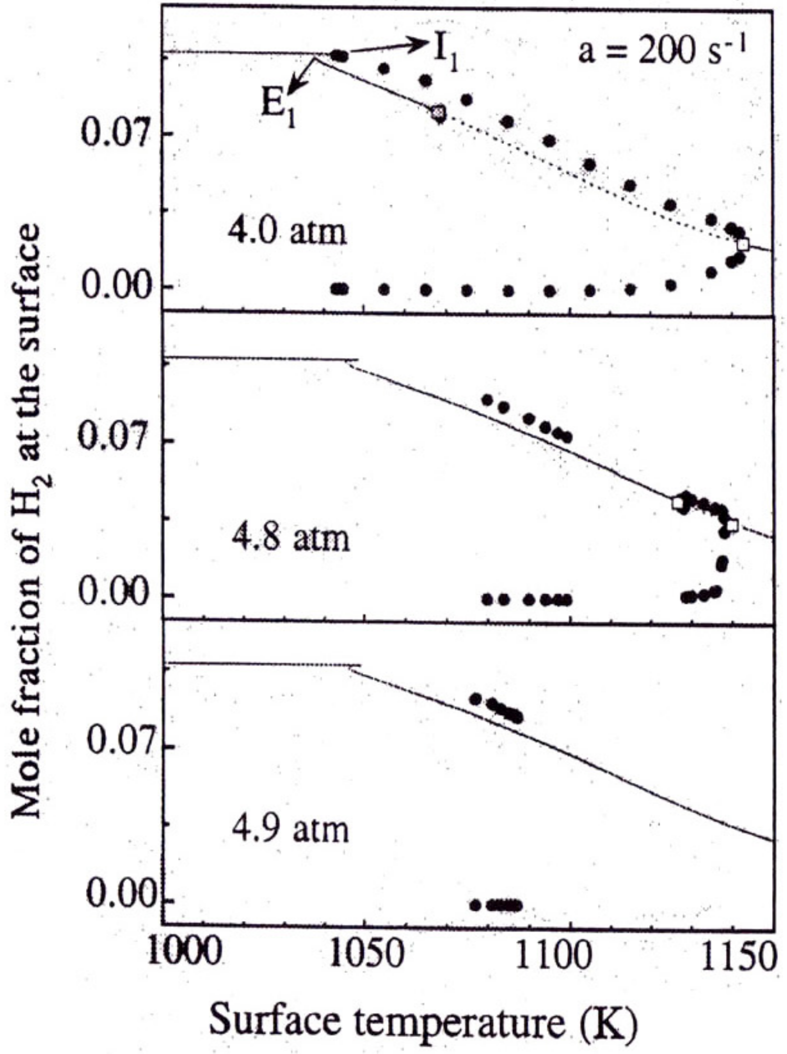
One-parameter bifurcation plots at 1 atm.



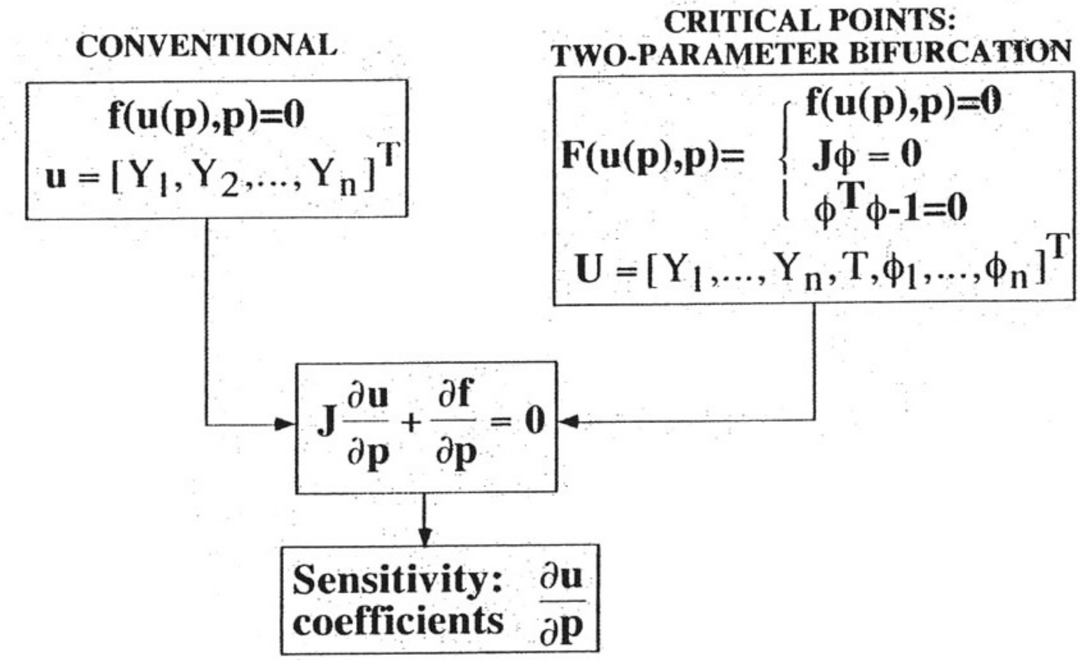
Period doubling route to chaos at 4.8 atm



Effect of Pressure on Oscillatory Instabilities



SENSITIVITY ANALYSIS



CONVENTIONAL

$$f(u(p),p)=0$$

$$u=[Y_1, Y_2, \ldots, Y_n]^T$$

CRITICAL POINTS: TWO-PARAMETER BIFURCATION

$$F(u(p),p)=\begin{cases} f(u(p),p)=0 \\ J\phi=0 \\ \phi^T\phi-1=0 \end{cases}$$

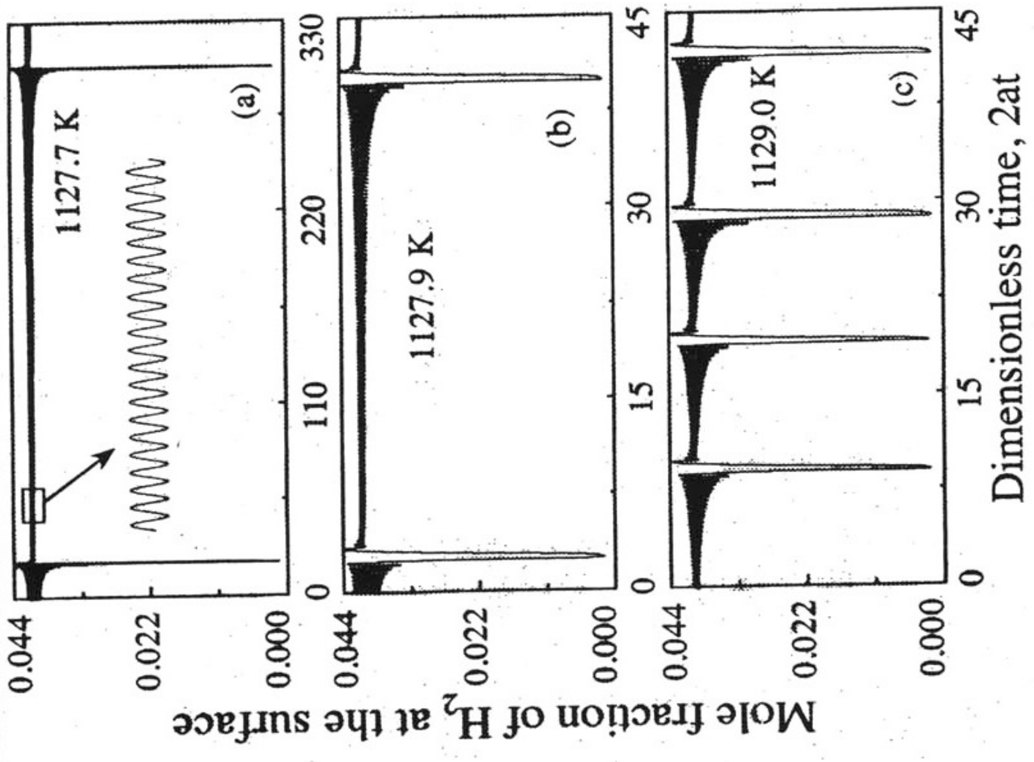
$$U=[Y_1, \ldots, Y_n, T, \phi_1, \ldots, \phi_n]^T$$

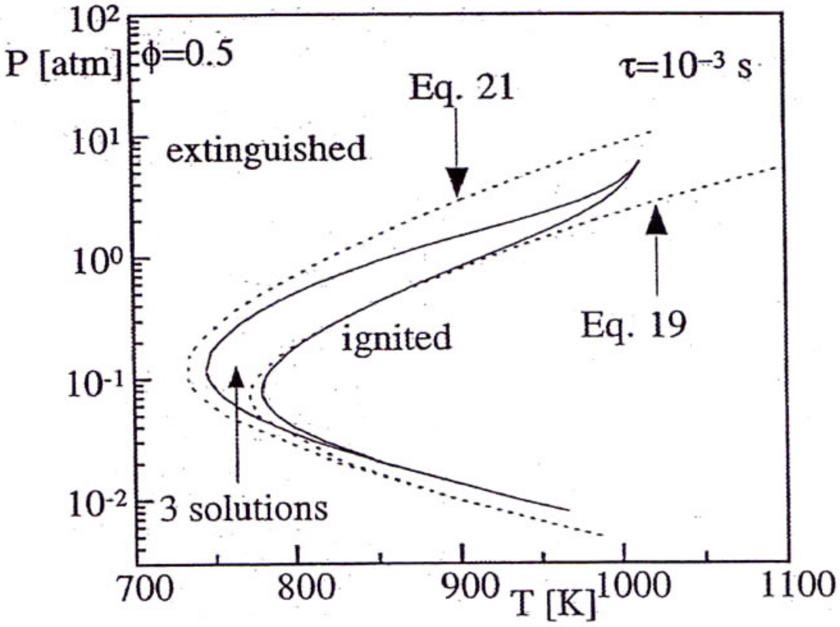
$$J\frac{\partial u}{\partial p}+\frac{\partial f}{\partial p}=0$$

Sensitivity: coefficients $\frac{\partial u}{\partial p}$

* * *

Intermittency route to chaos at 4.8 atm

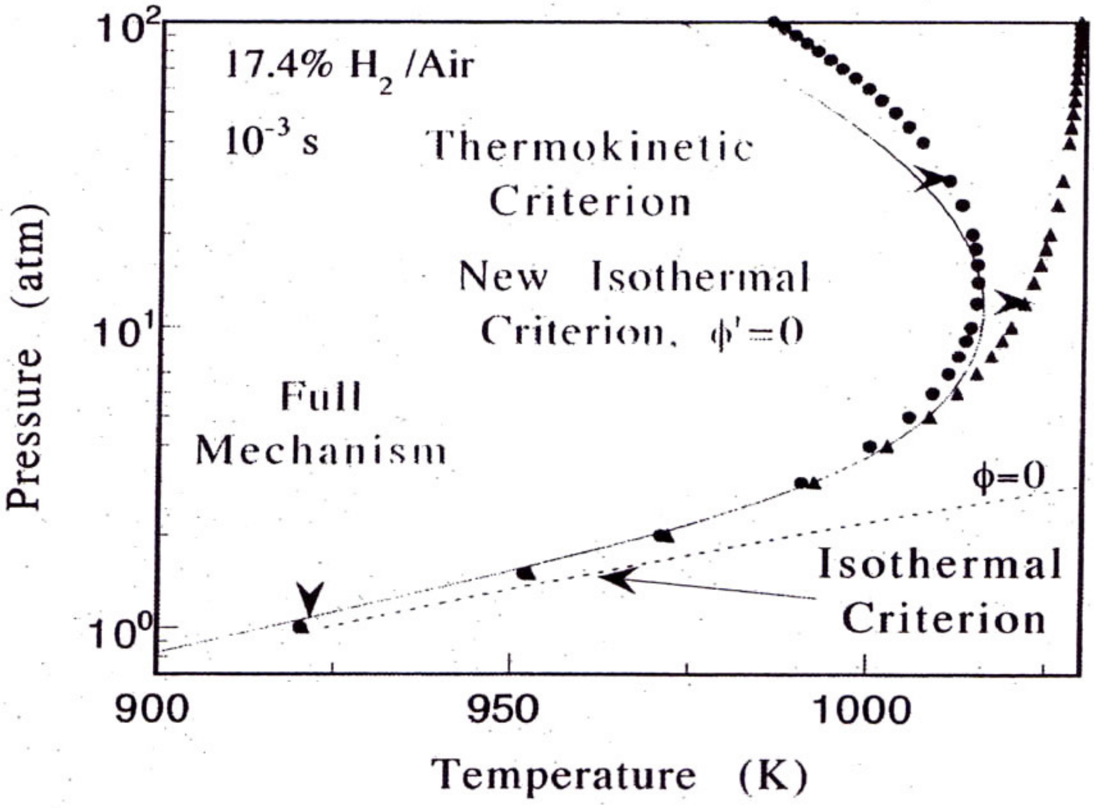


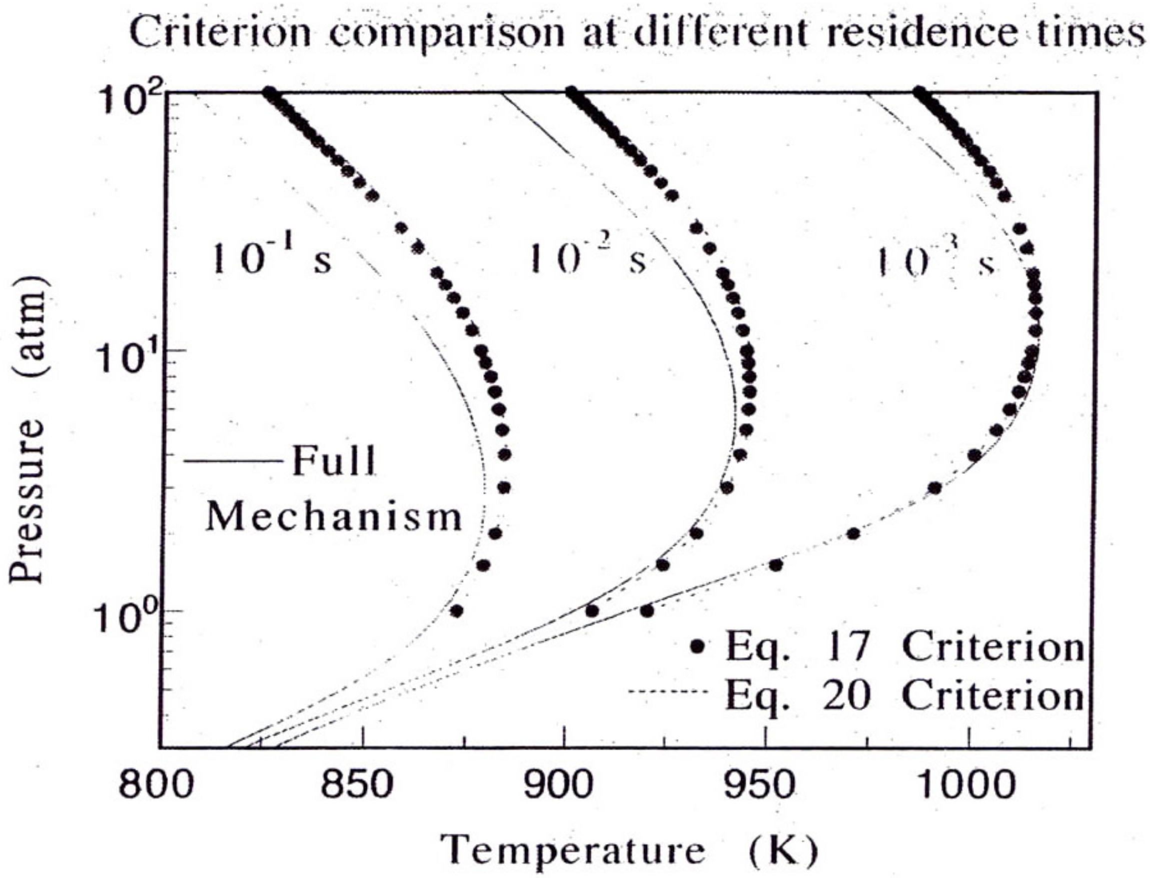


Ign. $2k_3 - k_5[M] - a_H(RT/PY_{O_2}) = 0$

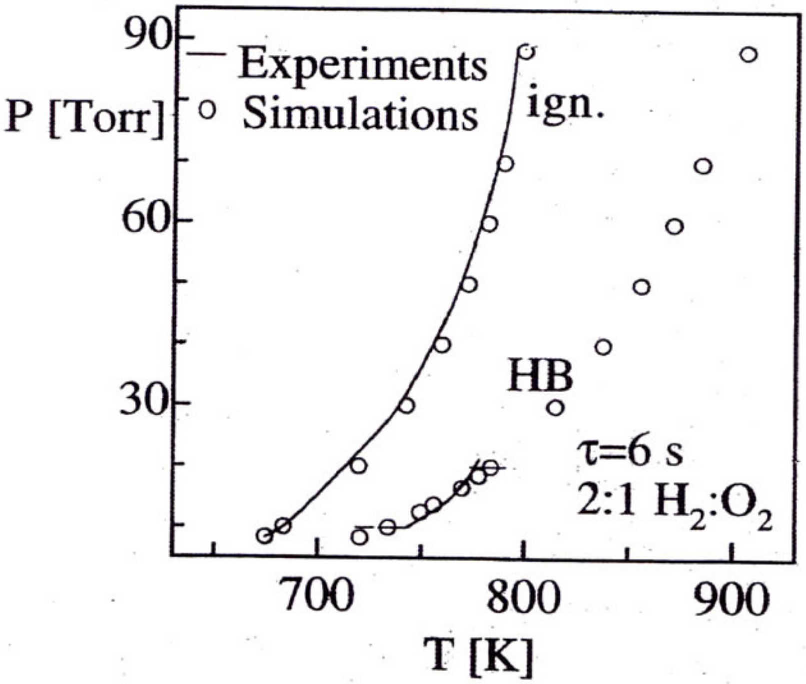
Ext. $2k_3 - 2k_5k_{16}[M]/(k_7 + k_{16}) - a_H(RT/PY_{O_2}) = 0$

Performance of different ignition criteria



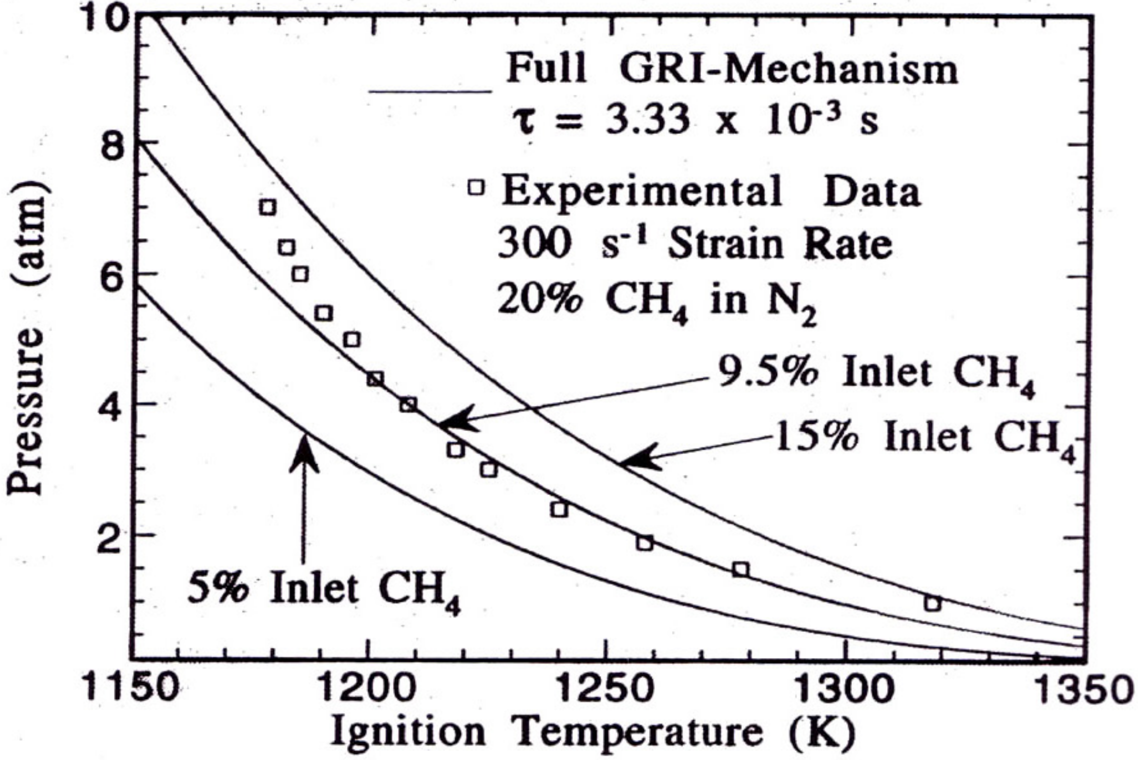


Criterion comparison at different residence times



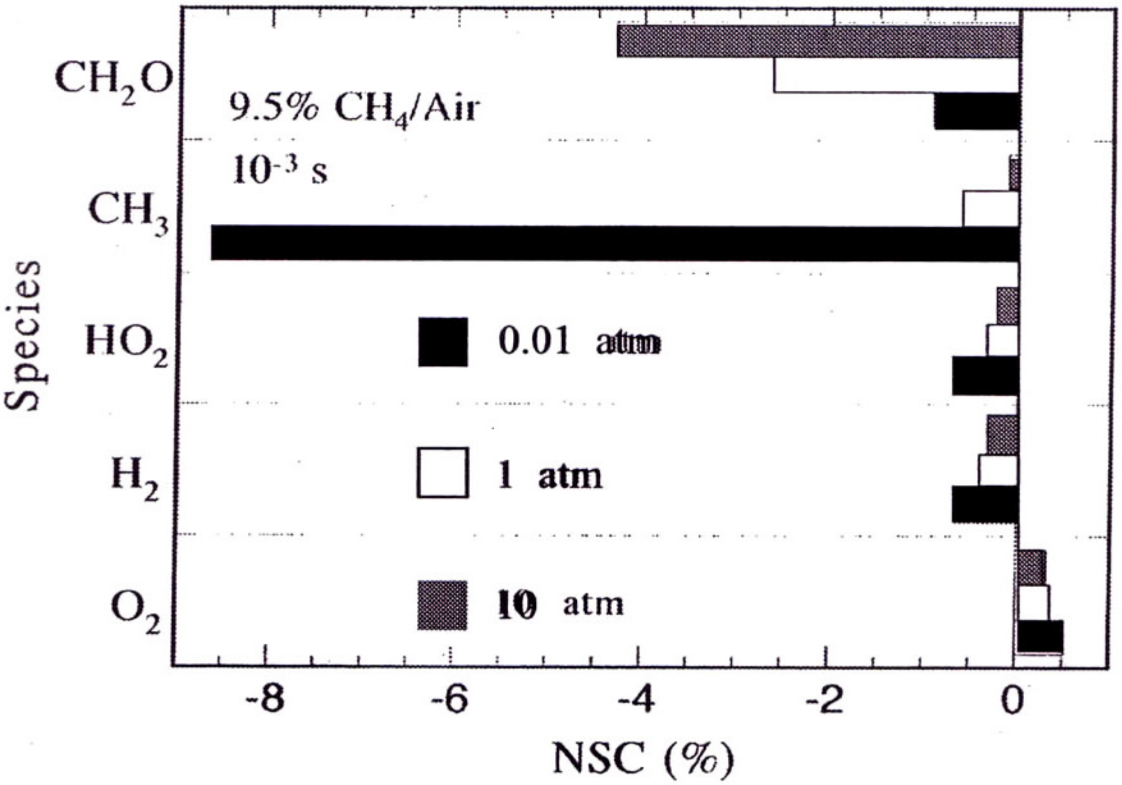
Experiments by D. L. Baulch et al.,
Combustion Flame 73, 163 (1988).

Comparison of CSTR Model Predictions to Diffusion Flame Experimental Data



Fotache, Kreutz, and Law, Combustion and Flame, 1997

Transport sensitivity analysis of non isothermal ignition



SUMMARY

- **Bifurcation tools can now be employed to study ignition, extinction, oscillations, and chaos of lumped and distributed reacting flows with detailed chemistry and transport**
- **Such simulations are much more efficient than time dependent simulations and can distinguish actual from false extinction**
- **Reduction tools can be extended for bifurcations to provide**
  - Insight into flame instabilities
  - Simplified models and criteria for instabilities
  - Chemistry validation from bifurcation experiments
- **While efficient algorithms are already in place, new algorithms must be implemented for larger problems**

Thermodynamic Database for Combustion Calculations

Alexander Burcat

Faculty of Aerospace Engineering
Technion – Israel Institute of Technology
Haifa 32000, Israel

A free thermodynamic database consisting of more than 800 stable chemical species and radicals, will be presented and discussed. All the species are used for combustion calculations or combustion related topics such as air pollution, detonations, fire suppression, etc. including among others use as a CHEMKIN database.

The different thermodynamic and thermochemical properties included in the database will be presented.

The policy of choosing the species, the different ways to calculate the thermodynamic properties, the ways to define their accuracy and uncertainties, the updating policy, as well as the implications of the above on their use, all will be exposed and discussed.

Thermodynamic Database for Combustion Calculations.

Alexander Burcat
Faculty of Aerospace Engineering, Technion - Israel Institute of Technology,
Haifa 32000, Israel

Abstract

A thermodynamic database is described, which is free of the main flaws of CHEMKIN's own database, and can be easily adapted for use with the program.

The main task of CHEMKIN, was to serve as a program that would provide kinetic modeling for gas phase reactions and other functions such as chemical equilibrium. For this purpose the user has to provide a series of elementary or pseudo-elementary reactions with their rate constants. In addition, the program needs the thermodynamic data of all the species in the model.

The use of the thermodynamic data has a few purposes. First it calculates the energy involved in each elementary step by calculating the enthalpy of reaction at the appropriate temperature, $\Delta_r H = \sum \Delta_f H(T)_{\text{products}} - \sum \Delta_f H(T)_{\text{reactants}}$ and then the entire energetic condition of the process. The second task is to calculate the back reaction rate of each elementary step, by using the equilibrium constant K_c of each reaction: $k_r = k_f/K$. K the equilibrium constant of the reaction, is calculated from the species coefficients of the thermodynamic polynomials through:

$$K_c = (R'T)^{-\Delta\nu} \left(\Delta a_1 (\ln T - 1) + \frac{\Delta a_2}{2} T + \frac{\Delta a_3}{6} T^2 + \frac{\Delta a_4}{12} T^3 + \frac{\Delta a_5}{20} T^4 + \frac{\Delta a_6}{T} + \Delta a_7 \right)$$

Where the mole number changes are $\Delta n = \sum n_j$ and the coefficient changes are $\Delta a_i = \sum n_j a_{ij}$. The summations are over all reactants and product species j with the mole numbers ν_j, positive for products and negative for reactants. R' is the gas constant given as 83.1451 when pressures are in bars and concentrations in mol/cm^3. Thus if the thermodynamic values of a species are substituted with other values, it will influence not only the energetic balance of the process, but also the kinetics itself through the calculation of the back reaction rate.

CHEMKIN is provided to users with a database of thermodynamic polynomials for a very large amount of species. However this database includes a large number of problems that the user has to deal with.

Since every species used has to include a thermodynamic polynomial in the database, the user has to search the provided database and find if the polynomial for his specific species is included and how is the polynomial assigned (for example CHO and HCO refer to the same species). But since the database is arranged in no order, and the species are not well identified, the user has to spend hours if not days trying to find the species and identify them. This could easily be avoided if the species were provided in an alphabetical or JANAF order, and some identification be supplied somewhere.

Databases are usually built according to two different philosophies. One approach is to build a database that is constantly or periodically corrected and/or revised and also expanded. The second approach, which was adopted by the CHEMKIN group since the beginning, (and blamed on budget shortage), was to abstain from any correction or revision of the species already included, and only add new species. This means that many problematic species have not been corrected during the last 20 years.

As an example of the first approach, another thermodynamic database[1] consisting of more than 800 stable chemical species and radicals, is presented. All the species are used for combustion calculations or combustion related topics such as air pollution, detonations, fire suppression, etc. including among others, serving as a CHEMKIN database.

This database is organized according to the JANAF alphabetical order. A header is included for each species to describe exactly what the species is, how it was calculated, where the data for the calculation were taken from, when was the calculation performed, and by whom.

There is no policy for choosing the species for this database. The species are chosen according to needs of specific projects either by the author or by requests, and also as their parameters become available in the literature. Because of that, the species are not all of the same quality. Some are very accurate and others are very approximate, including in between stages. As a result, each polynomial in the database is characterized by a letter A to F, stating the calculation accuracy of the polynomial. B is the standard quality of calculation of polyatomic species thermodynamics, defined as "rigid rotor harmonic oscillator" (RRHO) method. F is defined as very approximate estimations. All polyatomic species are calculated by the RRHO method if possible. If the data for that is unavailable, then polynomials are fitted to and extrapolated from limited experimental measurements of C_p, or Benson like group additivity method estimates, or others.

```
C2F6O2  CF3-OO-CF3 SIGMA=18 Calculated Using THERM (97) Extrapolated 1000-5000K
Using Wilhoit's Polynomials  HF298=360.2+/-3. kcal REF=Levy & Kennedy JACS 94
(1972) 3302  Max Lst Sq Error Cp @ 1000K 0.30%
CF3-O-O-CF3         T10/97C   2F   6O   2    0G   298.150  5000.000  F 170.01122 1
 1.87994539D+01 8.78358323D-03-3.68712829D-06 6.99609239D-10-4.92829440D-14    2
-1.88252514D+05-5.97973365D+01 9.11006951D+00 2.71182010D-02-1.23579087D-06    3
-2.30183402D-08 1.25085439D-11-1.85129629D+05-7.65920017D+00-1.81258643E+05    4

C2H ETHYNYL RADICAL SIGMA=1  STATWT=2   B0=1.457 NU=3328,372(2),1841  T0=4000
STATWT=4  B0=1.457 NU=3460,560(2),1850  REF=Kiefer, Sidhu, Kern, Xie, Chen,
Harding Comb Sci Technol 82,(1992),101  HF298=135.88 Kcal REF= NIST Webbook 1999.
MAX LST SQ ERROR CP @ 400 K 0.34 % .
C2H ETHYNYL RAD    T07/00C  2.H  1.   0.    0.G   200.000   6000.000  B  25.02994 1
 3.66459586E+00 3.82189487E-03-1.36509398E-06 2.13253692E-10-1.23098939E-14    2
 6.72238503E+04 3.91355399E+00 2.90180321E+00 1.32859725E-02-2.80508233E-05    3
 2.89300812E-08-1.07446930E-11 6.71171170E+04 6.17234595E+00 6.83770805E+04    4
```

Figure 1. Sample of species from the author's database. Pay attention to the header which states which species it is , how it was calculated and references for the data. The first row of the polynomial contains the location and date of the calculation (T stands for Technion), the atomic formula, G stands for a gas phase specie, the temperature range of the polynomial, the accuracy mark and the molecular weight. The following three rows of coefficients are the same as in CHEMKIN. The last coefficient, not read by CHEMKIN represents $\Delta_f H_{298}/R$. This format can be easily transformed to the CHEMKIN database format.

It is generally stated that the knowledge of the thermodynamics of a species is by far more accurate than our knowledge of the rest of the species properties such as the chemical kinetic rate. Nevertheless, since many of the species thermodynamics is available with a high degree of error, changing the thermodynamic values of some key species will effect drastically the entire model. Therefore one of the future tasks of the CHEMKIN developers should be to devise ways to test the kinetic results in view of the thermodynamics uncertainty limits.

Table 1. Enthalpies of formation of the C_5H_5 radical.

	ΔH_{298}	C_p	S_{298}
McMillen & Golden 1982	57.9		
Karni, Oref & Burcat 1991	63.6	18.3	66.8
Melius 1993	64.57		
Wang & Brezinski 1999	62.0		
Frank 1999	57.9		62.9
Zhong & Bozzelli 1999	57.17	17.86	63.58
Kern & Kiefer 1999	65.3		67

There are no known ways to establish if a thermodynamic evaluation is good or bad except by comparing it to experimental values. The main problem is that in most cases, the experimental value is not known or even impossible to measure directly. An example of this kind is given below for the cyclopentadienyl radical. There are debates among the researchers, regarding the proper way to configure this radical, and therefore its estimated values. Data from different authors are given in Table 1. As shown, the values differ from each other. Usually it is assumed that new data are better than old ones. But in this case four very recent values do not agree. Therefore the simplest way known to the author, to decide among the different values, is to see which of the data fits the experimental kinetics better, and in this case, the author decided according to what fits better his own data.

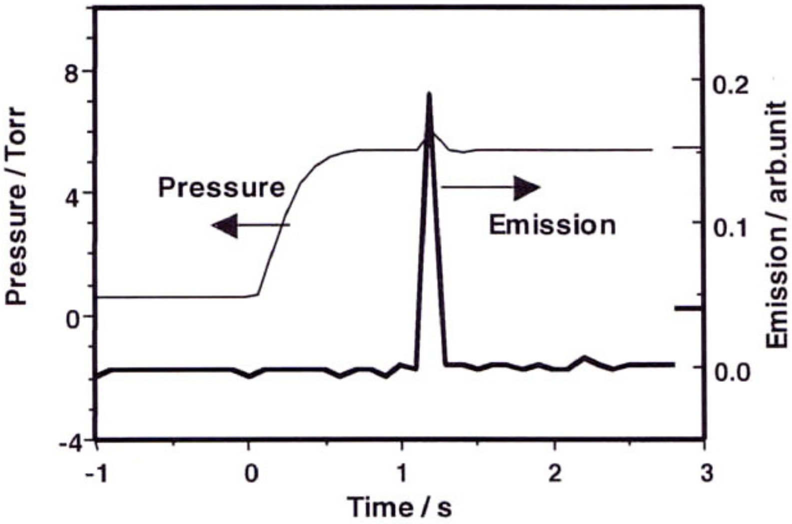
References

1. A. Burcat. Third Millennium Thermodynamic Database for Combustion Related Use. ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics.

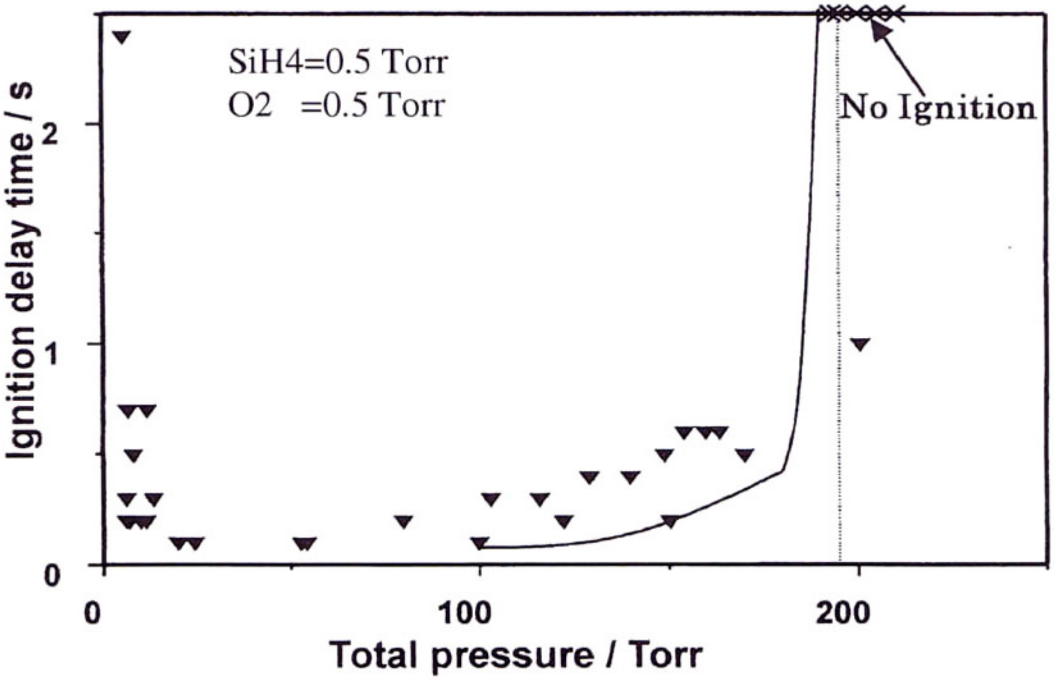
Experimental study- Ignition delay

Simple experiments

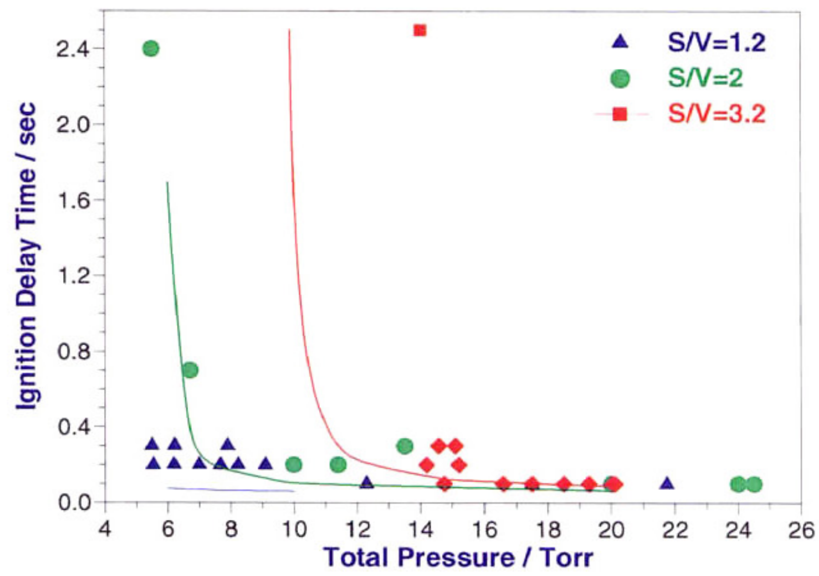
- measurement of ignition delay by monitoring emission.



Comparison with experimental results



Lower limiting pressures
- Effect of Surface Reactions



H-atom trap on

solid surfaces

H+_=><u>H</u>

Diffusion control

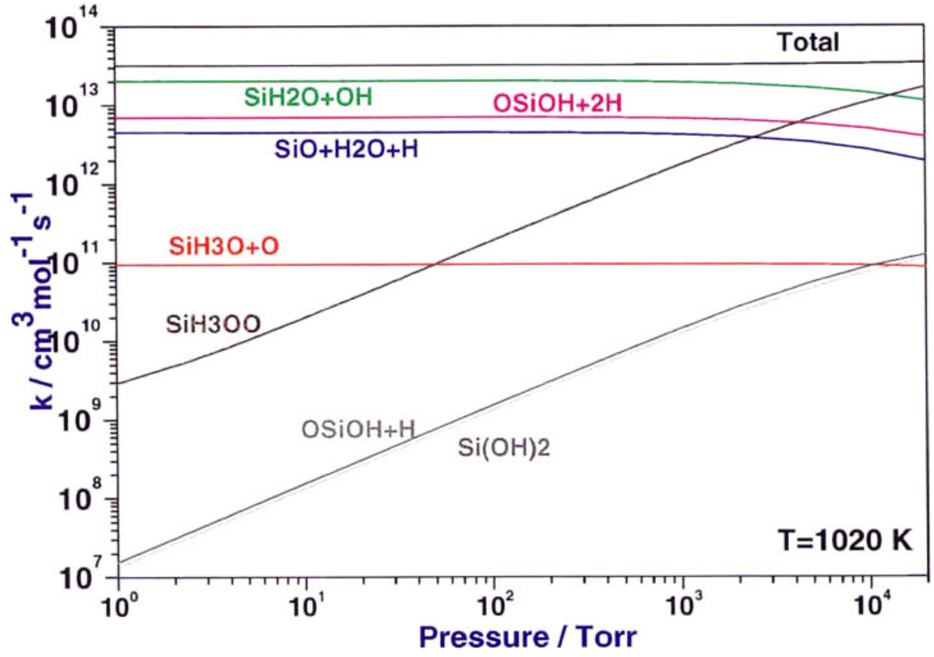
* * *

Summary

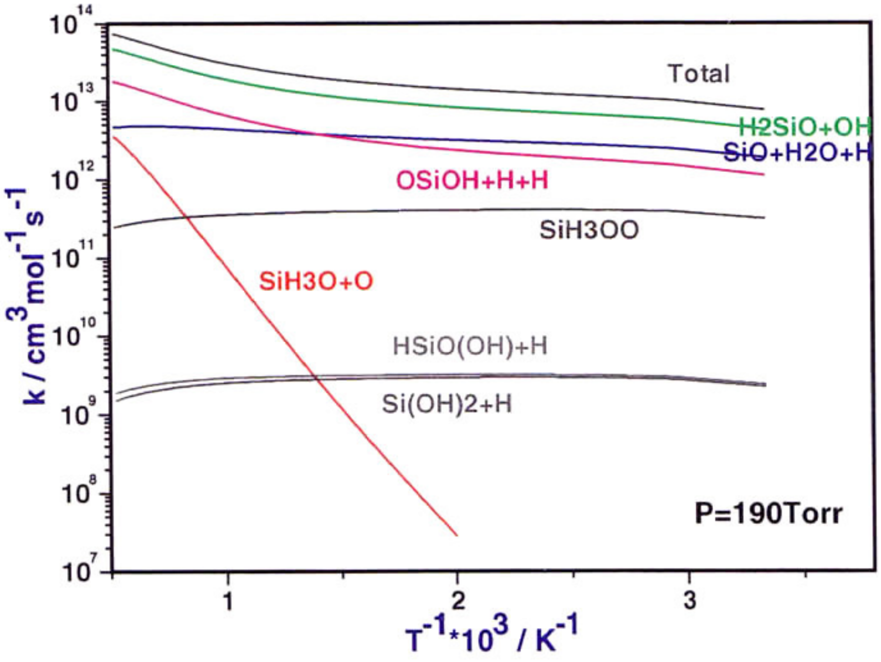
- Evaluation of the channel specific rate constants of chemical activation reaction can be very important in combustion.
  =>An example: SiH_4 combustion
- Temperature and pressure dependence of the rate constants can be very complex.
  =>Flexibility of input format for rate constants may be needed.

Pressure dependence

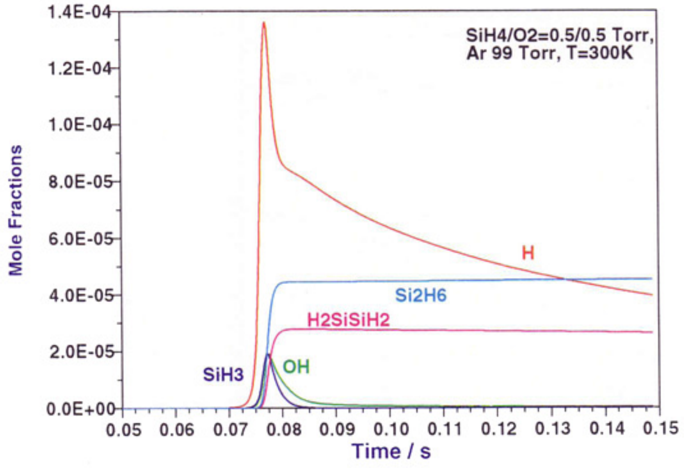
SiH_3+O_2=>Products

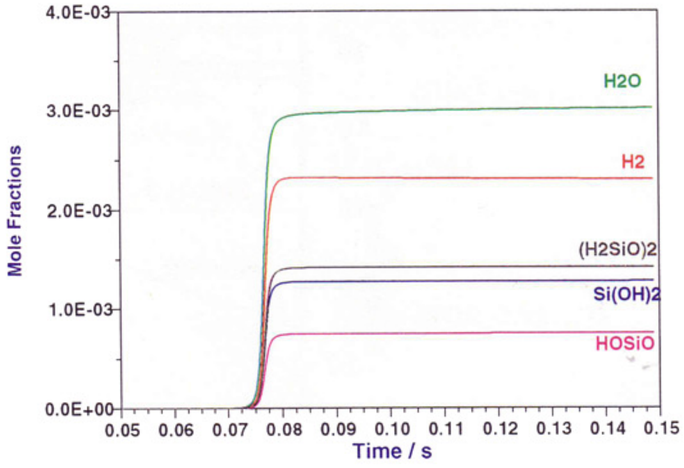


Temperature dependence

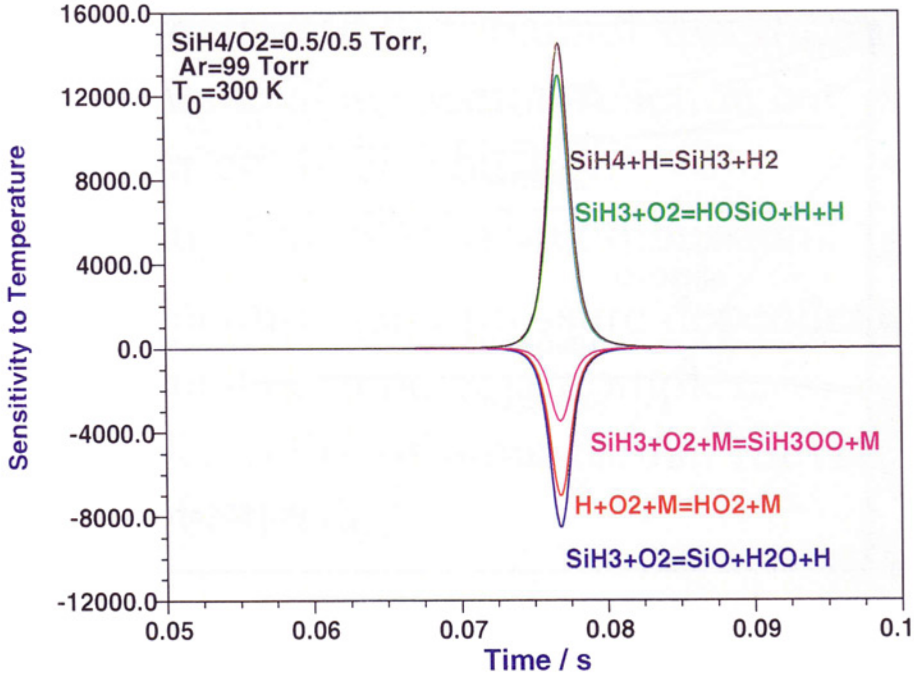


Kinetic Simulation

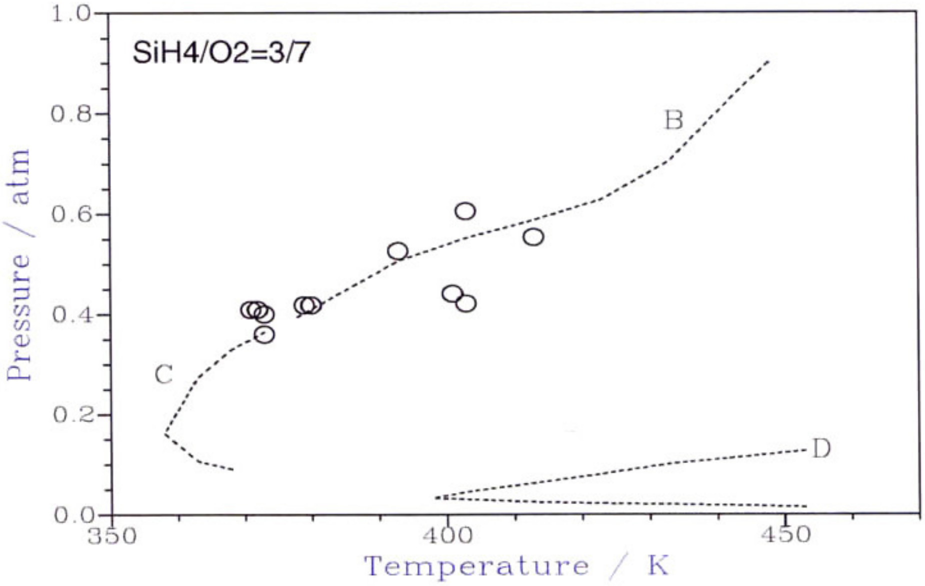




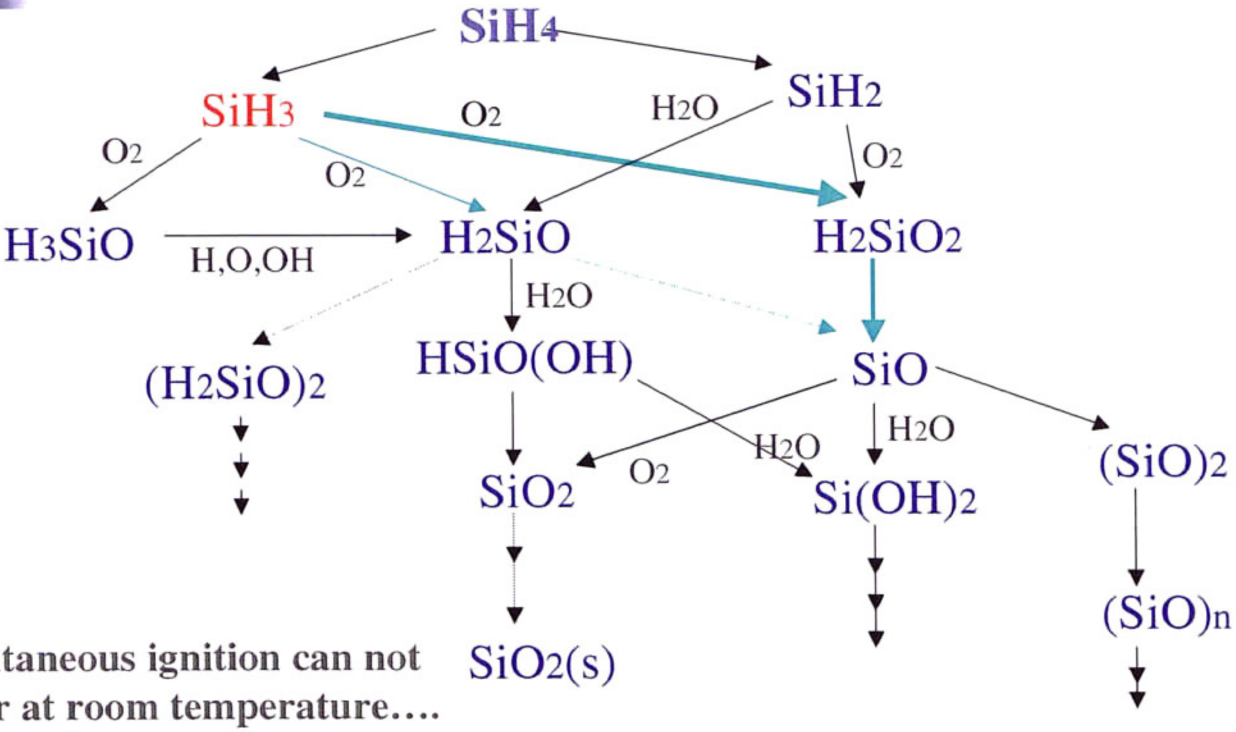
Sensitivity Analysis



Explosion Limit of SiH_4 Combustion

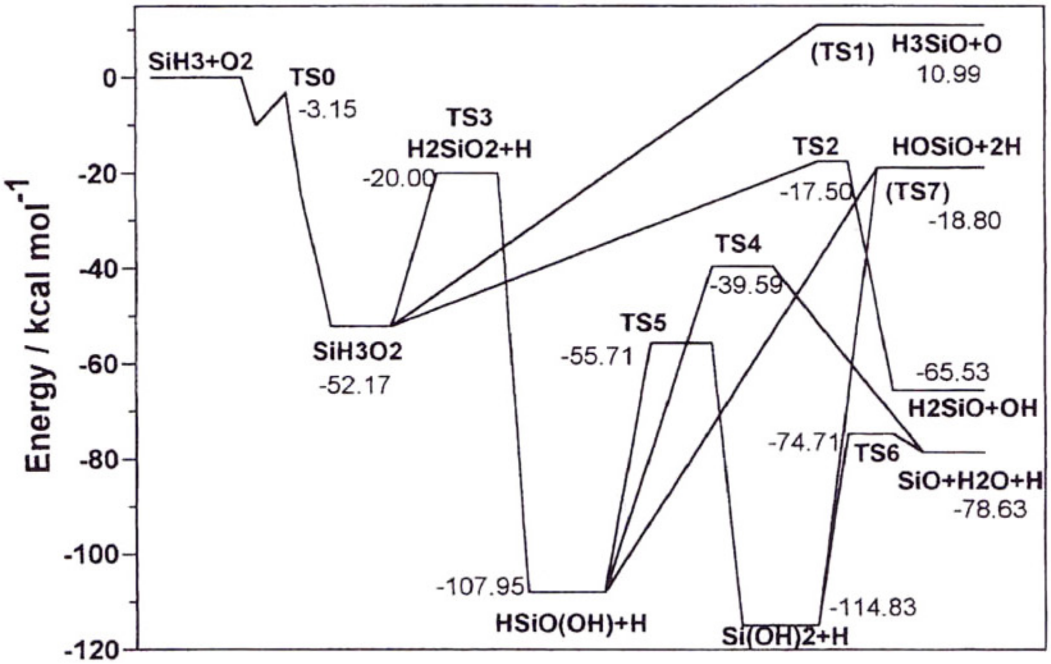


Proposed Mechanism for SiH_4 Combustion



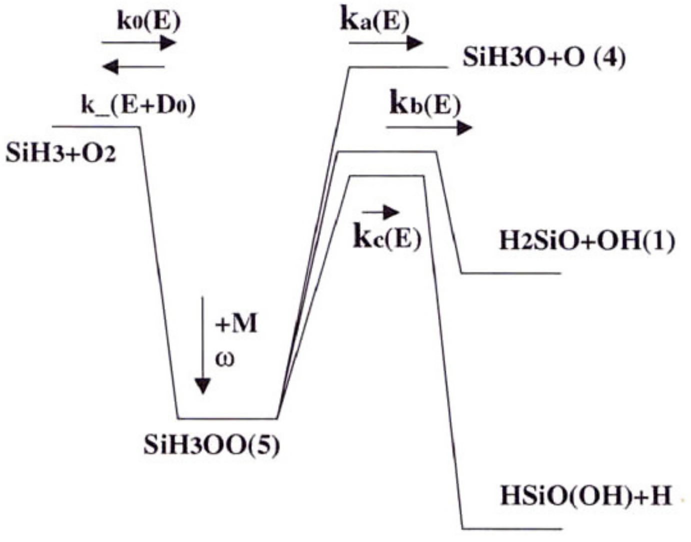
Spontaneous ignition can not occur at room temperature….

Potential Surfaces for SiH_3+O_2



Overall Reactions

Ex. SiH_3+O_2=>$H_2SiO+OH$ (1)



Conventional Treatment

$$k_A(E) = \omega + k_a(E) + k_b(E) + k_c(E)$$

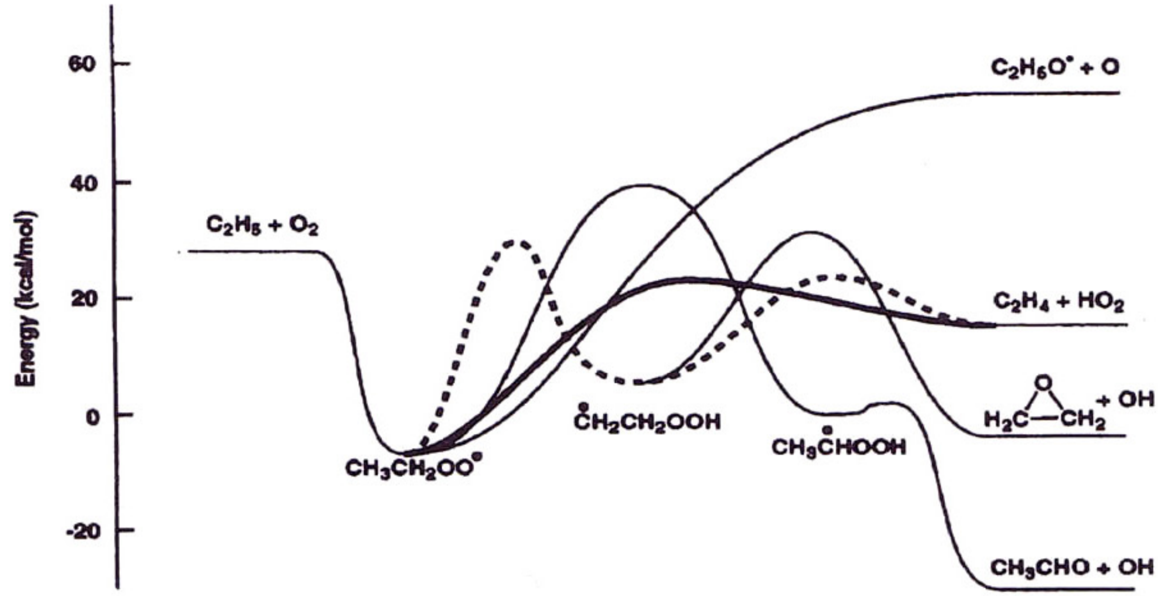
$$k_1(E) = \frac{1}{Q_{SiH3}Q_{O2}} \frac{k_b(E)}{k_A(E)} k_{=}(E+D_0)$$

$$\rho_{SiH3O2}(E+D_0)\exp(-\frac{E}{kT}$$

$$k_1(T) = \int_0^\infty k_1(E)dE$$

Exact treatment requires solution of Master equations.

Chemical Activation Reactions
Multi-well, multi-channel Reaction



P.K.Venkatesh et al. J.Chem.Phys., 111 (1999)

More Flexible Form of k(T,P)

An Example:

$$k(T) = (a_0 + a_1 T^{-1/2} + a_2 T^{-1} + a_3 T^{-3/2} + a_4 T^{-2}) \exp(-E_a / RT)$$

Multi-well, multi-channel reactions:

Modified Troe's formula (Gilbert et al. (1983))

$$F(T,P) = \exp(-L(T,P) F_{cent}(T))$$

Generalized-mean-of-limits (GML) formula (Kazakov et al.,(1994)

$$k(T,P) = [(k_0(T))^a + (k_\infty(T))^a]^{1/a}$$

$$a = h \exp\{-(\log p_r - \alpha)^2 / \sigma^2\} - 1$$

Chebyshev expansion of k(T,P) (Venkatesh et al., (1997)

Chemical Activation Reactions in Combustion

H_2 combustion as an example:

$H+O_2=OH+O$ $H+O_2+M=HO_2+M$

$O+H_2=OH+H$

$OH+H_2=H_2O+H$

$OH+OH=H_2O+O$ $OH+OH+M=H_2O_2+M$

$H+HO_2=H_2+O_2$ or $OH+OH$

$O+HO_2=OH+O_2$

$HO_2+HO_2=H_2O_2+O_2$

Role of Chemical Activation Reactions in Combustion

-An Example- SiH_4 Combustion

- Key Reaction : $SiH_3+O_2 \Rightarrow$ Many Products
  Complex chemical activation reaction
  Prediction of k(T,P) for each channel?
- Mechanism of self-ignition at room temp.?

- Effect of Surface Reactions to Explosion Limit

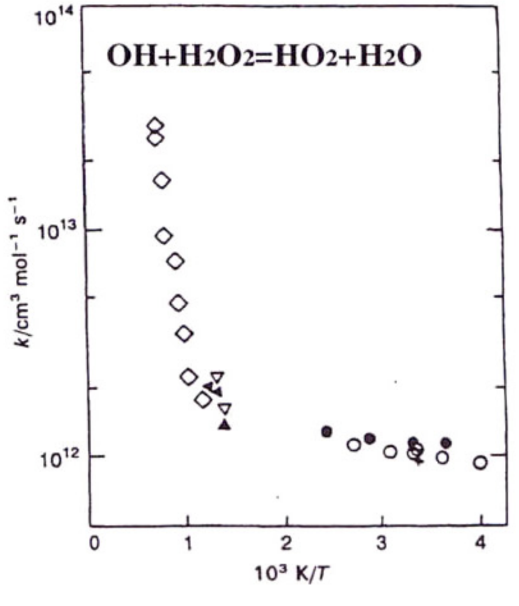
Pressure and Temperature Dependence of Rate Constants for Multi-Well, Multi-Channel Reactions

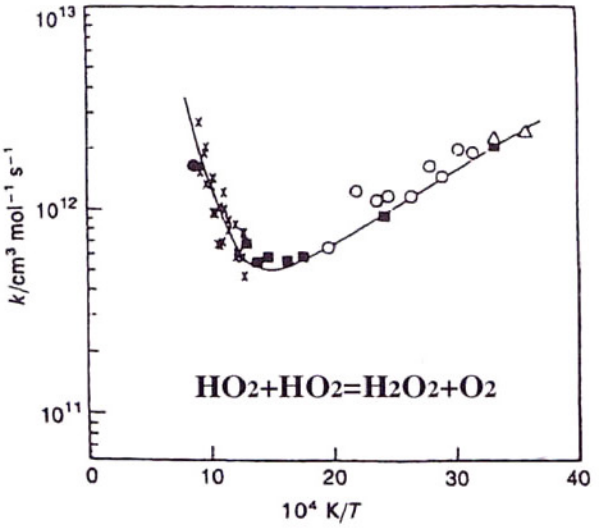
-Kinetics of SiH4 Combustion as an Example-

Mitsuo Koshi
University of Tokyo, Japan

Introduction:

Temperature dependence

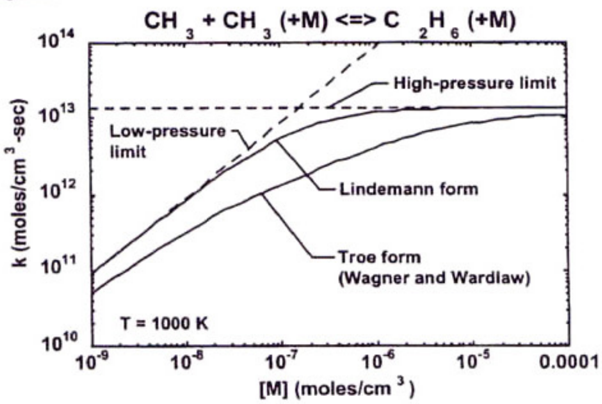


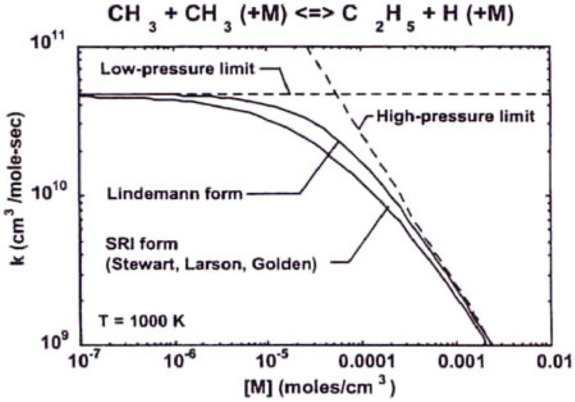


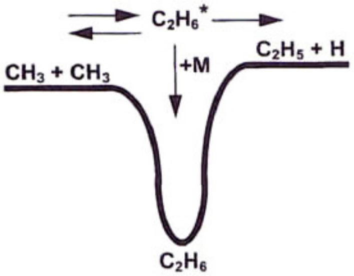
J.Troe, J.Chem.Soc.Fard.Trans.,90 (1994)

Sum of two channels: $k=k_1+k_2$

Introduction: Pressure dependence - Chemical activation reaction







From Chemkin III manual

---

k(T,P) in CHEMKIN

Bimolecular Reactions – Modified Arrehnius form

$$k = AT^b \exp(-E_a / RT)$$

Unimolecular Reactions– Modified Lindeman form

$$k(T,P) = k_\infty \left(\frac{p_r}{p_r + 1} \right) F(T,P) \quad p_r = \frac{k_0}{k_\infty}(M)$$

Chemical Activation Reactions (Single well/channel)

$$k(T,P) = k_\infty \left(\frac{1}{p_r + 1} \right) F(T,P) \quad p_r = \frac{k_0}{k_\infty}(M)$$

F(T,P) <= Troe formula or SRI form

Pressure and Temperature Dependence of Multi-well, Multi-product Reactions and Its Significance in Silane Combustion

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Recently, the importance of properly treating the pressure and temperature dependence of bimolecular chemically activated reactions and termolecular recombination reactions has been widely recognized [1]. Pressure dependence of bimolecular reactions proceeding via multiple long-lived intermediates can be very complex. Once formed, there are several possible fates for such an intermediate. It may be stabilized by collisional deactivation to produce a stable association product. It may also undergo to another reaction intermediates (i.e., isomerization), or it may dissociate to some products if the energy barrier for the reaction is sufficiently low. Reverse dissociation back to reactants may also be possible. Evaluation of the rate constants for each reaction channel requires the knowledge of potential energy surfaces for all possible channels and the structures of all intermediates and activated complexes. With such information, channel specific rate constants can be calculated on the basis of multi-channel RRKM theory or master equation analysis [2].

If one of the product channels produces a chain-carrier radical, the channel specific rate constant can be very sensitive to the overall characteristics. A good example is the SiH3+O2 reaction in complex silane combustion mechanisms. This reaction proceeds via several reaction intermediates and has many product channels, as shown below [3,4];

(a) SiH3+O2 ⇒ SiH3O + O
(b) SiH3+O2 ⇒ SiH3O2* ⇒ SiH2O+OH
(c) SiH3+O2 ⇒ SiH3O2* ⇒ HSiO(OH)*+H ⇒ HOSiO+2H
(c') SiH3+O2 ⇒ SiH3O2* ⇒ HSiO(OH)*+H ⇒ Si(OH)2+H ⇒ HOSiO+2H
(d) SiH3+O2 ⇒ SiH3O2* ⇒ HSiO(OH)*+H ⇒ SiO+H2O+H
(d') SiH3+O2 ⇒ SiH3O2* ⇒ HSiO(OH)*+H ⇒ Si(OH)2+H ⇒ SiO+H2O+H
(e) SiH3+O2+M ⇒ SiH3O2+M
(f) SiH3+O2+M ⇒ HSiO(OH)+M
(g) SiH3+O2+M ⇒ Si(OH)2+M

Reaction (a) is endothermic and all other steps are exothermic. Rate constants for these products channels are calculated as functions of pressure and temperature. It is shown that the pressure dependence of reactions (c) and (c') is extremely sensitive to the ignition delay times of Silane/O2 mixtures at low temperatures. Competition between reactions (c)+(c') and H+O2+M=>HO2+M determines the second explosion limit of silane combustion. A detailed reaction mechanism including the above reactions has been constructed and simulations for silane combustion have been tried. However, since the present version of the CHEMKIN interpreter does not accept rate constants that are complex function of pressure, only constant pressure calculations are possible. Calculated ignition delay times are compared with experimental data, and the significance of the pressure dependence of these reactions is discussed.

References

[1] P. K. Venkatesh, A. Y. Chang, A. M. Dean, M. H. Cohen, R. W. Carr, AIChE J. 43, 1331 (1997).
[2] T. J. Frankcombe, S. C. Smith, K. E. Gate, S. H. Robertson, Phys. Chem. Chem. Phys., 2, 793 (2000).
[3] M. Koshi, N. Nishida, Y. Murakami, H. Matsui, J. Phys. Chem., 97, 4473 (1993).
[4] S. Kondo, S. Tokuhashi, H. Nagai, A. Takahasi, M. Aoyagi, et al., J. Phys. Chem. A101, 6015 (1997).

Mechanism Development

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In many technologically important situations, e.g. rich combustion, a very large number of chemical species are reacting simultaneously. Computer methods for constructing large chemical kinetic mechanisms, and estimating the many required rate parameters, will be outlined. Ultimately these complex chemistry models will need to be coupled with transport, leading to even more complex models. It is quite difficult for humans to work with, understand, and assess the large models created by these model-construction programs, even with tools like CHEMKIN which improve the human/computer interface. For very large models, it is necessary to move up one level of abstraction from the individual-reaction, individual-species focus of CHEMKIN. Some of the unresolved problems, and progress towards their solution, will be briefly described.

Recent success in accurately calculating reaction rates a priori suggest that reasonably reliable large kinetic models, even including coupling with transport in reacting flow simulations, could be rapidly constructed and solved completely a priori by computer with minimal human input. The progress we have made towards this goal is summarized, highlighting:

1. How molecules are represented and handled by the computer;
2. Selection of the chemical species to be used in the kinetic model;
3. "supergroup" methods for computing transition state free energies and rates via TST;
4. computerized falloff and chemical-activation analysis for large molecules; and
5. the "adaptive chemistry" method for reacting flow simulations.

It is anticipated that this approach will eventually allow users to ignore the details of the rate constants, species lists, and individual species concentration profiles, and instead focus on the higher-level inputs (group additivity parameters for thermo and physical properties, reaction rate estimation rules) and outputs (e.g. ignition delay, flame speed, total hydrocarbon emissions). This is in many ways analogous to the way in which CHEMKIN allowed the modelers to hide all the details about the differential equations and the numerical solvers in a reliable black box program.

The very large kinetic models which can be easily constructed using this new simulation technology pose many challenges for CHEMKIN. Tools are needed to:

1. identify the range of validity of a kinetic model;
2. specify the uncertainties in model predictions, including errors due to model incompleteness;
3. compare huge models with each other;
4. ease comparisons of model predictions with experimental data;
5. identify what features of a huge model are really important; and
6. develop reduced models that replicate the huge model in some range.

Development of these tools will require advances in numerical analysis, e.g. development of very rapid sensitivity analysis, model reduction, and range of validity tools, as well as some conceptual developments (what do we really want out of a huge model?).

Mechanism Development

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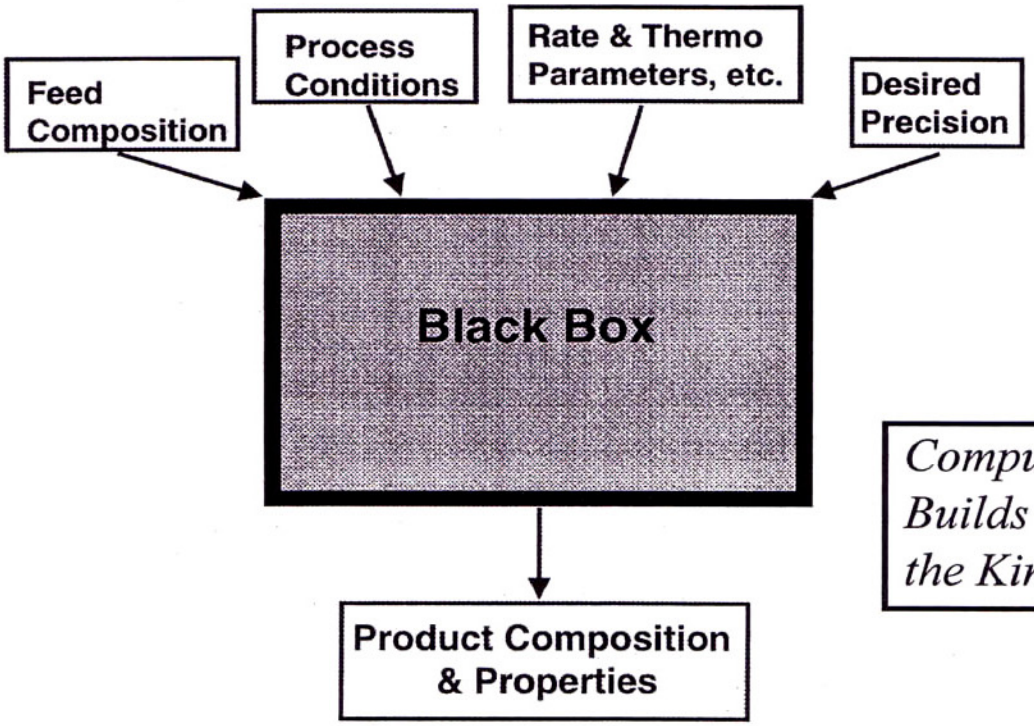
2nd International Workshop on CHEMKIN in Combustion
Edinburgh, Scotland
July 30, 2000

Huge Models Pose New Challenges

- **Now: Computer-made Kinetic Models**
- **Soon: Computer-made reactor simulations**
- **Obstacle: Reaction Rate Estimation**
- **Challenges:**
  - **When are Models Valid? How accurate?**
  - **Comparing Big Models**
  - **Comparing Model Predictions with Experiment**
  - **Identifying What is Important in a Big Model**
  - **Make the computer handle all the details!**

The Dream



Feed Composition

Process Conditions

Rate & Thermo Parameters, etc.

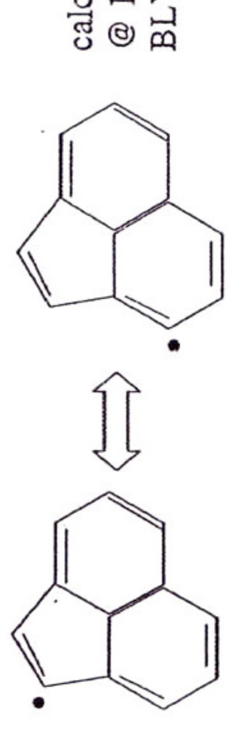
Desired Precision

Black Box

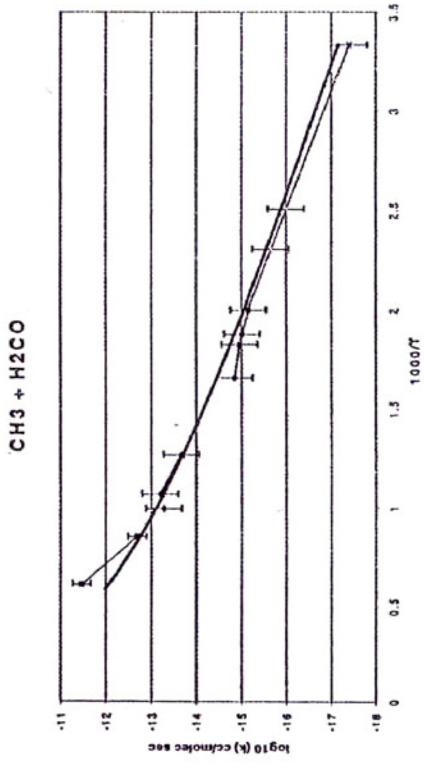
Product Composition & Properties

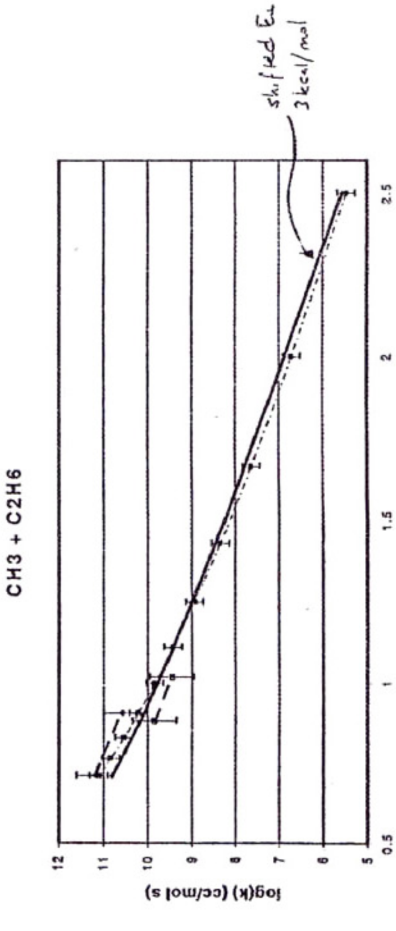
Computer Builds & Solves the Kinetic Model

Quantum Thermo & Rates



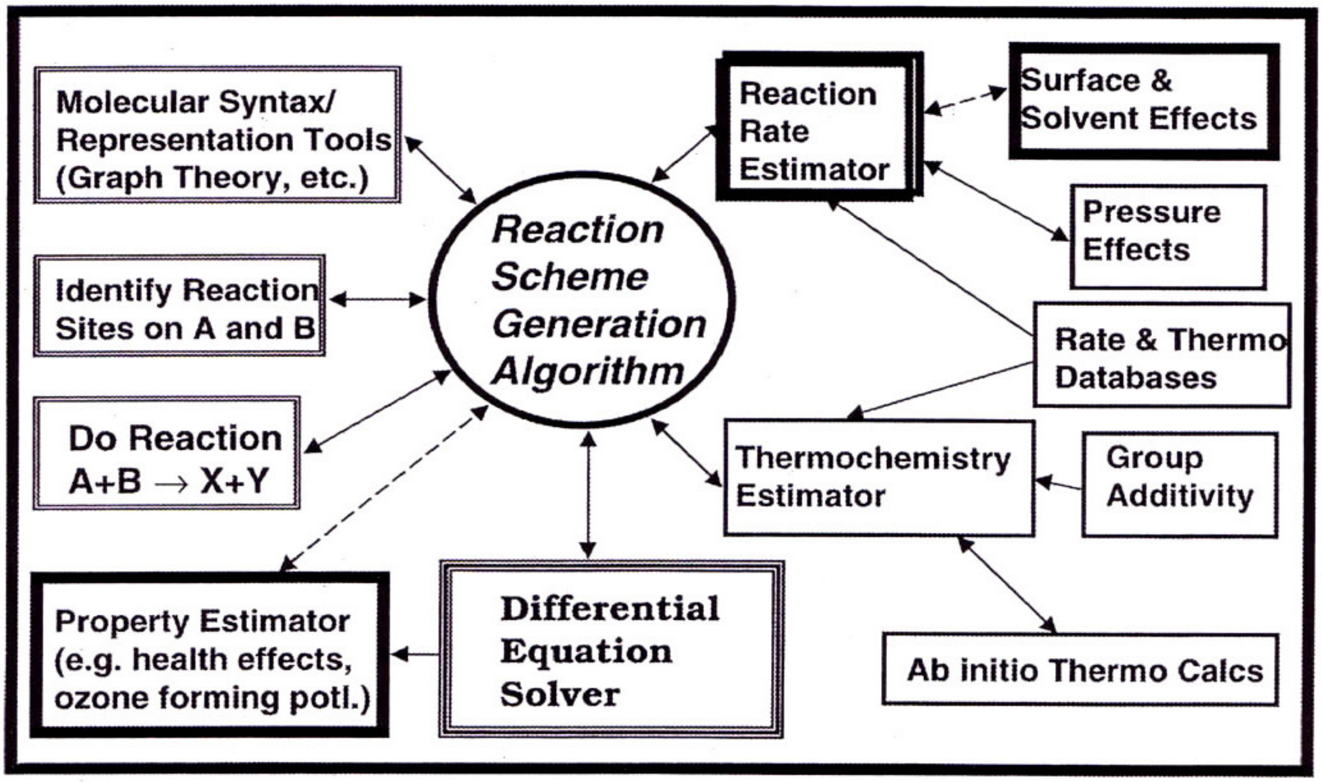
calc $K_{eq} = 0.46$
@ 1800 K
BLYP(DZVP)


CH3 + H2CO


CH3 + C2H6

shifted Ea
3 kcal/mol

Inside the Black Box



Teaching a Computer to Keep Track of Molecules

("NetGen": Broadbelt, Stark, & Klein 1994)

Ranzi
Come
Blurock
Warnatz
Ugi
Ayscough
Jorgensen
DiMaio
. . .

- \+ Matrix Representation of Bonding & Chemical Reactions
- \+ Uniqueness: Many Possible Representations of Same Molecule
- \+ Recognizing Reactive Sites Appropriate to Each Reaction Family

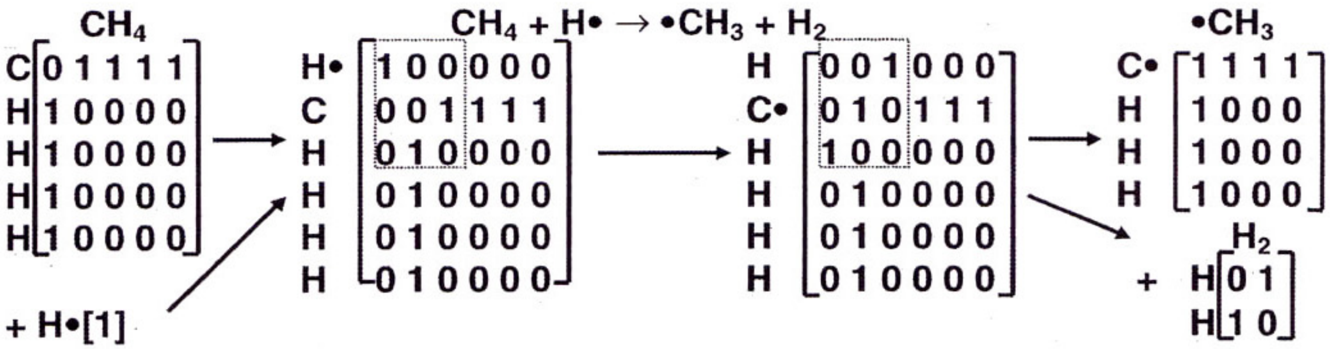
An Example: H-abstraction by H atoms H• + H-C

Reaction Operator: $\begin{array}{c} H\bullet \\ C \\ H \end{array}\begin{bmatrix} -1 & 0 & 1 \\ 0 & 1 & -1 \\ 1 & -1 & 0 \end{bmatrix}$

$k = A \exp(-E_a/RT)$

$A = 2\times10^{10}\ M^{-1}s^{-1}$

$E_a = 11.5\ \text{kcal/mol} + 0.5\ \Delta H_{rxn}$



CH_4 $\begin{array}{c} C \\ H \\ H \\ H \\ H \end{array}\begin{bmatrix} 0&1&1&1&1 \\ 1&0&0&0&0 \\ 1&0&0&0&0 \\ 1&0&0&0&0 \\ 1&0&0&0&0 \end{bmatrix}$ + H•[1]

$CH_4 + H\bullet \rightarrow \bullet CH_3 + H_2$

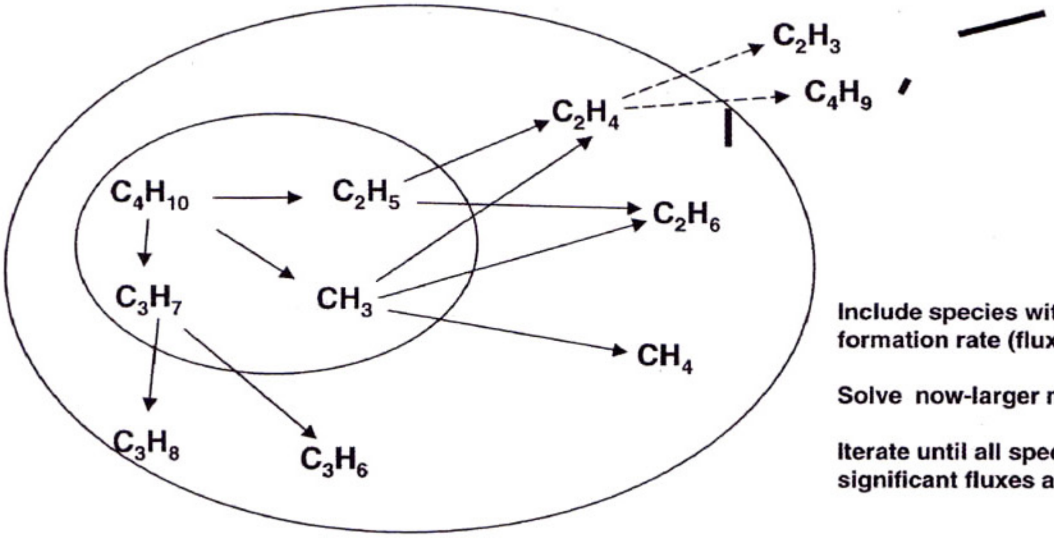
$\begin{array}{c} H\bullet \\ C \\ H \\ H \\ H \\ H \end{array}\begin{bmatrix} 1&0&0&0&0&0 \\ 0&0&1&1&1&1 \\ 0&1&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&1&0&0&0&0 \end{bmatrix} \longrightarrow \begin{array}{c} H \\ C\bullet \\ H \\ H \\ H \\ H \end{array}\begin{bmatrix} 0&0&1&0&0&0 \\ 0&1&0&1&1&1 \\ 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&1&0&0&0&0 \end{bmatrix}$

$\bullet CH_3$ $\begin{array}{c} C\bullet \\ H \\ H \\ H \end{array}\begin{bmatrix} 1&1&1&1 \\ 1&0&0&0 \\ 1&0&0&0 \\ 1&0&0&0 \end{bmatrix}$

$+\ H_2$ $\begin{array}{c} H \\ H \end{array}\begin{bmatrix} 0&1 \\ 1&0 \end{bmatrix}$

What Species Belong in the Model?

- Infinite number of possible intermediates and by-products
- Rate-Based Selection Algorithm [*J.Phys.Chem. A* 101, 3731 (1997)]
  - feasible for $O(10^{3)}$ species in model, considering $O(10^6)$ reactions
- Model Depends on Reaction Conditions
  - temperature, pressure, timescale, initial concentrations, precision



Include species with highest formation rate (flux).

Solve now-larger model.

Iterate until all species with significant fluxes are included.

Super-Group-Additivity for Transition States

'supergroup' : The Part of a Transition Structure with Partially Broken and Formed Bonds which are not Describable by the Existing Groups for Stable Species (including Radicals).

Example:

$\text{R-CH2-H} + CH_3 \rightarrow [\text{R-CH2--H--}CH_3]^{\#} \rightarrow \text{R-}CH_2 + CH_4$

$\Delta_f H$ (TS): {R} + {C/CH_2/-H/CH_3}

$\Delta_f H$ (Reactants): {R} + {C/C/H_3} + {C/H_3}

=> $\Delta H^{\#} = \Delta_f H$ (TS) - $\Delta_f H$ (Reactants) = {C/CH_2/-H/CH_3} - {C/C/H_3} - {C/H_3}

Concept of Group Additivity Demands Supergroups to Have Constant Contributions of H^{298}, S^{298} and c_p's in Transition Structures.

As supergroups Consist of Several Polyvalent Atoms, they are not Groups in the Framework of GA. A Way to Split the above Supergroup into real Groups Could be :

{C/CH_2/-H/CH_3} => (C/H_3/-H) and (C/C/H_2/-H)

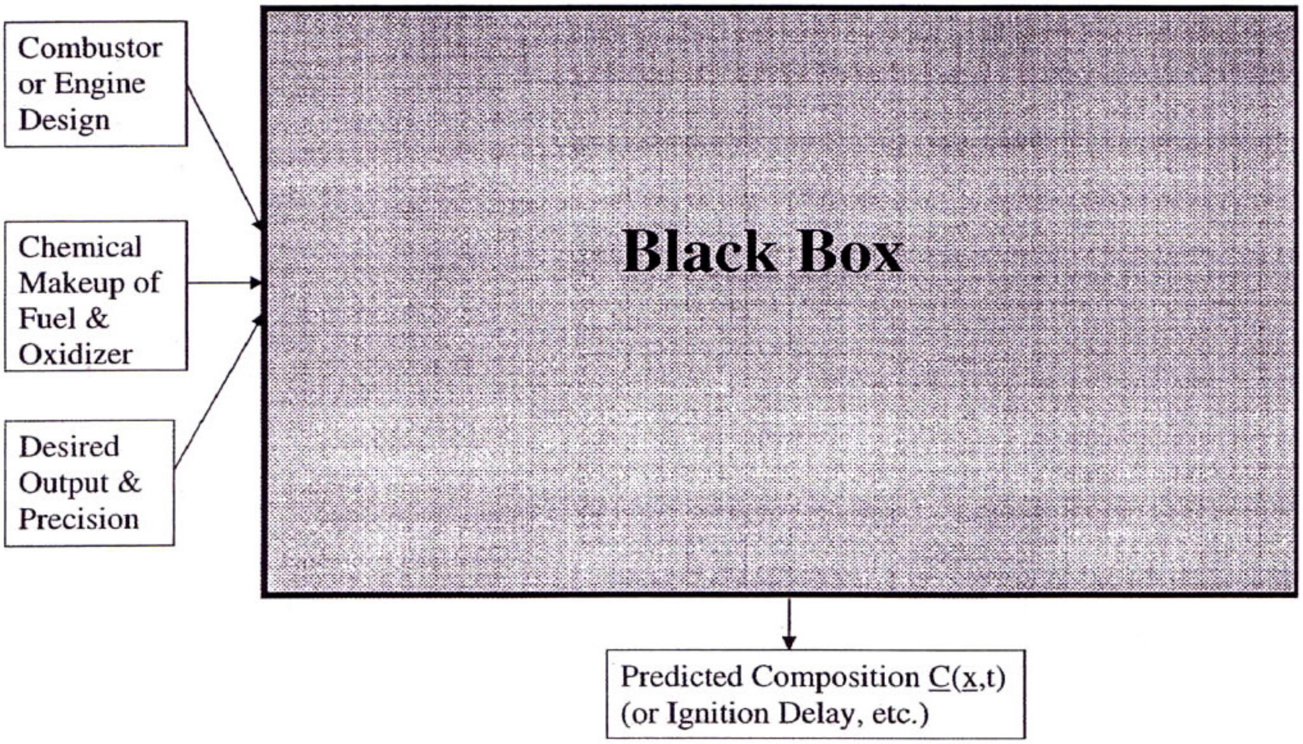
Through the Use of Symmetric Reactions,

CH_3 - - H - - CH_3 => 2 {C/H_3/C}
CH_3–CH_2 - - H - - CH_2—CH_3 => 2 {C/H_3/-H} + 2 {C/C/H_2/-H}

Individual Group Values could be derived.
Efforts were made to Demonstrate the Existence of 'Supergroups' and to Subdivide Them Into Groups.

See poster R412, 6Thu5B

The Dream



Combustor or Engine Design

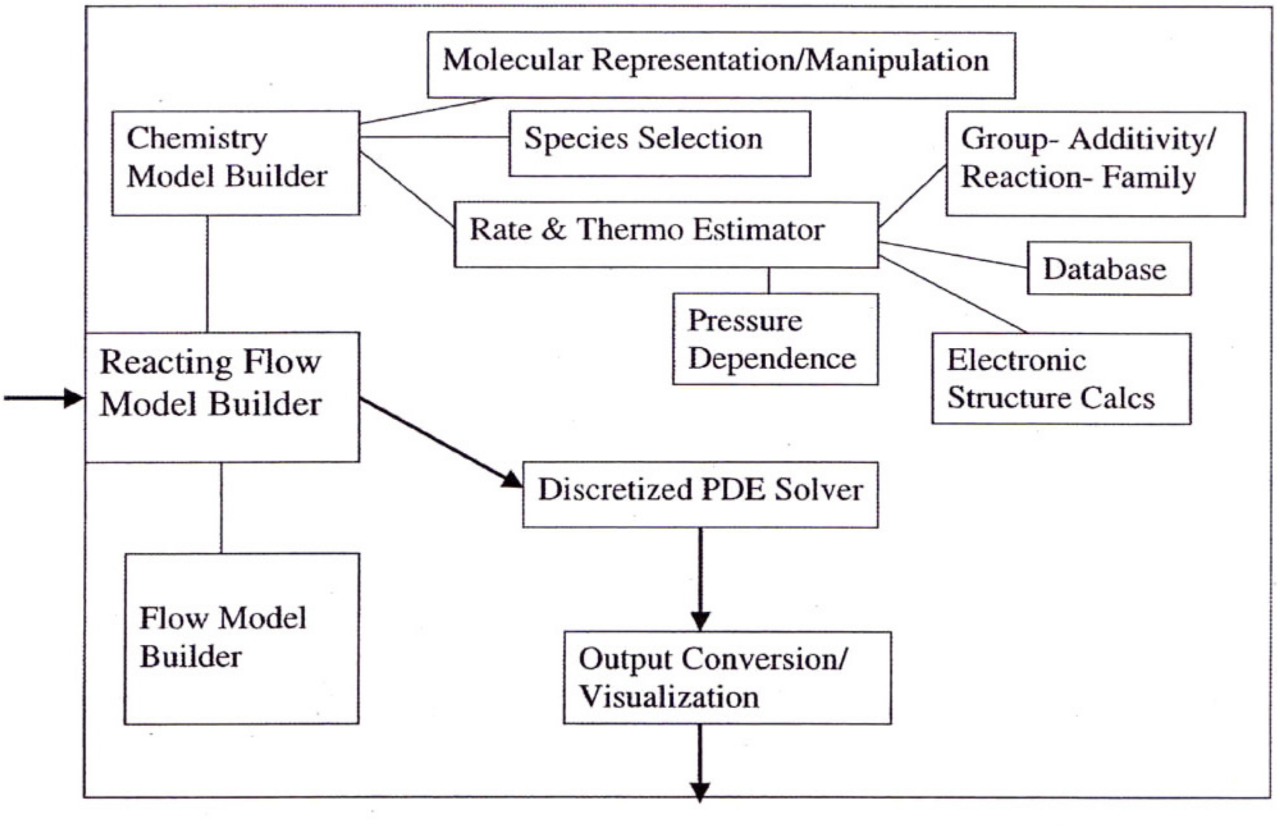
Chemical Makeup of Fuel & Oxidizer

Desired Output & Precision

Black Box

Predicted Composition $\underline{C}(\underline{x},t)$ (or Ignition Delay, etc.)

Inside the Black Box



Molecular Representation/Manipulation

Chemistry Model Builder

Species Selection

Group- Additivity/ Reaction- Family

Rate & Thermo Estimator

Database

Pressure Dependence

Electronic Structure Calcs

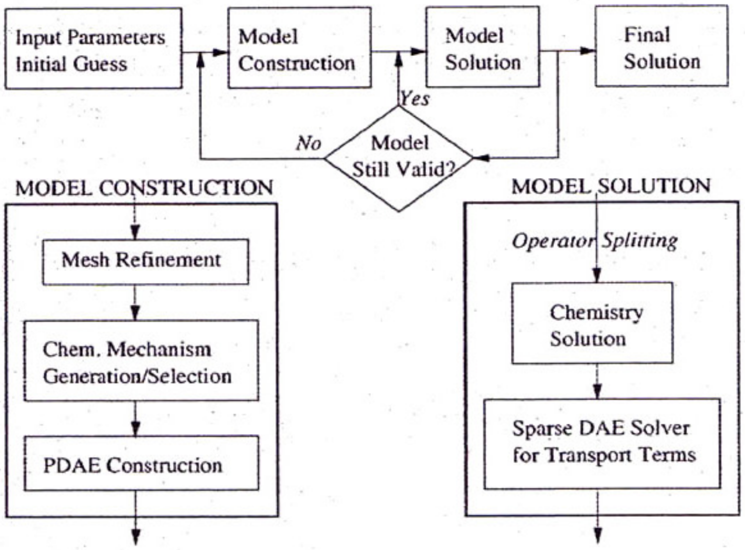
Reacting Flow Model Builder

Discretized PDE Solver

Flow Model Builder

Output Conversion/ Visualization

Adaptive Chemistry Procedure



Input Parameters
Initial Guess

Model Construction

Model Solution

Final Solution

Model Still Valid?

Yes

No

MODEL CONSTRUCTION

Mesh Refinement

Chem. Mechanism Generation/Selection

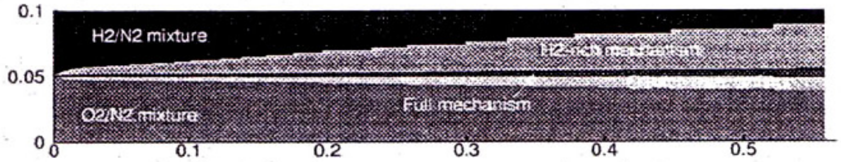
PDAE Construction

MODEL SOLUTION

Operator Splitting

Chemistry Solution

Sparse DAE Solver for Transport Terms



D. Schwer P405
6 thu B19

When is Model Valid? Accurate?

- Chemistry Depends on Reaction Conditions
- Model only valid under certain conditions
  - Neglects side reactions/species
  - Uncertainties in rate estimates more important in some conditions than in others
- Tool needed to identify Range of Validity!
- Method needed to specify uncertainties in model predictions!
- Models with Ranges and Accuracies needed for Adaptive Chemistry.

Comparing Big Models a Chore

- Same species? Same thermo? transport?
- Same reactions? Same rates?
- Which of the hundreds of discrepancies matter? Sensitivity computation feasible?
- MANY models in Adaptive Chemistry...
- Much worse in multi-d! e.g. Why do two mechanisms give different flame speeds?

Comparing with Experiment

- **Many uncertainties in Model Predictions**
  - **Rate Estimates**
  - **Thermo, Transport Estimates**
  - **Which Species/Reactions Belong in Model?**
  - **Tolerances in Numerical Solver**
  - **How to do Uncertainty Propagation?**
- **Uncertainties in the Data**
  - **Referees: please force both modelers and experimentalists to estimate uncertainties!**

Identifying what is Important

- **Nice tools in CHEMKIN, KINALC**
  - become less useful with thousands of reactions
- **Tool for Model Reduction?**
- **Want real input/output sensitivities**
  - Group additivity & rate estimation parameters
  - What is the real output from a Big Model?
- **What sensitivities do we want for multi-d simulations?**

Where We are Going

- CHEMKIN put the <u>numerics</u> in a Black Box
- Time to put <u>molecules</u> in a Black Box, too.
  - Too many species/reactions for humans
  - Focus instead on group additivity parameters, reaction family rate rules as inputs
  - What observables are the outputs? Not all the concentration profiles of hundreds of species!
- Challenge: Creating a bug-free Black Box!

Acknowledgements

Collaborators

Prof. A.M. Dean (Col. Sch. of Mines)
Dr. J.M. Grenda (ExxonMobil)
Prof. J.W. Bozzelli (NJIT)

$$$

DOE Basic Energy Sciences
(ABB) Alstom Power
EPA Center for Airborne Organics
National Science Foundation
Dow Chemical
General Motors

MIT People

David Matheu
Dr. Hans Carstensen
Dr. R. Sumathy
Dr. Doug Schwer
Tom Lada
Dr. Oleg Mazyar
Jing Song
Binita Bhattacharjee
Dr. Henning Richter
Prof. Paul Barton
Dr. John Tolsma

CHEMKIN in Education

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Many educators recognize the usefulness and power of the CHEMKIN routines and related Sandia combustion codes in the formal teaching of combustion. Results from a survey of combustion educators on their use of CHEMKIN for formal instruction will be presented and discussed. Included in this discussion will be examples of how the various codes are employed for instruction, issues of software availability and cost for instruction, and the need for user-friendliness in an instructional environment. The presentation will conclude with a description of how CHEMKIN has influenced the latest generation of combustion textbooks.

CHEMKIN IN EDUCATION

Stephen R. Turns

Propulsion Engineering Research Center
&
Department of Mechanical & Nuclear Engineering

Penn State University

CHEMKIN IN EDUCATION

- SURVEY & SURVEY RESULTS
- EXAMPLES OF INSTRUCTIONAL USE
- ISSUES FOR INSTRUCTIONAL USE
- A PROPOSAL
- DISCUSSION

SURVEY

1. In the past 5 years or so, have you taught a combustion course?
2. Were the students in your class mostly graduates or undergraduates?
3. Did you use any of the CHEMKIN and related Sandia combustion codes in your course?
    a. Which codes?
    b. Describe how you used the codes.
    c. How did you obtain access to the software?
    d. Describe any difficulties you have experienced.

SURVEY - Continued

4. If you do not currently use the CHEMKIN/Sandia software in your course, would you use it if it were more readily available for instructional use? Less costly?
5. Do you have any other comments related to the use of the CHEMKIN/Sandia software in education?

SURVEY RESULTS

REQUESTS: 52
RESPONSES: 25 (48%)

In the past 5 years or so, have you taught a combustion course?

Yes: 25
No: 0

Were the students in your class mostly graduates or undergraduates?

Graduate Students Mostly: 16
Mix of Grads & Undergrads: 9

SURVEY RESULTS – Continued

Did you use any of the CHEMKIN combustion codes in your course?

Yes: 17
No: 8

Which codes?

PREMIX: 7
PSR: 4
PFR: 3
EQUIL: 3
STANJAN: 3

OPPDIF: 2
SENKIN: 1
AURORA: 1
CONP: 1
TRANFIT: 1

SURVEY RESULTS - Continued

Describe how you used the codes.

Lectures:

- Species mole fractions in premixed flames
- Premixed flame examples
- Laminar flame speed calculations
- Reaction pathway analysis
- Generate various graphs & conclusions

Projects:

- Parametric studies
- Duplicate published results & extend
- Simple models of ignition & blowoff
- Adiabatic flame temperatures versus stoichiometry
- Evolution & falloff of radical concentrations & pollutant formation
- Flame speeds
- Reaction pathway analysis

Homework & Exams

EXAMPLE: ME 516 ASSIGNMENT 4

COMPLEX CHEMISTRY, CHEMKIN SOFTWARE, AND THE WELL-STIRRED REACTOR

Due Date: To be announced in class

The **objectives** of this assignment are for you to:

- Develop an awareness of the various components of the CHEMKIN package and other associated software
- Obtain firsthand experience in using some of these codes
- Explore the characteristics of a well-stirred reactor model which includes detailed chemistry
- Explore the details of complex H_2-air and CH_4-air combustion chemistry

Need Help? If you have a question or a problem with either the SGI workstations and/or the codes, you should contact our TA...

PART I. THE CHEMKIN LIBRARY AND GRI MECH 2.11

a. Read Appendix A. This is a list of some of the reports or manuals for the CHEMKIN library and associated codes.

b. Read Kee and Miller (Ref. 1 from Appendix A). This is available ...

c. Read Glarborg, Kee, Grcar, and Miller, also available...

d. Visit the GRI Mech web site: http://euler.Berkeley.edu./gri_mech/index.html....

APPENDIX A: CHEMKIN AND RELATED SOFTWARE

1. R. J. Kee and J. A. Miller, "A Structured Approach to the Computational Modeling of Chemical Kinetics and Molecular Transport in Flowing Systems," Report No. SAND86-8841, February, 1991.

2. R. J. Kee, F. M. Rupley, J. A. Miller, "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics," Report No. SAND89-8009/UC-401, March, 1991.

3. A. E. Lutz, R. J. Kee, J. A. Miller, "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics With Sensitivity Analysis," Report No. SAND87-8248/UC-401, August, 1991.

4. R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, J. A. Miller, "A Fortran Computer code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties," Report No. SAND86-8246/UC-401, December, 1990.

5. R. J. Kee, F. M. Rupley, J. A. Miller, "The Chemkin Thermodynamic Data Base," Report No. SAND87-8215B/UC-4, March, 1991 (Supersedes SAND87-8215).

6. P. Glarborg, R. J. Kee, J. F. Grcar, and J. A. Miller, "PSR: A FORTRAN Program for Modeling Well-Stirred Reactors," Report No. SAND86-8209/UC-4, February, 1991.

7. R. J. Kee, J. F. Grcar, M. D. Smooke, and J. A. Miller, "A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames," SAND85-8240/UC-401, March, 1991.

PART II. WSR WITH DETAILED H_2-AIR COMBUSTION CHEMISTRY

a. Read Appendices C and D on the use of the PSR code with the SGI cluster. Run the PSR H_2-air test case. Print out...

b. Explore the effect of residence time in a well-stirred reactor for H_2-air reactants. Use $\Phi = 1.0$, $T_{inlet} = 298$ K, $V_{reactor} = 67.4$ cm^3.

   i. Determine the equilibrium composition ($\tau_{res} \to \infty$ or, say, 1s).

   ii. Make several runs, shortening the residence time with each run, ...

   iii. Plot the temperature and the mole fractions of the following species... Discuss these results.

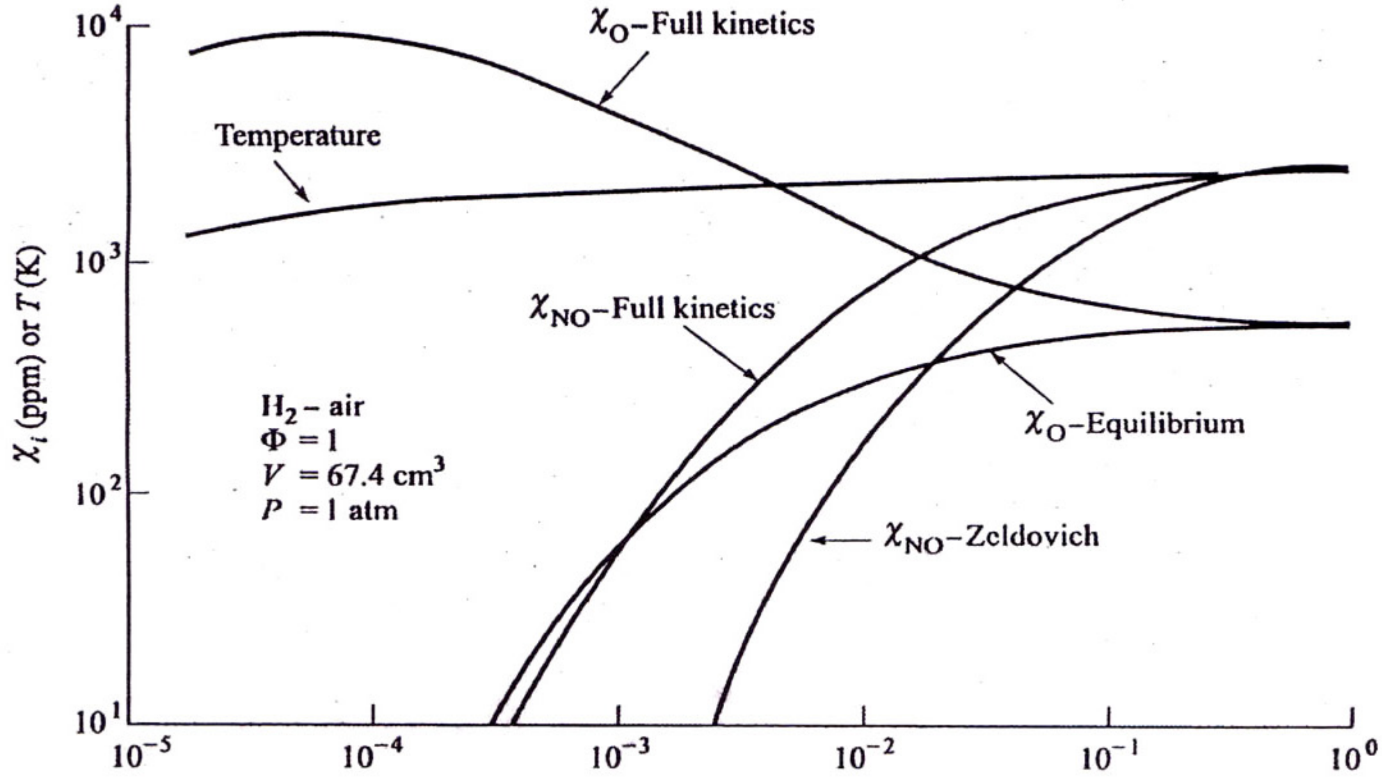
   iv. Draw a reaction-path diagram for the oxidation of H_2 for $\tau_{res} = 1$ s. **Include only the major paths.** List the molar flux (mole/s) and reaction number associated with each path alongside each arrow. **Note:** This **might** happen to be trivial.

PART III. SIMPLE MODEL FOR NO FORMATION IN WSR

a. Write out the NO species conservation equation for ...

b. Complete your model above using only the simple Zeldovich chain-reaction pair. Assume...

c. Solve your NO formation model... Compare your results with the PSR predictions using detailed chemistry. Discuss.



PART IV. WSR WITH DETAILED CH_4-AIR COMBUSTION CHEMISTRY

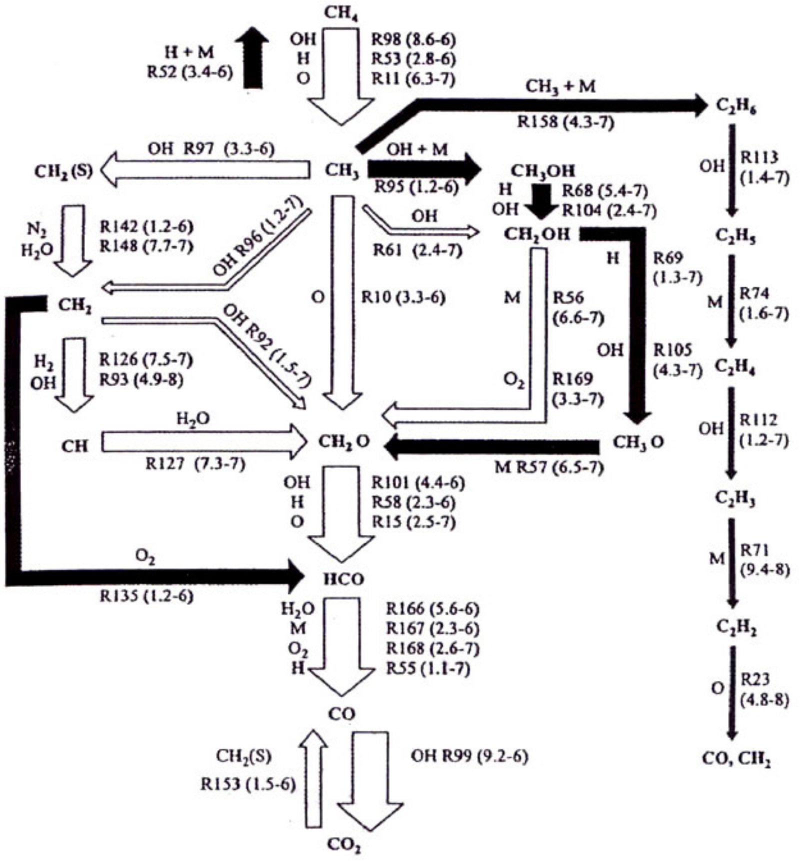
a. Run the PSR code for CH_4-air reactants with $\Phi = 1$, $T_{in} = 298$ K, $\tau_{res} = 0.1$ s, and $V_{reactor} = 67.4\ cm^3$. Set the heat loss to zero (adiabatic case).

b. Construct a reaction path diagram. Show only the major pathways. **Keep it simple.** Give numerical values for the molar fluxes and the reaction number beside each reaction-path arrow.

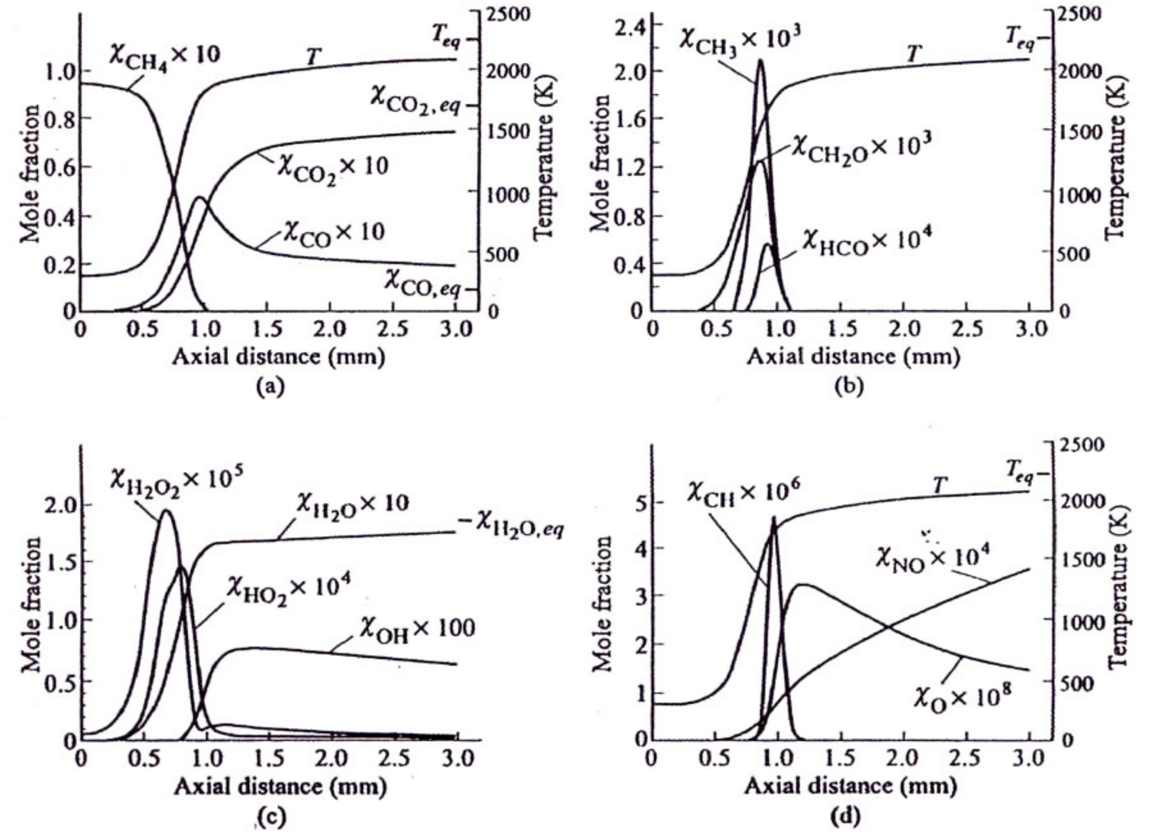
c. Repeat a and b above, but now incorporate a heat loss of **55** cal/s. Do the reaction paths change significantly? For example, how do the CH_3 destruction pathways change? Discuss.

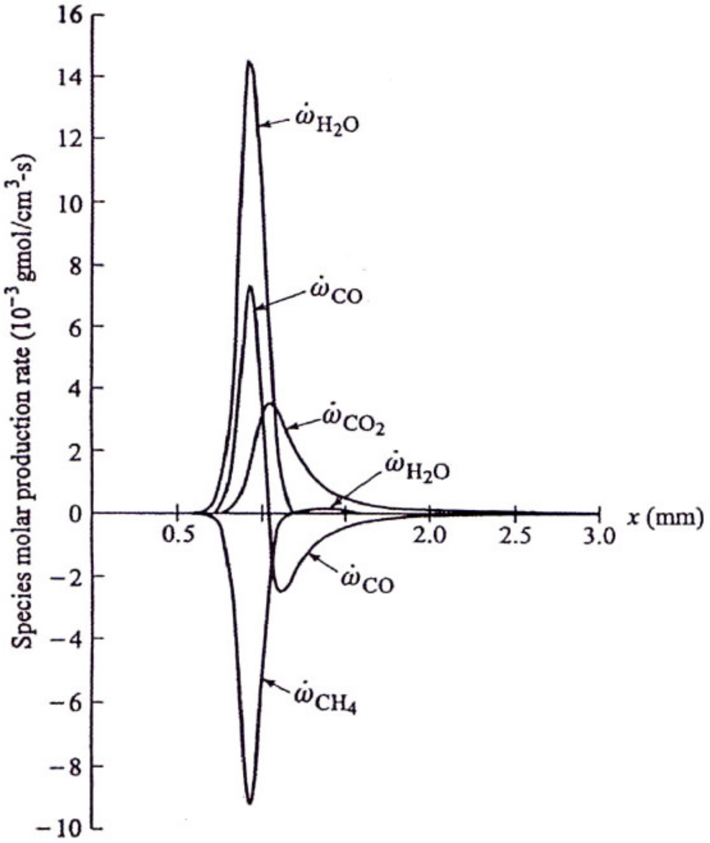
REPORT

- Label each part of your work to correspond with the parts of the assignment.
- Do not turn in reams of computer output. Turn in only what you think is particularly useful. If you have a difficult time deciding, put the material in an appendix.


CH₄
H + M
R52 (3.4-6)
OH H O
R98 (8.6-6)
R53 (2.8-6)
R11 (6.3-7)
CH₃ + M
R158 (4.3-7)
C₂H₆
OH R97 (3.3-6)
CH₂(S)
CH₃
OH + M
R95 (1.2-6)
CH₃OH
H OH
R68 (5.4-7)
R104 (2.4-7)
OH R113 (1.4-7)
N₂ H₂O
R142 (1.2-6)
R148 (7.7-7)
OH R96 (1.2-7)
OH
R61 (2.4-7)
CH₂OH
C₂H₅
H R69 (1.3-7)
CH₂
O R10 (3.3-6)
M R56 (6.6-7)
M R74 (1.6-7)
OH R92 (1.5-7)
OH R105 (4.3-7)
C₂H₄
H₂ OH
R126 (7.5-7)
R93 (4.9-8)
O₂ R169 (3.3-7)
OH R112 (1.2-7)
H₂O
CH
R127 (7.3-7)
CH₂O
CH₃O
M R57 (6.5-7)
OH H O
R101 (4.4-6)
R58 (2.3-6)
R15 (2.5-7)
C₂H₃
M R71 (9.4-8)
O₂
R135 (1.2-6)
HCO
H₂O M O₂ H
R166 (5.6-6)
R167 (2.3-6)
R168 (2.6-7)
R55 (1.1-7)
C₂H₂
O R23 (4.8-8)
CO
CO, CH₂
CH₂(S)
R153 (1.5-6)
OH R99 (9.2-6)
CO₂

* * *


χ_CH4 × 10
T
T_eq
χ_CO2,eq
χ_CO2 × 10
χ_CO × 10
χ_CO,eq
Mole fraction
Temperature (K)
Axial distance (mm)
(a)
χ_CH3 × 10³
χ_CH2O × 10³
χ_HCO × 10⁴
(b)
χ_H2O2 × 10⁵
χ_H2O × 10
χ_H2O,eq
χ_HO2 × 10⁴
χ_OH × 100
(c)
χ_CH × 10⁶
χ_NO × 10⁴
χ_O × 10⁸
(d)
0 0.5 1.0 1.5 2.0 2.5 3.0
0 500 1000 1500 2000 2500



SURVEY RESULTS - Continued

How did you obtain access to the software?

Old Freeware: 13
RD License: 2 (using same license)
Bowman Version: 2

Comments:

We would love to see a lower license fee…

Too expensive for classroom.

Will not use the RD versions unless they become a lot cheaper for the educational market.

Will not use new versions because they are expensive & not very adaptable to special needs.

SURVEY RESULTS - Continued

If you do not currently use the CHEMKIN software in your course, would you use it if it were more readily available for instructional use? Less costly?

Yes: 4
No: 2
Maybe: 2

Comments:

I would use a more up-to-date version if it were less costly, e.g., if students could purchase a license for using the software in class for about $10 a piece.

The cost is a major issue. Since it is such a specialized software, the university will not pay for 25 seats.

Yes, if less than, say, $200.

...

SURVEY RESULTS – Continued

Describe any difficulties you have experienced in the instructional use of CHEMKIN & related software.

Same old problem, poor interface for students with limited UNIX experience...

I have to offer an extra session on "survival UNIX and VI" to enable the use of CHEMKIN on a UNIX platform. Students would be happier running something under Windows...

The code I have is DOS based; wish it was Windows based.

The most significant difficulties originate from students' computer knowledge: code compilation, porting codes to different platforms.

When desperate, throw up your hands: I am sick to death of workstations and FORTRAN. I want to use CHEMKIN routines from the comfort of Windows using my slick Delphi computer. You would think that by now someone would have converted CKLIB.F into a DLL that can be used from a real, live modern language. I think this individual should come forward and share with the rest of us.

SURVEY RESULTS – Continued

Do you have any other comments related to the use of the CHEMKIN/Sandia software in education?

A clearinghouse for CHEMKIN problems, with example input files, would be very helpful.

They have the potential for being very useful, especially if a version of a reactor network code with a good GUI (like the GRI calculator that was never released because of haggling between GRI and RD) becomes available.

I use CHEMKIN in my research, but have not implemented it into teaching because of the user license restrictions.

It is obviously a powerful tool, and I suppose that is why it was commercialized. I would welcome any opportunity to use it in education so that students continue to use in industrial/academic settings. Just try to get these guys to provide CHEMKIN and SURFACE CHEMKIN for educational purposes. It would add a lot to combustion education.

A PROPOSAL

Make available a special ***CHEMKIN-for-Education*** package that

- ☺ *Contains the most popular codes: PREMIX, PSR, PFR, EQUIL, etc.*
- ☺ *Contains a library of instructional examples.*
- ☺ *Has a user-friendly graphical interface for input & post-processing.*
- ☺ *Operates in a WINDOWS environment.*
- ☺ *Is free, or available for a nominal fee, to qualified users.*

Other Comments – Continued

I think it is a great tool. It would have been nice to have the students themselves use it on a PC, but I have not compiled it there and didn't have the time to work out the bugs so I could answer their questions. In following years, I will probably use PSR and SENKIN to generate more examples.

A majority of the students that I teach will not have a job that requires them to do laminar flame calculations. If they will work in the area of combustion, they will probably work for utility companies and do boiler calculations. Thus a good interface between CHEMKIN and codes that do more practical combustion calculations will help, both in the effectiveness of instruction and to broaden the CHEMKIN market.

A version more amenable to instructional use would definitely be a plus! This includes a free version without all the bells and whistles which the students could get used to and thus would then be more likely to use and purchase later in their career.

Flame Synthesis of Materials:
Modeling Combustion Synthesis Systems

Margaret S. Wooldridge

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Ann Arbor, MI 48109-2125 USA

Combustion synthesis (CS) is an important research topic in both the combustion and materials communities. An enormous range of substances (from high-cost-per-gram materials such as electronics, optics and specialty catalysts, to low-cost-per-gram materials, such as fillers and opacifiers) and quantity of materials are produced annually using combustion synthesis methods. Combustion synthesis research has potential for considerable impact, particularly in the area of molecularly designed materials and nanosized materials.

Combustion synthesis systems are inherently multi-phase, and are generally categorized by the phase of the reactants. The paramount issue in CS studies is the quality of the product materials, in particular, the product composition and microstructure (primary particle size, morphology, etc.). Therefore, both modeling and experimental efforts focus on goals of developing improved techniques and predictive capabilities for enhancing and enabling combustion synthesis technologies.

Depending on the type of CS system, gas-phase chemical reactions may or may not be a dominant physical mechanism in determining the product characteristics. Two specific examples of CS systems will be discussed in the context of current and desired modeling capabilities, and interfacing with CHEMKIN software. The examples include gas-phase combustion synthesis of silica (SiO_2) particles and self-propagating high-temperature synthesis (SHS) of transition metal carbides and borides. Important transport processes for each of these systems will be presented. Short-term and longer-term needs in combustion synthesis modeling will be highlighted. Some of the topics that will be covered include: key gas-phase reactions in the Si/H/O system, modeling particle nucleation and polymerization reactions, surface reactions, and adsorption and migration of gas-phase species on surfaces. Experimental needs also will also be briefly reviewed.

Flame Synthesis of Materials: Modeling Combustion Synthesis Systems

Second International Workshop on CHEMKIN in Combustion
Edinburgh, Scotland

Margaret S. Wooldridge
Department of Mechanical Engineering

Outline

- ➢Introduction and Motivation
- ➢Case Study I: Gas-Phase Combustion Synthesis (GPCS)
- ➢Modeling Approaches for GPCS
- ➢CHEMKIN and GPCS
- ➢Case Study II: Self-Propagating High-Temperature Combustion Synthesis
- ➢Modeling Approaches for SHS
- ➢Summary

Motivation

Combustion synthesis material systems:

- High value/low volume materials:
  - Microelectronics, optics, biomaterials,
  - nanostructured materials
  - Silicon, carbon nanotubes, diamond films
- Medium value/medium volume materials:
  - Catalysts, fiber optics
  - Transition metal carbides, silica
- Low value/high volume materials:
  - Filler, strengtheners, opacifiers
  - Titania, silica, carbon black

Introduction to Combustion Synthesis

Categories of combustion synthesis processes:

TABLE I

Most common combustion patterns (for the $X \rightarrow Z$ or $X + Y \rightarrow Z$ reactions taken as an example, where the initial temperature for X and Y is T_o, and Z is present at the maximum combustion temperature T_m).

	Classical combustion of gasses	$X(\text{gas}) + Y(\text{gas}) \rightarrow Z(\text{gas})$
➡	Condensation combustion of gasses	$X(\text{gas}) + Y(\text{gas}) \rightarrow Z(\text{gas + particles})$
	Combustion of suspensions in gas	$X(\text{particles or drops}) + Y(\text{gas}) \rightarrow Z(\text{gas or gas + particles})$
	Heterogeneous combustion	$X(\text{surface}) + Y(\text{gas}) \rightarrow Z(\text{gas})$
	Permeation combustion	$X(\text{porous system}) + Y(\text{gas}) \begin{array}{l} \nearrow Z(\text{gas}) \\ \searrow Z(\text{solid}) \end{array}$
	Combustion of monofuels	
	liquid	$X(\text{liquid}) \rightarrow Z(\text{gas})$
	solid	$X(\text{solid}) \rightarrow Z(\text{gas})$
	Combustion of blends	
	liquid	$X(\text{liquid}) + Y(\text{liquid}) \rightarrow Z(\text{gas})$
	solid	$X(\text{solid}) + Y(\text{solid}) \rightarrow Z(\text{gas})$
	Combustion of thermites (liquid flame)	$X(\text{powder}) + Y(\text{powder}) \rightarrow Z(\text{liquid})$
➡	Solid-state combustion (solid flame)	$X(\text{powder}) + Y(\text{powder}) \rightarrow Z(\text{solid})$

Merzhanov, A.G., *Combust. Sci. Tech.* 98:307-336 (1994)

Modeling Combustion Synthesis Systems

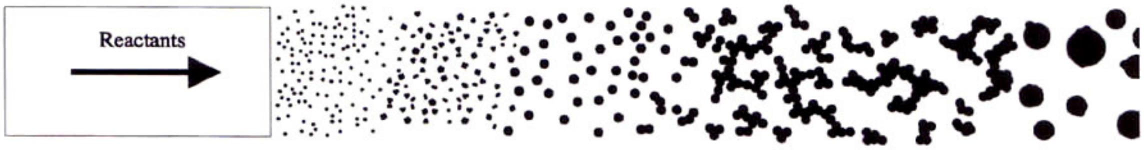
Objective: To reliably and accurately predict product composition, morphology and production rates.

System I

System II

Case Study I: Gas-Phase Combustion Synthesis of Particles

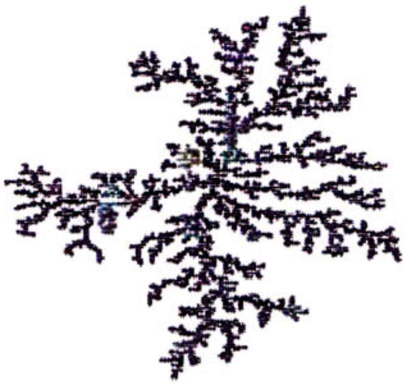
Modeling approaches	CHEMKIN	Molecular dynamics	Solutions to the ADE	Monte Carlo methods
Particle size range	~Angstrom	~nanometers	~100s nanometers	~micron



Physical mechanisms: Monomer Formation, Cluster Formation, Homogeneous Nucleation (Primary particles), Agglomeration, Surface Growth, Coalescence

Sintering/Surface Growth Growth Models

Monte Carlo simulation of simultaneous agglomeration and sintering



a

Unsintered agglomerate,
(no sintering)

b

Sintered agglomerate,
(sintering rate = 4*growth rate)

Akhtar, M.K., Lipscomb, G.G., and Pratsinis, S.E., *Aerosol Sci. Tech.* 21:83-93 (1994)

Issues: relating simulation times to real times, particle-gas reactions may be important

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Agglomeration Models

Aerosol Dynamic Equation: $$\frac{dn_i}{dt} = I_i + \frac{1}{2}\sum_{j=1}^{i-1}\beta_{j,i-j}n_jn_{i-j} - \sum_{j=i}^{\infty}\beta_{i,j}n_in_j$$

Assumes: primary particle building blocks, source rate from decomposition kinetics

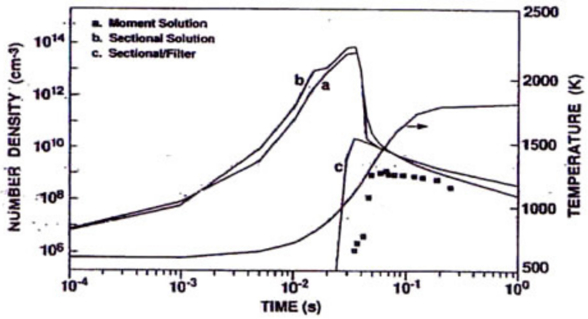

Figure 4. Number density vs. residence time in flame 1.
Curve *a*, moment method solution
Curve *b*, sectional method solution
Curve *c*, sectional solution with 40 nm cutoff
Open squares, experimental measurements
Silane mole fraction in fuel stream – 0.365%

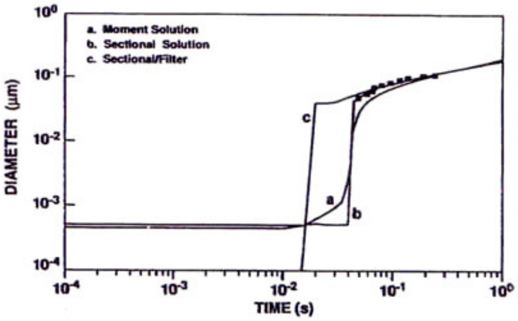

Figure 5. Particle diameter vs. residence time in flame 1.
Curve *a*, moment method solution
Curve *b*, sectional method solution
Curve *c*, sectional solution with 40 nm cutoff
Open squares, experimental measurements
Silane mole fraction in fuel stream – 0.365%

Zachariah, M.R., and Semerjian, H.G., *AIChE J.*, 35:2003-2012 (1989)

Issues: gas-phase chemical kinetics may be important for certain conditions, particle-gas reactions may be important, presumes particle shape

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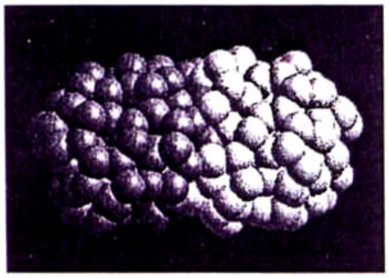
Nucleation models

Molecular dynamics models model range from ~10mer to 1000 atoms

Collision between two 120 Si atom clusters

T = 2000 K

Rapid sintering



T = 600 K

Slow sintering

Zachariah, M.R., Carrier, M.J., and Blaisten-Barojas, E., *Mat. Res. Soc. Symp. Proc.* 334:75-80 (1994)

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CHEMKIN Modeling of GPCS

Issues:

Do nucleates or monomers chemically resemble the final particle product? ***Probably not!***

At the early stages of nucleation, sticking coefficients are << 1.

Result: RRKM analysis of nucleation reactions such as:

Polymerization:
$SiO + SiO = Si_2O_2$

Reaction:
$Si_2O_2 + H_2O = Si_2O_2H(OH)$

Zachariah, M.R., and Tsang, W., *J. Phys. Chem.*, 99:5308-5318 (1995).

Facilitating CHEMKIN modeling for simulating early time nucleation (<10mer)

Nucleation is arguably the most important step in gas-phase combustion synthesis of particles, particularly in synthesis of nanoparticles.

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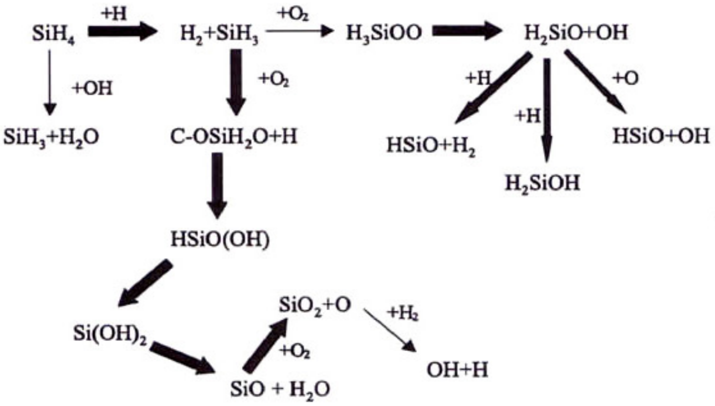
CHEMKIN Modeling of GPCS

CHEMKIN modeling for simulating gas phase chemistry

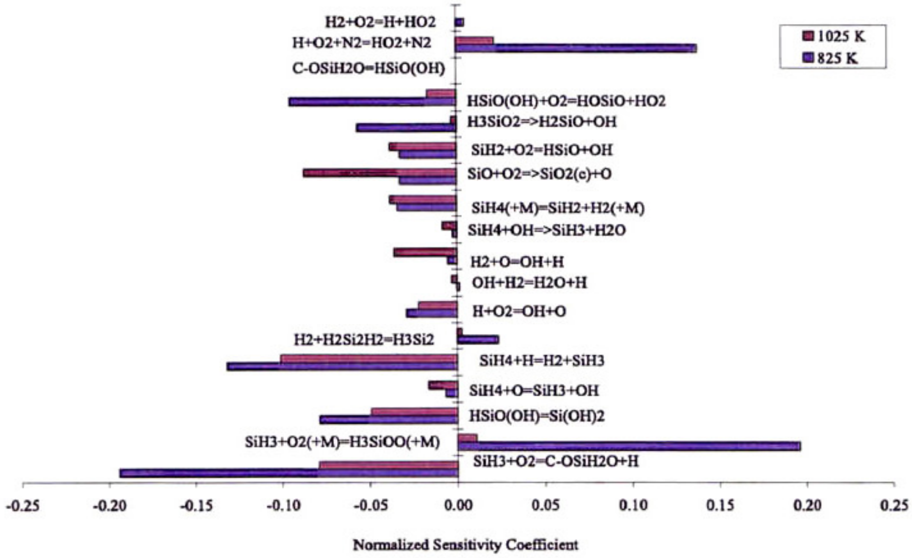


Reaction path diagram for $SiH_4/O_2 \Rightarrow SiO_2$ Combustion Modeling

Michigan**Engineering** Wooldridge, Bozzelli and Kim, in preparation, *Comb. Flame*, 2001

$SiH_4/O_2 \Rightarrow SiO_2$ Combustion Modeling

CHEMKIN modeling for identification of important reactions

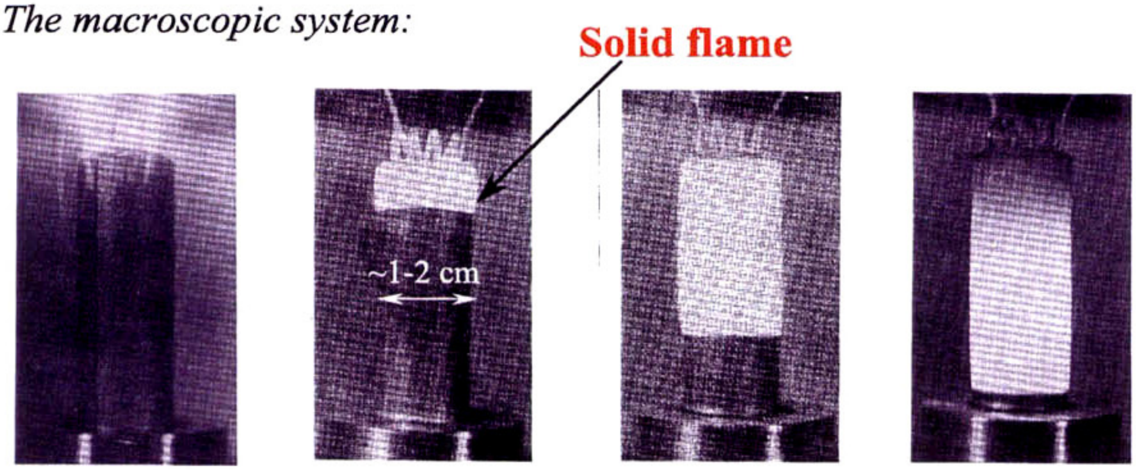


Sensitivity analysis: ignition delay times, SiH_4/O_2 combustion

Michigan**Engineering** Wooldridge, Bozzelli and Kim, in preparation, *Comb. Flame*, 2001

Self-Propagating High-Temperature Combustion Synthesis (SHS)

The macroscopic system:



t = 0　t = 0.05s　t = 0.3s　t = 0.4s

Ti/2B system

Merzhanov, A.G., *Combust. Sci. Tech.* 98:307-336 (1994)

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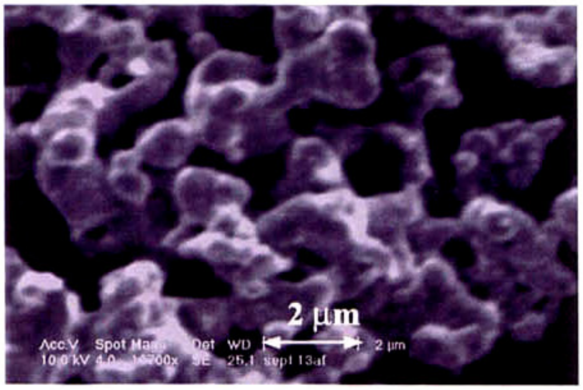
Variations on Traditional SHS

Methods to affect transport processes

- Fluidized-bed combustion synthesis, K. Brezinsky, University of Illinois at Chicago
- Electric-field activated SHS, Z. Munir, University of California at Davis
- Catalytically-assisted SHS (gas-phase additives), M. Wooldridge, University of Michigan at Ann Arbor



SEM image of TaC product ($Ta = 1.88\ \mu m$, $\chi_{I2} = 37.9\%$, $P = 0.26$ bar)

Kim and Wooldridge, *J. Am. Cer. Soc.*, 2000

Are SHS systems diffusion or kinetics limited?

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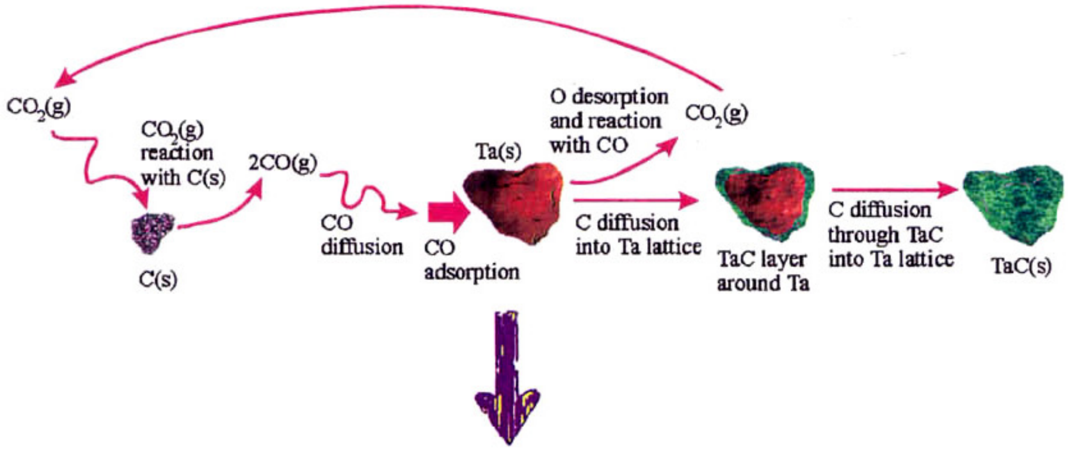
Catalytically-Assisted SHS

Proposed transport mechanisms in the CO2/Ta/C system



Net Result:
C is transported to Ta

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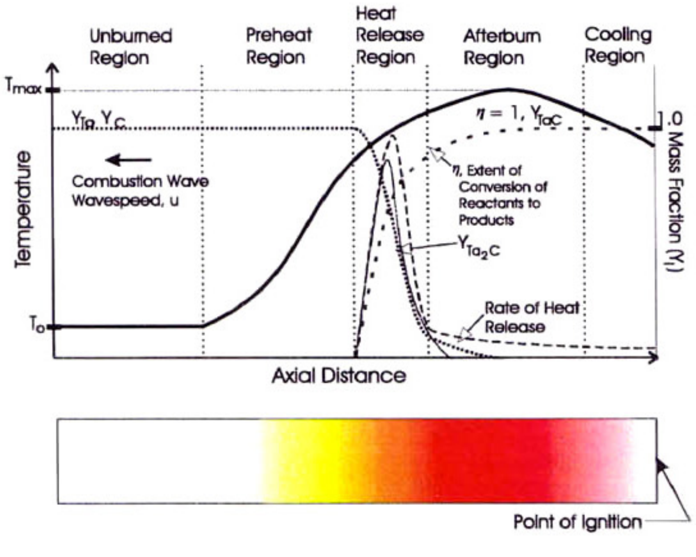
Kim and Wooldridge, *J. Am. Cer. Soc.*, 2001, in press

* * *

SHS Modeling

- **Modified 1-D laminar flame models**



- **Quasi-microscopic gap/layer approach (Law, Merzhanov, Munir)**
- **Microscopic single cell model (one particle surrounded by another) (Kostogorov, Dorozhevets)**
- **Multi-level (specimen, particle, particle ensembles) (Kaviany)**

Parameters influencing SHS combustion characteristics: packing density, particle size, stoichiometry, temperature, pressure, etc.

Can Surface Chemkin be extended to modeling gas-assisted SHS systems?

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Future Opportunities and Challenges for Modeling of Combustion Synthesis Systems

- Thermodata to support additional high-temperature materials systems
    - e.g. TiO_2, Sb_2O_3, SnO_x, non-oxide ceramics
- Rate coefficient data to support additional material systems
    - Detailed rate coefficients for GPCS
    - Overall or multistep rate coefficients for SHS
- Interfacing capabilities between modeling GPCS approaches
- Continued development of early time nucleation models for GPCS
- Generalized approach to modeling SHS which is relatively material independent
- Microscopic models for SHS which incorporate and retain particle morphology

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Paul Torek
Jianfan Wu (Texas A&M)

Undergraduate Students:
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Steve Lenick
Scott Matula
Srin Nagali
Annie Wang

High School Students
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Chemistry in Multi-Dimensional Fluid Flow

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There is increasing interest in simulating chemically reacting flows in complex geometries for a wide range of applications. For example, more stringent regulatory requirements for air and surface transports have led to a need to fine-tune combustors in IC and gas turbine engines to reduce emissions of pollutants such as NOx and soot. Combustion CFD (Computational Fluid Dynamics) is a tool being increasingly used to aid in the design process to achieve these emissions goals. CFD coupled with detailed kinetics also offers the potential for aiding the design of other systems where complex multi-dimensional fluid flows interact with complex chemistry. In the chemical processing industry for example, minor changes in reactor geometries can sometimes lead to unexpected effects in product yields, etc. Reacting-flow CFD may provide useful insights into these geometry-related effects.

This presentation will start with the status and examples of the coupling of CHEMKIN and SURFACE CHEMKIN with STAR-CD, a commercial CFD program. Examples will include premixed and spray injection laboratory flame tubes and gas turbine combustors. Data comparisons will be shown for emission and temperature distributions. For additional comparison purposes, calculations with simplified global reaction mechanisms and NOx post-processors will also be shown.

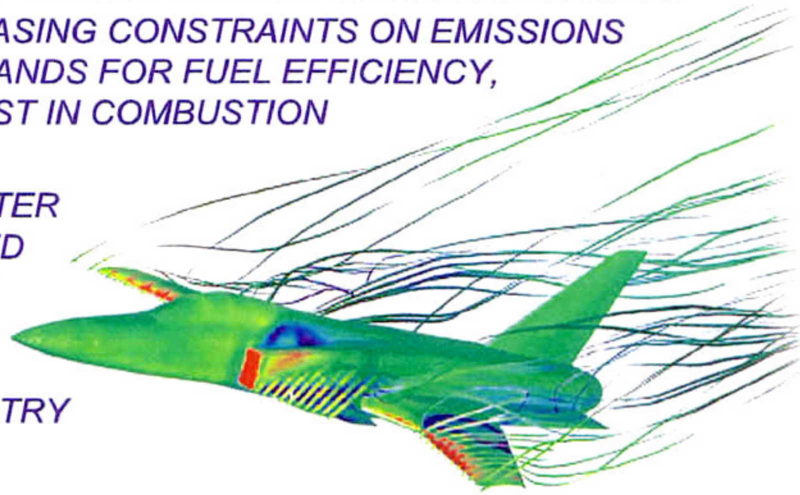
In addition, methods for combining chemistry with turbulence, the combustion-turbulence interaction, will be discussed. This will include simple approaches (such as Eddy Breakup) widely used in industry through more advanced Monte Carlo approaches. Several examples will also be discussed here.

CHEMISTRY IN MULTI-DIMENSIONAL FLUID FLOW

J. M. DEUR

OVERVIEW

- ☐ COMPUTATIONAL FLUID DYNAMICS (CFD) IS COMMONLY USED ENGINEERING TOOL – PARTICULARLY FOR AERODYNAMICS.
- ☐ BECAUSE OF INCREASING CONSTRAINTS ON EMISSIONS AND GROWING DEMANDS FOR FUEL EFFICIENCY, INDUSTRIAL INTEREST IN COMBUSTION CFD IS GROWING.
- ☐ DEMAND FOR GREATER YIELDS, ETC. HAS LED TO MORE INTEREST IN REACTING FLOW CFD IN CHEMICAL PROCESSING INDUSTRY AS WELL.



COMMERCIAL CFD

- *INDUSTRIAL USERS COMMONLY USE COMMERICAL CFD CODES SUCH AS FLUENT, CFX, STAR-CD, ETC.*
- *STAR-CD IS A GENERAL PURPOSE COMMERCIAL CFD CODE FOR FLOWS INCLUDING TURBULENCE, SPRAYS, AND CHEMISTRY.*
- *STANDARD STAR-CD CHEMISTRY OPTIONS INCLUDE:*
  - *FINITE RATE KINETICS – ONLY SIX REACTIONS FOR NOW, BUT...*
  - *SIMPLE MIXING CONTROLLED MODELS – EDDY BREAK-UP, ETC.*
  - *PRESUMED PDF MODEL – BASED ON EQUILIBRIUM CHEMISTRY.*
  - *FLAME AREA MODELS – WELLER, CFM, ETC.*
  - *COAL COMBUSTION MODELS.*
  - *NO_X MODELS – THERMAL, PROMPT, AND FUEL.*

USE OF COMBUSTION CFD IN DIESEL DESIGN

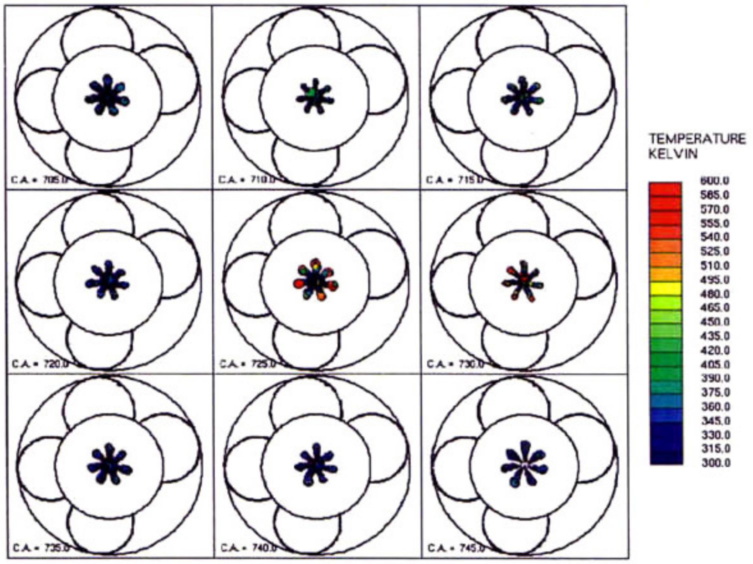
BASELINE (REOP)

MODIFIED BOWL (EOP3)

4-VALVE DI DIESEL DESIGN STUDY

BASELINE
(REOP)

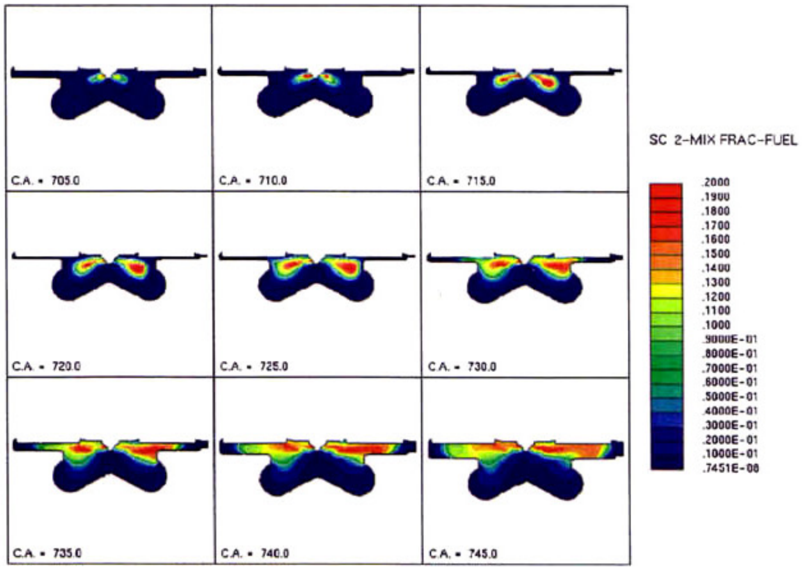
SPRAY
PATTERN



4-VALVE DI DIESEL DESIGN STUDY

BASELINE
(REOP)

FUEL VAPOR
CONTOURS

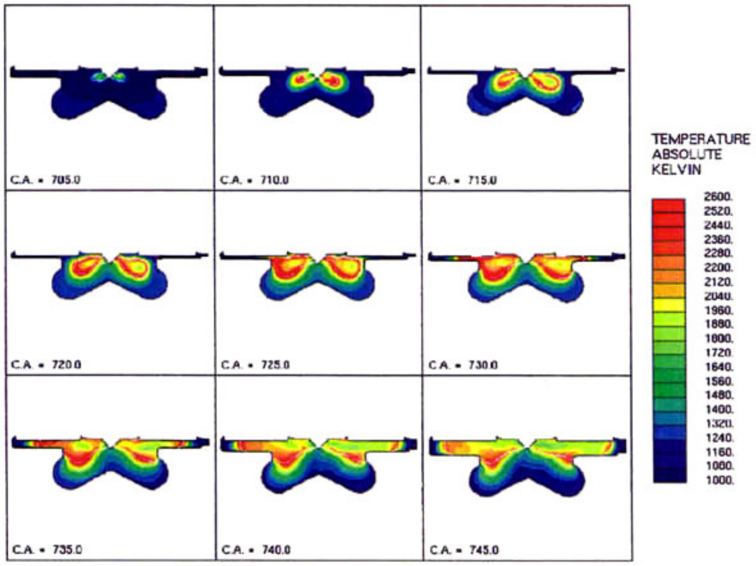


adapco
Analysis & Design Application Co., Ltd.

4-VALVE DI DIESEL DESIGN STUDY

BASELINE (REOP)

TEMPERATURE CONTOURS



2ND INTERNATIONAL WORKSHOP ON CHEMKIN IN COMBUSTION

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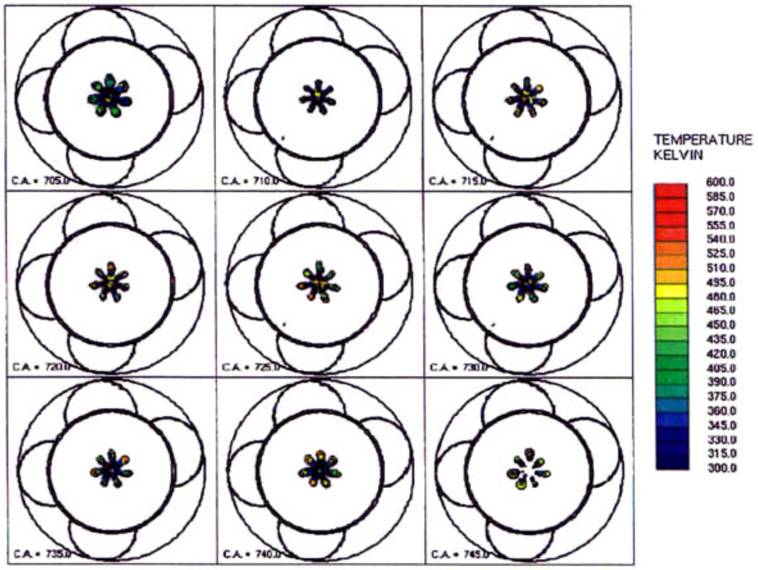
4-VALVE DI DIESEL DESIGN STUDY

MODIFIED BOWL (EOP3)

SPRAY PATTERN

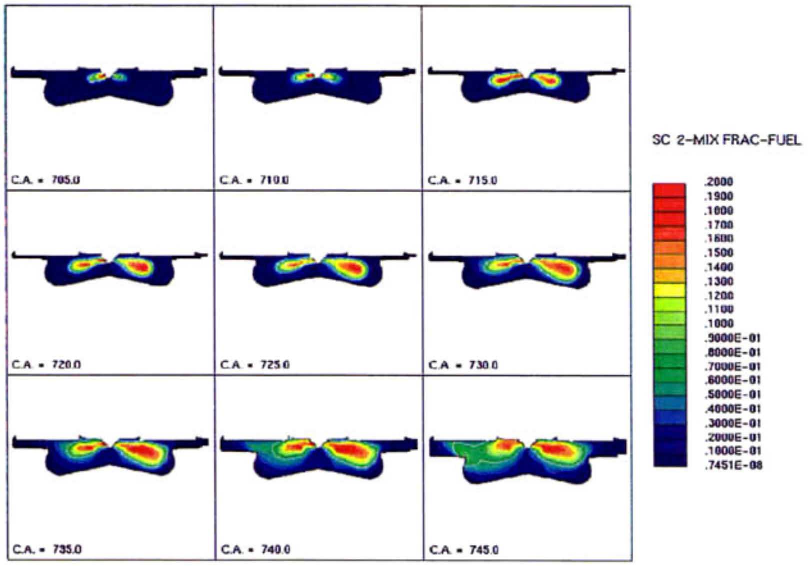


2ND INTERNATIONAL WORKSHOP ON CHEMKIN IN COMBUSTION

4-VALVE DI DIESEL DESIGN STUDY

MODIFIED
BOWL (EOP3)

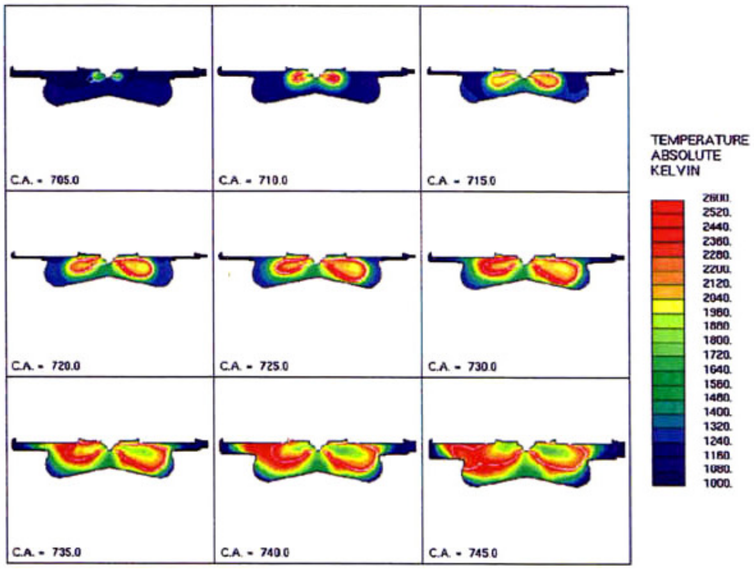
FUEL VAPOR
CONTOURS



4-VALVE DI DIESEL DESIGN STUDY

MODIFIED
BOWL (EOP3)

TEMPERATURE
CONTOURS



HOW IS COMBUSTION IN DIESEL SIMULATED?

- ☐ *SHELL DIESEL IGNITION MODEL BASED ON GENERIC MECHANISM:*

$RH + O_2 \Rightarrow 2R^*$ $\quad R^* \Rightarrow R^* + Q$ $\quad R^* \Rightarrow$ TERMINATION

$R^* \Rightarrow R^* + P$ $\quad R^* + Q \Rightarrow R^* + B$ $\quad 2R^* \Rightarrow$ TERMINATION

$R^* \Rightarrow R + B$ $\quad B \Rightarrow 2R^*$

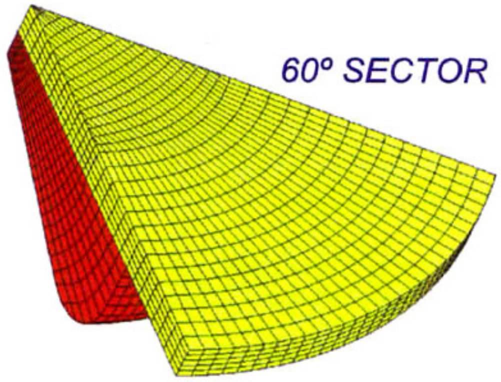
RH – FUEL, R - RAD., B – BRANCHING AGENT, Q – INTERMED., P – PROD.*

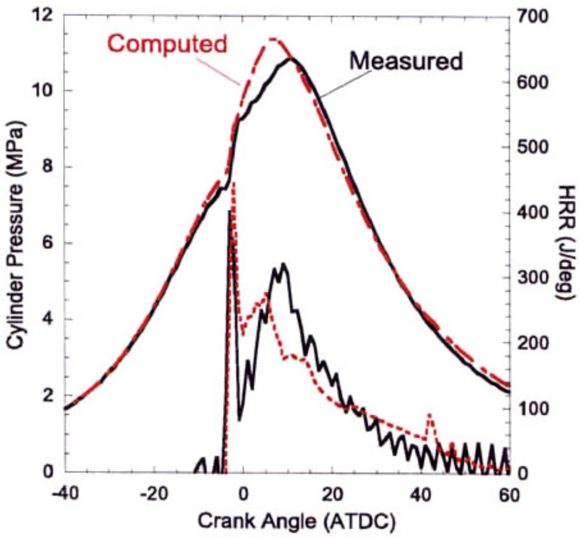
- ☐ *ONCE CELL TEMPERATURE OR GRADIENT REACHES SPECIFIED VALUE, CHEMISTRY SWITCHES TO MIXING CONTROLLED MODEL, E.G., LATCT:*

$$m\acute{Y}_f = -A \frac{\min\left(m_f, \dfrac{m_o}{s_o}, B\dfrac{m_p}{s_p}\right)}{\dfrac{\mathrm{m_f}}{\mathrm{m}\acute{\mathrm{Y}}_{\mathrm{f}_{kin}}} + f_c \dfrac{\mathrm{k}}{\varepsilon}}$$

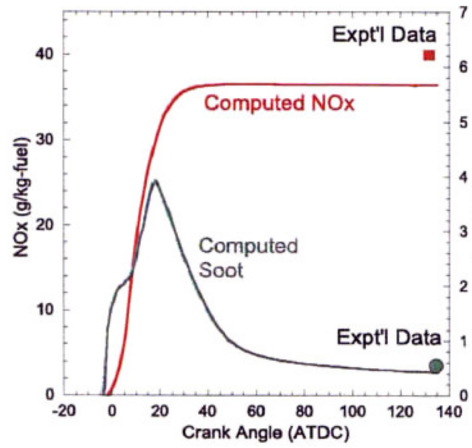
U OF W/ERC MODELS + STAR-CD: CAT 3400

- ☐ *SHELL IGNITION AND LATCT COMBUSTION MODELS.*
- ☐ *SOOT AND NO_X MODELS.*
- ☐ *ATOMIZATION MODEL.*

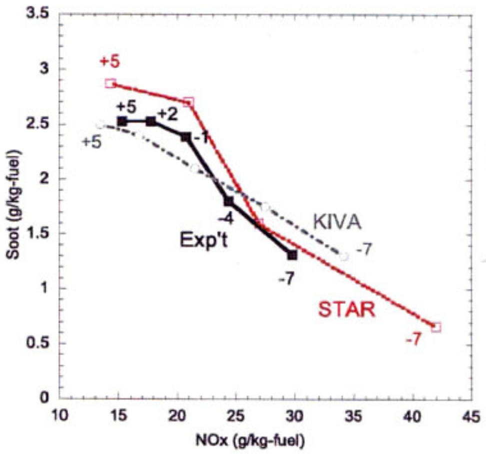




CAT 3400 HEAVY DUTY DIESEL STUDY



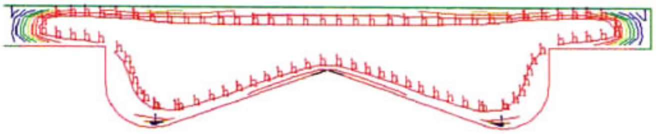
BASELINE



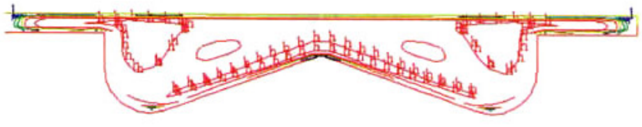
HIGH LOAD, SINGLE INJECTION

DETAILED CHEMISTRY IN DIESEL SIMULATION

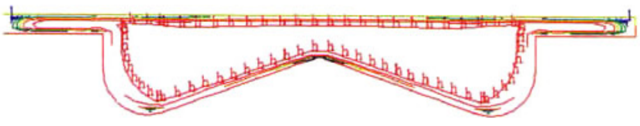
- ☐ *CALCULATIONS WITH KIVA AND CHEMKIN II BY U OF WISCONSIN.*
- ☐ *ANALYSIS OF VOLVO TD-100 HEAVY DUTY DIESEL.*
- ☐ *EXPERIMENTS RUN WITH NATURAL GAS AT LUND INST. OF TECHNOLOGY.*
- ☐ *WESTBROOK MECHANISM WITH 211 SPECIES IN 1174 REACTIONS.*
- ☐ *STAR-CD + CHEMKIN III NEXT?*



-17º ATDC 792 - 879 K

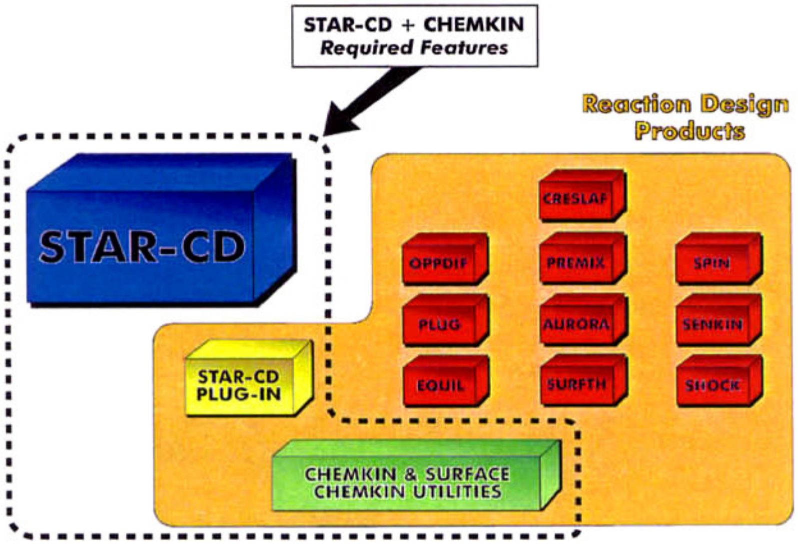


-3º ATDC 1850 - 2010 K



ATDC 1790 - 2000 K

CHEMKIN + STAR-CD



NASA GLENN 26-STEP MECHANISM

$C_3H_8 + N_2 \Rightarrow 3CH + 5H + N_2$

$CH + OH \leftrightarrow CO + H_2$

$CH + O \leftrightarrow CO + H$

$2CH + M \leftrightarrow C_2H_2 + M$

$C_2H_2 + O_2 \leftrightarrow 2CO + H_2$

$N_2 + O \leftrightarrow N + NO$

$N_2 + H_2 + M \leftrightarrow 2NH + M$

$NH + O \leftrightarrow NO + H$

$N_2O + OH \leftrightarrow N_2 + HO_2$

$H_2 + OH \leftrightarrow H_2O + H$

$H + O_2 \leftrightarrow O + OH$

$O + HO_2 \leftrightarrow OH + O_2$

$H + HO_2 \leftrightarrow H_2 + O_2$

$CO + OH \leftrightarrow CO_2 + H$

$N + O_2 \leftrightarrow NO + O$

$CH + NO \leftrightarrow NH + CO$

$N_2O + O \leftrightarrow 2NO$

$N_2O + H \leftrightarrow N_2 + OH$

$H_2 + O \leftrightarrow H + OH$

$H + O_2 \leftrightarrow HO_2$

$H_2 + 2H \leftrightarrow 2H_2$

$O_2 + M \leftrightarrow 2O + M$

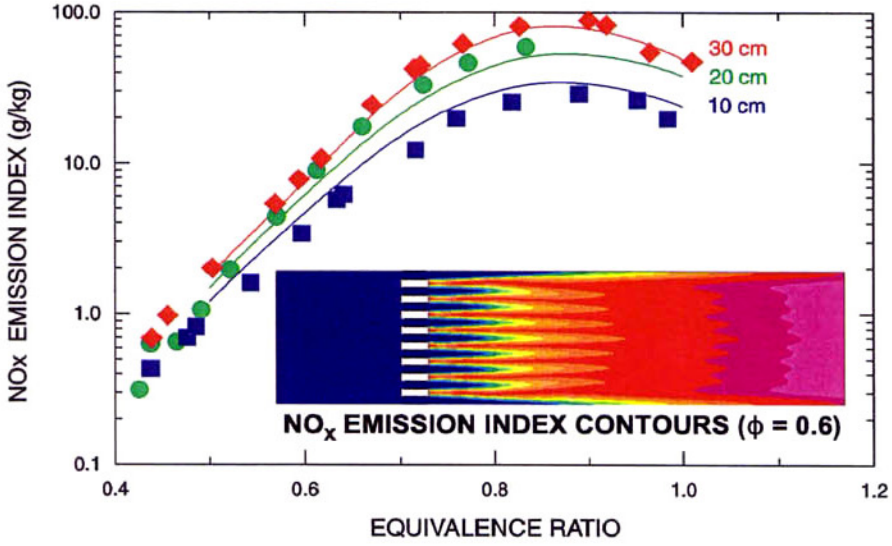
$CO + HO_2 \leftrightarrow CO_2 + OH$

$N + OH \leftrightarrow NO + H$

$NH + NO \leftrightarrow N_2O + H$

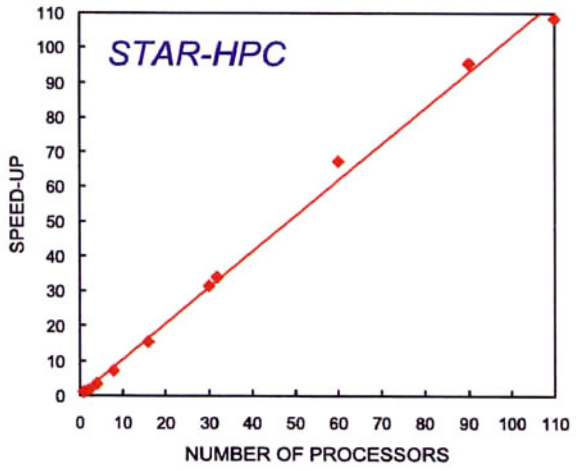
$N_2O + O \leftrightarrow N_2 + O_2$

NASA LeRC LPP FLAME TUBE ANALYSIS



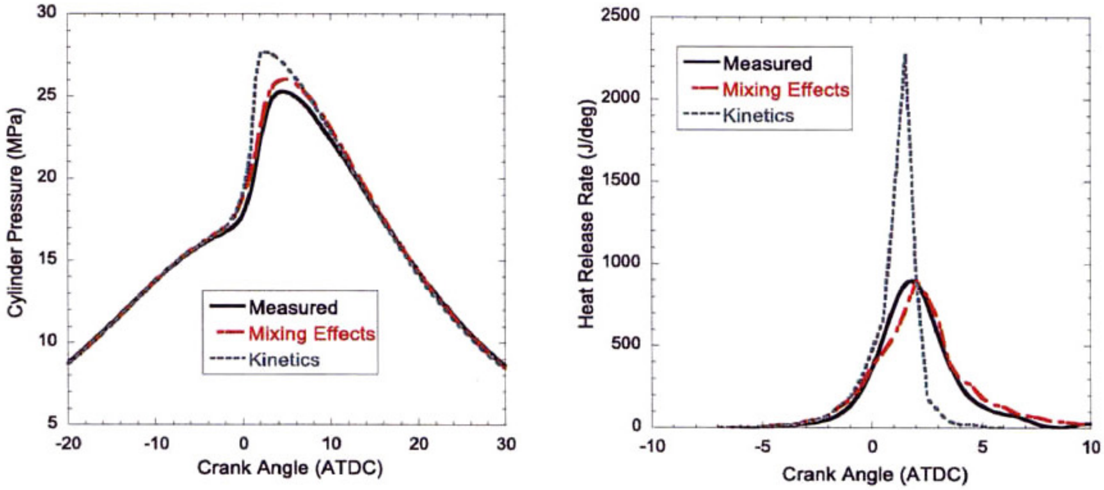
PARALLEL COMPUTING

- *PARALLEL COMPUTING AND COMPUTER ADVANCES MAKE ANALYSES WITH DETAILED CHEMISTRY POSSIBLE.*
- *MILLION+ CELL STAR-CD GE COMBUSTOR ANALYSIS TOOK 75 CPU HOURS IN 1997 ON 4 SP2 NODES – LESS THAN A DAY ON WINTERHAWK II TODAY.*
- *DAIMLER PERFORMS FULL CYCLE ENGINE SIMULATIONS (INCLUDING SPRAYS AND COMBUSTION) OVERNIGHT WITH 64 CPU SGI ORIGIN.*



KINETICS AREN'T ALWAYS ENOUGH!

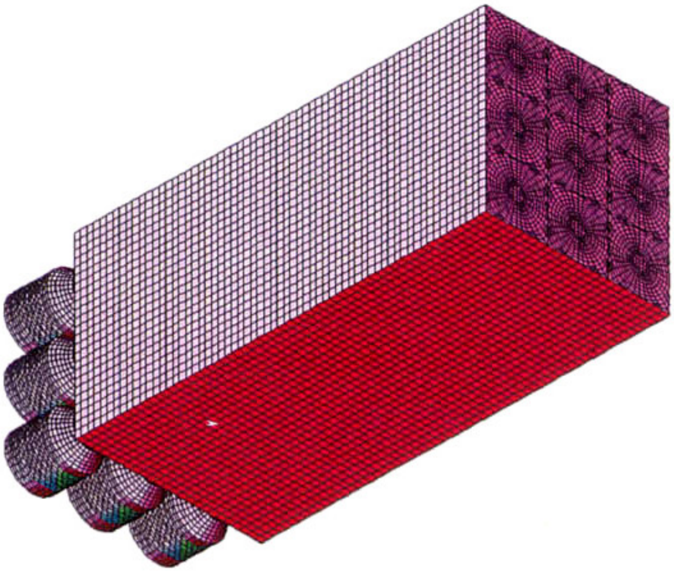
VOLVO TD-100 HEAVY DUTY DIESEL ANALYSIS BY U OF WISCONSIN



COMBUSTION-TURBULENCE INTERACTION

- ☐ *TURBULENCE CAN STRONGLY AFFECT THE COMBUSTION PROCESS.*
- ☐ *A NUMBER OF APPROACHES ARE AVAILABLE TO DESCRIBE THIS INTERACTION IN STAR-CD:*
  - ○ *EDDY BREAK-UP (EBU).*
  - ○ *COMBINED TIMESCALE (ALSO COMBINED KINETICS AND EBU).*
  - ○ *EQUILIBRIUM PRESUMED PROBABILITY DENSITY FUNCTION (PPDF).*
  - ○ *LAMINAR FLAMELET PPDF (COMING SOON).*
  - ○ *FLAME AREA MODELS.*
- ☐ *EVOLVED PDF METHOD – MONTE CARLO TECHNIQUE FOR EXAMPLE – MAY PROVIDE A BETTER DESCRIPTION OF THE COMBUSTION-TURBULENCE INTERACTION, BUT THE COST IS PROHIBITIVE NOW.*

LeRC LDI FLAME TUBE ANALYSIS



LeRC LDI FLAME TUBE ANALYSIS

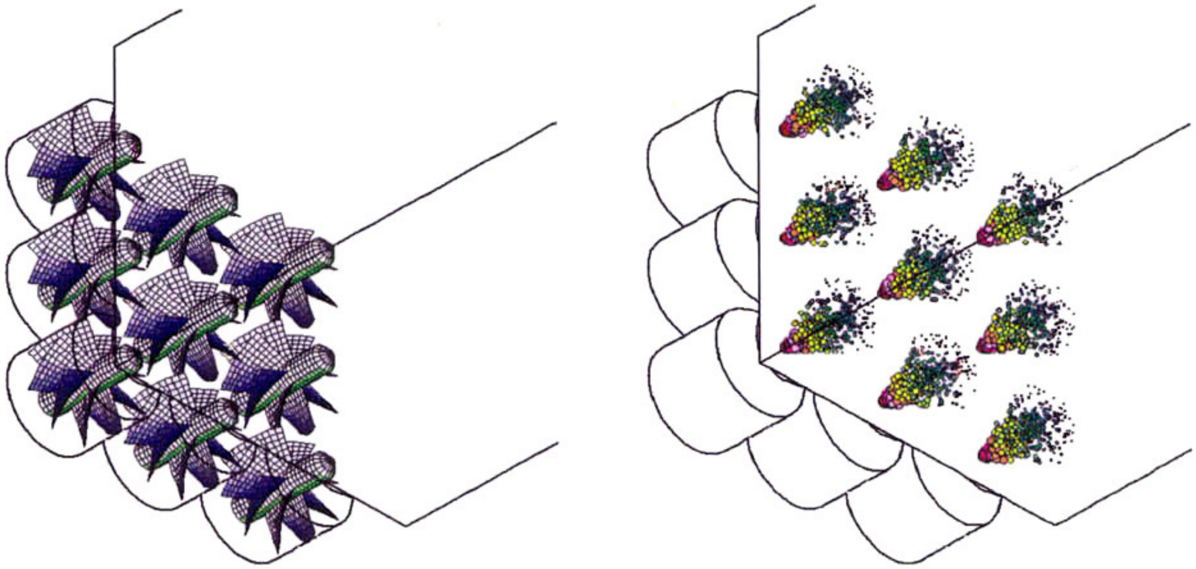
- ☐ *FUEL INJECTION DESCRIBED WITH EFFECTIVE NOZZLE MODEL – INJECTION CAN ALSO BE DESCRIBED WITH USER CODING.*
- ☐ *SPRAY DESCRIBED BY STOCHASTIC LAGRANGIAN MODEL WITH BREAKUP, TURBULENT DISPERSION, AND COLLISION SUB-MODELS.*
- ☐ *TURBULENCE MODELED WITH CHEN k-$\varepsilon\epsilon$ MODEL WITH WALL FUNCTIONS.*
- ☐ *COMBUSTION SIMULATED BY MONGIA COMBINED TIMESCALE MODEL:*

$$C_XH_Y + (1/2\,X + 1/2\,Y)\,O_2 \Rightarrow X\,CO + 1/2\,Y\,H_2O$$

$$CO + 1/2\,O_2 \Rightarrow CO_2$$

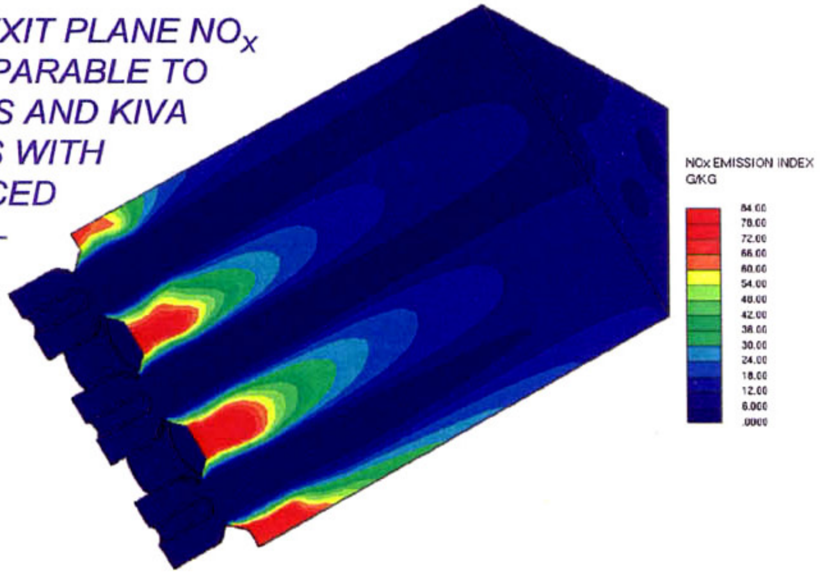
- ☐ *THERMAL NO_X FORMATION DETERMINED WITH JOINT SCALAR PPDF POST-PROCESSOR.*

LeRC LDI FLAME TUBE ANALYSIS



LeRC LDI FLAME TUBE ANALYSIS

PREDICTED EXIT PLANE NO_X LEVELS COMPARABLE TO EXPERIMENTS AND KIVA PREDICTIONS WITH LEWIS REDUCED MECHANISM – CHEMKIN + STAR-CD NEXT!



JOINT SCALAR PPDF NO$_X$ POST-PROCESSOR

- ☐ *ASSUME THAT THERMAL NO$_X$ FORMATION CAN BE DECOUPLED FROM COMBUSTION CHEMISTRY AND, HENCE, "POST-PROCESSED."*
- ☐ *EXTENDED ZEL'DOVICH THERMAL NO$_X$ MECHANISM WITH QUASI-STEADY STATE N ATOM AND EQUILIBRIUM O ATOM, ETC. ASSUMPTIONS.*
- ☐ *CHEMISTRY-TURBULENCE INTERACTION (NUMERICALLY INTEGRATED):*

$$\bar{R} = \frac{\int_0^1 R_{\bar{C}_1, \bar{C}_2 \ldots \bar{?}}\, \mathrm{q}^{a-1}(1-\mathrm{q})^{b-1}\, d\mathrm{q}}{\int_0^1 \mathrm{q}^{a-1}(1-\mathrm{q})^{b-1}\, d\mathrm{q}}$$

$$a = \frac{1-S}{S}\bar{\mathrm{q}} \qquad b = \frac{1-S}{S}\left(1-\bar{\mathrm{q}}\right) \qquad \mathrm{q} = \frac{T - T_{\min}}{\mathrm{T_b} - T_{\min}}$$

PRESUMED (ASSUMED SHAPE) PDF MODEL

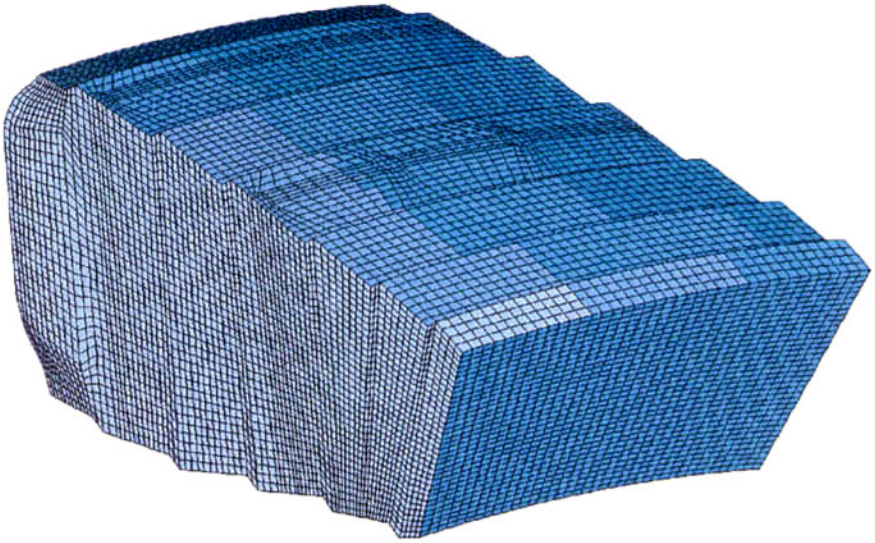
- ☐ *DUE TO TURBULENCE, LOCAL MIXTURE FRACTION, f, IS A RANDOM VARIABLE. SCALAR CONCENTRATIONS DEPEND ON MIXTURE FRACTION. THUS, AVERAGE SCALAR FIELD IS GIVEN BY:*

$$\mathrm{f} = \int_0^1 \hat{\mathrm{f}}\,(f)\,P(f)\,df$$

WHERE P(f) IS PROBABILITY DENSITY FUNCTION (PDF) REPRESENTING TURBULENT FLUCTUATIONS OF MIXTURE FRACTION (BETA FUNCTION USED IN STAR-CD) AND $\hat{\mathrm{f}}(\mathrm{f})$ DESCRIBES CHEMISTRY RELATION BETWEEN SCALARS AND MIXTURE FRACTION.

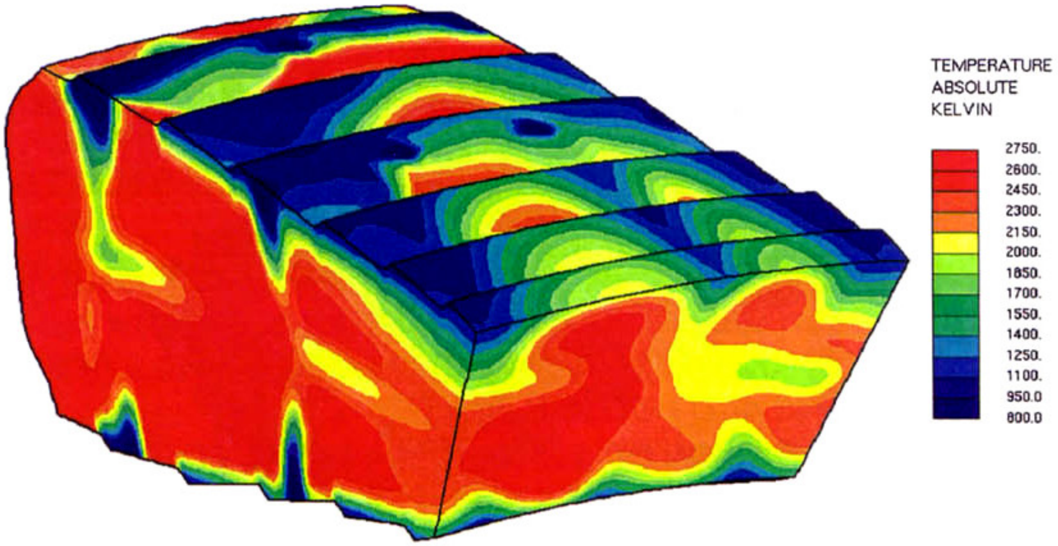
- ☐ *IN THE PRESENT VERSION OF STAR-CD, CHEMICAL EQUILIBRIUM PROVIDES THIS CHEMISTRY RELATIONSHIP – IN NEXT VERSION, LAMINAR FLAMELET PPDF USING OPPDIF WILL BE AVAILABLE.*

GE CFM56 COMBUSTOR SECTOR ANALYSIS



2ND INTERNATIONAL WORKSHOP ON CHEMKIN
IN COMBUSTION

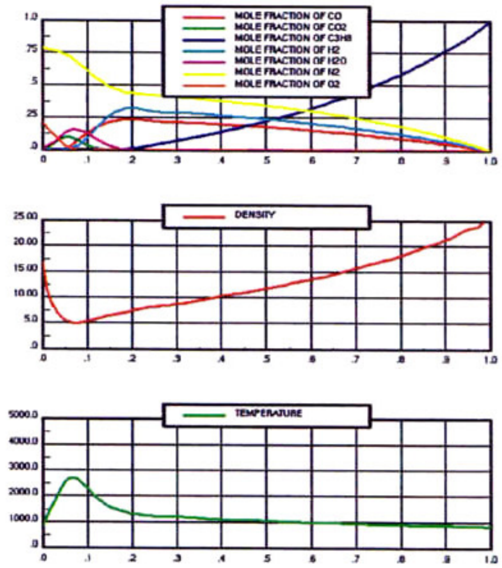
GE CFM56 COMBUSTOR SECTOR ANALYSIS



2ND INTERNATIONAL WORKSHOP ON CHEMKIN
IN COMBUSTION

GE CFM56 COMBUSTOR SECTOR ANALYSIS

- COMBUSTION ANALYSIS WITH EQUILIBRIUM PPDF MODEL – SEVEN SPECIES CONSIDERED.
- INJECTOR SWIRL FLOW AND VAPORIZED FUEL DISTRIBUTION DEFINED WITH USER CODING FROM EXPERIMENTAL DATA.
- EXIT TEMPERATURE PATTERN MATCHES EXPERIMENTAL DATA.
- ANALYSIS TOOK ~11 HOURS ON AN IBM 590 WORKSTATION – MODEL HAS 150,000 CELLS.



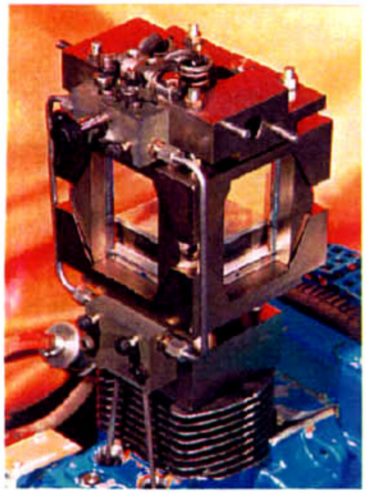
WELLER FLAME AREA MODEL

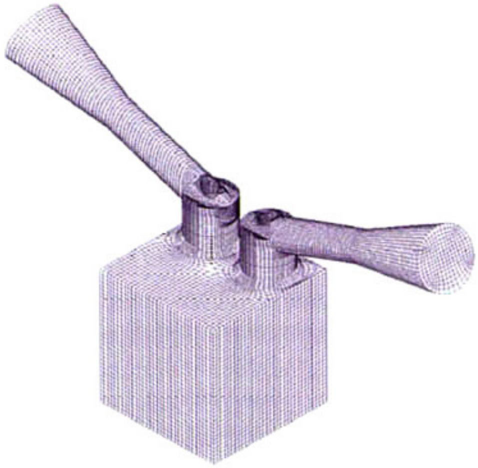
- FLAME ASSUMED TO BE INFINITESIMALLY THIN INTERFACE BETWEEN BURNT AND UNBURNT GASES – TURBULENCE WRINKLES FLAME SURFACE.
- REGRESS VARIABLE (VARIES FROM 1 → 0 DURING BURN) CALCULATED WITH TRANSPORT EQUATION:

$$\frac{\partial(\bar{r}\ \tilde{b})}{\partial t} + \nabla\circ\left(\bar{r}\ \tilde{U}\tilde{b}\right) - \nabla\circ\left(\bar{r}\ \tilde{D}_b\nabla\tilde{b}\right) = -\,\bar{r}_u\,\Xi\,\mathrm{U}_l\left|\nabla\tilde{b}\right|$$

- WRINKLE FACTOR, X , IS TURBULENT TO LAMINAR FLAME AREA RATIO.
- LAMINAR FLAME SPEED, U_l , BASED ON EXPERIMENTAL MEASUREMENT OR NUMERICAL SIMULATION USING DETAILED CHEMISTRY WITH CHEMKIN.

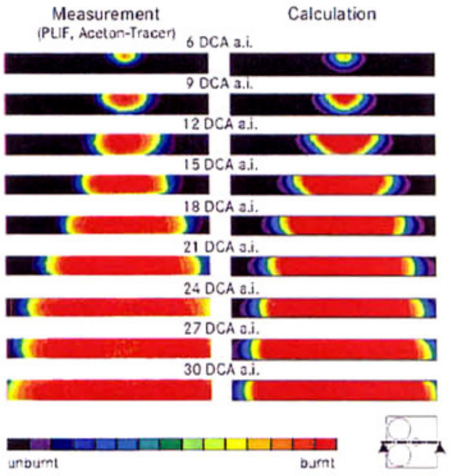
SQUARE PISTON RESEARCH ENGINE STUDY

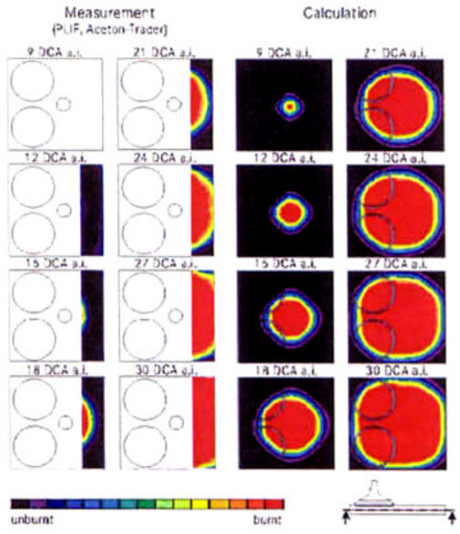




HEEL, B., ET AL., "VALIDATION OF SI COMBUSTION MODEL OVER RANGE OF SPEED, LOAD, EQUIVALENCE RATIO, AND SPARK TIMING," INTERNATIONAL SYMPOSIUM COMODIA 97 (1997).

SQUARE PISTON RESEARCH ENGINE STUDY





RWTH G-EQUATION MODEL

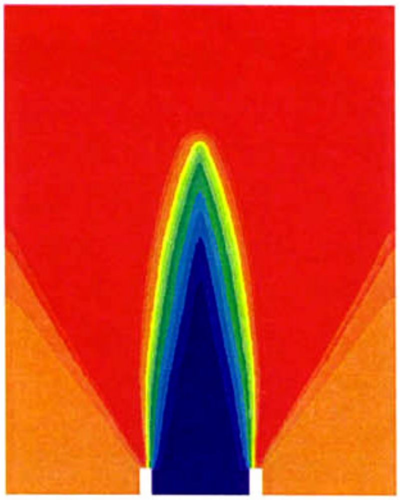
☐ *ADAPCO IS TEAMING WITH RWTH TO ADD THE G-EQUATION MODEL TO STAR-CD.*

☐ *$G(x,t)$ IS SCALAR QUANTITY WHERE $G(x,t) = G_o$ CORRESPONDS TO SPECIFIED ISO-SURFACE IN FLAME. $G > G_o$ IS PRODUCT REGION, AND $G < G_o$ IS REACTANT SIDE.*

☐ *MODEL BASED ON G-EQUATION:*

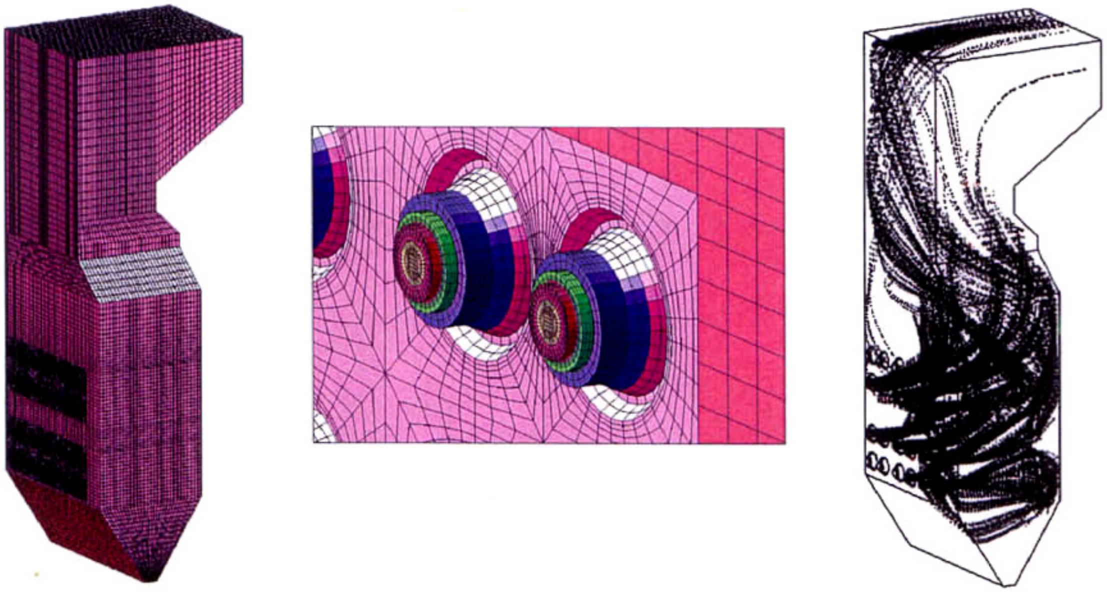
$$\rho\frac{\partial G}{\partial t} + \rho\vec{v}\circ\nabla G = \rho s_L|\nabla G|$$

WHERE THE BURNING VELOCITY, s_L, IS BASED ON UNSTRETCHED LAMINAR FLAME SPEED, FLAME FRONT CURVATURE, AND FLAME STRAIN.



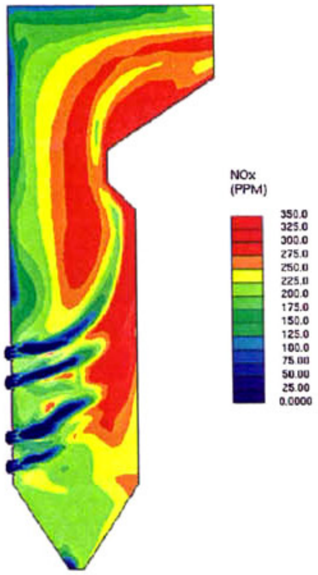
TURBULENT BUNSEN FLAME

DIDCOT COAL FIRED BOILER ANALYSIS



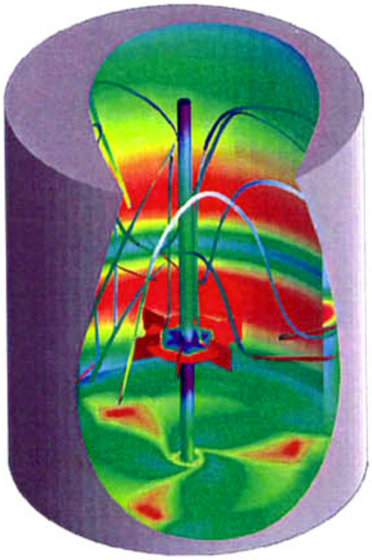
DIDCOT COAL FIRED BOILER ANALYSIS

- *PULVERIZED COAL COMBUSTION MODELS:*
  - *DEVOLATILIZATION.*
  - *VOLATILES COMBUSTION.*
  - *CHAR COMBUSTION.*
  - *THERMAL, PROMPT, AND FUEL NO_X.*
  - *PARTICIPATING MEDIA RADIATION.*
- *COAL PARTICLES UTILIZE STOCHASTIC LAGRANGIAN "SPRAY" MODEL.*
- *EXIT NO_X AND % GCV LOSS WITHIN 10% OF MEASURED VALUES.*
- *ADDITION OF ADVANCED ACERC MODELS UNDERWAY – CHEMKIN MAY BE VERY USEFUL FOR SCR, REBURN, ETC.*



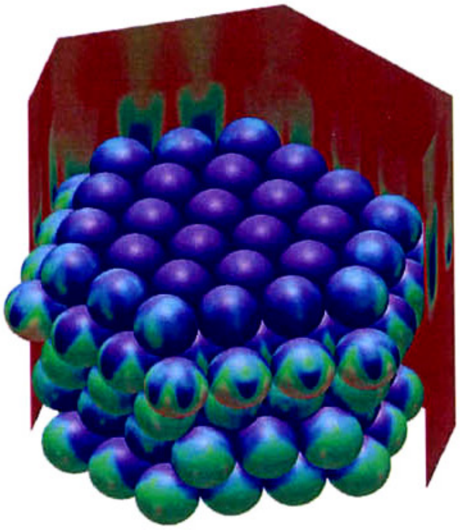
CHEMICAL PROCESSING INDUSTRY

- *STAR-CD HAS BEEN USED TO ANALYZE MANY PROBLEMS OF INTEREST TO THE CHEMICAL PROCESSING INDUSTRY, BUT MOST OF THESE ANALYSES HAVE NOT INCLUDED THE CHEMISTRY ITSELF.*
- *EXAMPLE: PHARMACEUTICAL FERMENTATION PROCESS HAD LOWER YIELD IN TANK WITH MINOR GEOMETRY CHANGES. STAR-CD USED TO STUDY FLOW DIFFERENCES DUE TO THESE MODIFICATIONS.*
- *CHEMKIN + STAR-CD WILL ALLOW DETAILED CHEMISTRY TO BE ADDED.*



CFD AND CATALYTIC REACTING SYSTEMS

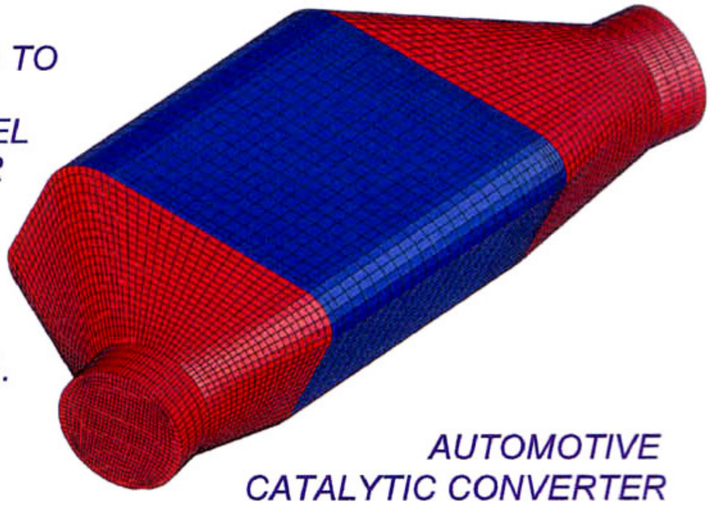
- CATALYSTS ARE INCREASINGLY BEING USED TO ENHANCE REACTOR YIELDS, REDUCE POLLUTANT EMISSIONS, ETC.
- AT PRESENT, USER CODING IS NEEDED IN STAR-CD TO MODEL SIMPLIFIED CHEMISTRY, SPECIES TRANSPORT, AND HEAT TRANSFER BY REPRESENTATIVE CHANNEL OR THIN FILM METHODS.
- SURFACE CHEMKIN IS ALSO BEING COMBINED WITH STAR-CD TO MODEL THESE SYSTEMS.



FIXED BED REACTOR

CFD AND CATALYTIC REACTING SYSTEMS

- ADAPCO IS COMBINING CHEMKIN, SURFACE CHEMKIN, AND STAR-CD TO IMPROVE ITS MODELS AUTOMOTIVE AND DIESEL CATALYTIC CONVERTER SYSTEMS, INCLUDING:
  - SELECTIVE CATALYTIC REDUCTION (SCR).
  - LOW NO_X TRAP (LNT).
  - CONTINUOUS REGENERATION TRAP (CRT).



AUTOMOTIVE CATALYTIC CONVERTER

CONCLUSIONS

- *COMMERCIAL CFD CODES, LIKE STAR-CD, ARE POWERFUL TOOLS FOR ANALYZING REACTING FLOW SYSTEMS.*
- *HOWEVER, ROOM EXISTS FOR IMPROVEMENT OF CHEMISTRY AND OTHER PHYSICAL MODELS.*
- *ADAPCO'S APPROACH IS TEAMING WITH UNIVERSITIES, LABORATORIES, AND COMMERCIAL VENDORS (LIKE REACTION DESIGN) TO MERGE THEIR MODELS WITH STAR-CD.*
- *ADAPCO IS ALWAYS LOOKING FOR BETA TESTERS TO TRY OUT THESE NEW CAPABILITIES.*

ADAPCO MODELING PARTNERSHIPS

REACTION DESIGN

RHEINISCH-
WESTFÄLISCHE
TECHNISCHE
HOCHSCHULE
RWTH

FOR MORE INFORMATION CONTACT:
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Advanced
Combustion
Engineering
Research
Center

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VIVAT COMBUSTO SEMPER

Catalytic Combustion: State of the Art and Modeling Needs

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Catalytic combustion has been applied in numerous devices such as catalytic igniters, portable heaters, home heating appliances, exhaust treatment systems, and removal of volatile organic compounds. For some years, research and development of catalytic combustion technology have been focusing on gas turbine burners in power generation systems again. Despite recent advances in non-catalytic gas turbine technology to meet NO_x emission limits, gas turbines operated with a catalytic combustion stage are proceeding from laboratory-scale to commercial-scale testing. Use of biomass-derived fuels, fuel cell technology, and chemical synthesis seem to be becoming further driving forces for catalytic combustion R&D. A better understanding of the physical and chemical processes, the establishment of reliable models, and the development of computational tools for numerical simulation will help to overcome the challenges in catalytic combustion technology. Here, the CHEMKIN software has been proved to be a useful package for modelers.

Catalyst Materials and Reaction Kinetics

The ultimate goal of kinetics research is the development of detailed reaction mechanisms based on elementary steps. Heterogeneous reactions in catalytic combustion can principally be treated by a formalism very similar to that for gas phase reactions. A fundamental problem however is that the binding states of adsorption on the surface varies with the surface coverage of all adsorbed species, hence all reaction rates depend on all surface coverages. Furthermore, the variation in surface coverage may even lead to a change of surface structures and consequently to a completely different set of reaction rates. SURFACE CHEMKIN is capable of modeling these features, but almost no kinetic data are available describing these phenomena in detail.

Nevertheless, several surface reaction mechanisms with associated rate expressions were published based on the mean field approximation in the last decade. The mechanisms are often based on limited experimental data for a limited range of conditions. Furthermore, potential gas phase reactions have been neglected, or oversimplified models for the simulation of the surrounding flow have been used for the development of the mechanism. In some cases, the kinetic data of a published mechanism have been modified to fit new measurements, and then it is claimed that the *real* reaction mechanism has been found. The following ideas may help to overcome this unsatisfying situation: (1) distribution of reaction mechanisms in an electronic format using the same nomenclature, (2) establishment of a set of well-defined experiments for mechanism validation, (3) critical evaluation of uncertainties in the flow field and homogeneous chemistry models used, and (4) study of elementary reaction kinetics at relevant conditions (pressure and materials gap), which eventually is the basis for any reliable reaction scheme.

Among the catalyst materials applicable for catalytic combustion, platinum has been studied most extensively. However, platinum based catalysts are not used for gas turbine applications; palladium or metal-substituted hexaluminate are more common. Thus there is substantial need to establish suitable reaction mechanisms for these materials. Given their complex behavior (hysteresis, chemical interactions with the support, lack of fundamental kinetic data) it is unlikely that a reliable elementary-step based mechanism can be developed. Nevertheless, even semi-detailed mechanisms that can predict overall chemical behavior would be very useful. These mechanisms have at least to be independent of the particular flow situation.

Even though reaction kinetics of homogeneous combustion seems to be understood quite well, uncertainties remain about the low-temperature gas phase chemistry associated with catalytic combustion.

Device Geometry and Flow Field Models

Stagnation point flows on reactive disks (application: CVD) and flows through catalytic channels (application: gas turbines) have been studied extensively. The most accurate modeling approach is the solution of the multi-dimensional Navier-Stokes equations combined with a multi-component transport model and detailed homogeneous and heterogeneous reaction schemes. CFD software has therefore been coupled with packages modeling reaction kinetics. The complexity of these simulations can lead to tremendous computing time and convergence problems due to the stiffness introduced by the chemistry models. Therefore, simplified flow models are frequently used. Here, one has to make sure that the flow model and behavior in the technical device really match (e.g., impact of edge effects in stagnation flows or mass transport limitation in channel flows), otherwise any conclusions and extrapolations are risky.

Accurate numerical simulation of more complex systems such as herringbone monolithic structures and membrane reactors is still a challenge. Also the interaction of very different time scales of energy exchange in devices such as catalytic radiant burners (heat conduction in gas and solid, thermal radiation, heat release by chemical reactions) is far away from being trivial to simulate. When turbulent channel flows are simulated the poorly understood flow behavior near the (catalytic) channel wall has to be considered carefully. Using washcoat in catalytic monoliths can lead to transport limitation by pore diffusion inside the washcoat. Because this process is strongly coupled with the catalytic reaction rates more sophisticated models are needed to take this effect into account.

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Catalytic Combustion: State of the art and modeling needs

OLAF DEUTSCHMANN
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http://reaflow.iwr.uni-heidelberg.de/~dmann

- Flow field simulation
- Catalyst materials and reaction kinetics

Olaf Deutschmann, Second International Workshop on CHEMKIN in Combustion, Edinburgh/Scotland, July 30, 2000

OD_00_081

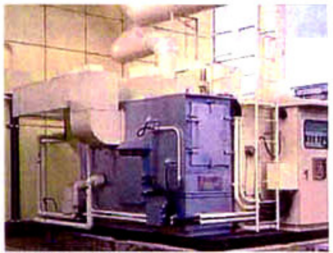
Catalytic combustion: Wide variety of applications, mainly driven by environmental concerns

IWR Universität Heidelberg

Stationary gas turbine

XONON Combustor
Catalytica Combustion Systems, Inc.

VOC removal



Catabrun, Taikisha Ltd.
www.taikisha.co.jp (15/6/2000)

Domestic gas stove

Interpid II, L&S Fireplace Shoppe,
www.lsfireplace.com (15/6/2000)

Portable radiant heater

Catalyst SystemTechnologies, Har Hotzvim, Israel

Catalytic converter

Courtesy of J. Eberspächer GmbH & Co.

Olaf Deutschmann, Second International Workshop on CHEMKIN in Combustion, Edinburgh/Scotland, July 30, 2000

OD_00_082

Reactive flow in a single channel of a catalytic monolith: Varying levels of modeling the transport processes

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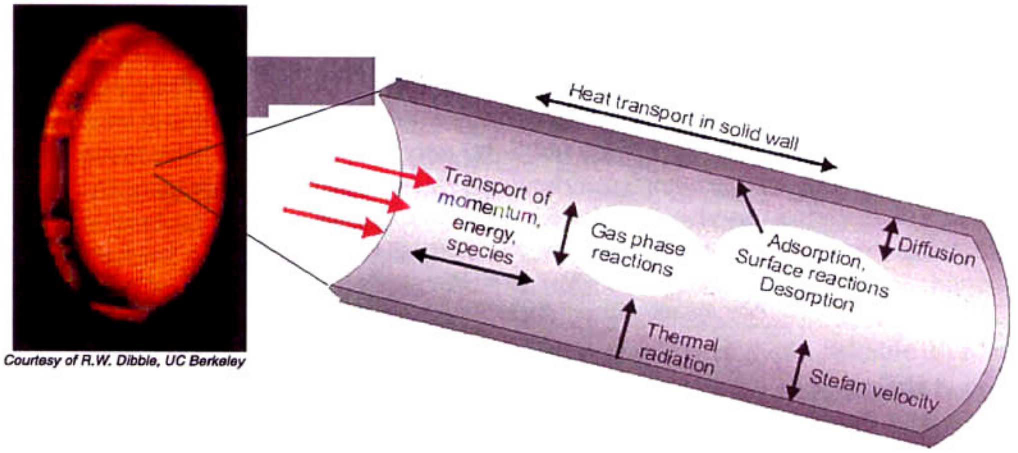

Courtesy of R.W. Dibble, UC Berkeley

	Navier-Stokes	Boundary-Layer	Plug-Flow
Axial convection	yes	yes	yes
Axial diffusion	yes	no	no
Radial diffusion	yes	yes	no

L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, Catal. Today 59 (2000) 47

Olaf Deutschmann, Second International Workshop on CHEMKIN in Combustion, Edinburgh/Scotland, July 30, 2000

OD_00_083

Ultra-Low-Emission Gas-Turbine Technology: Modeling of the Catalytic Combustion Stage

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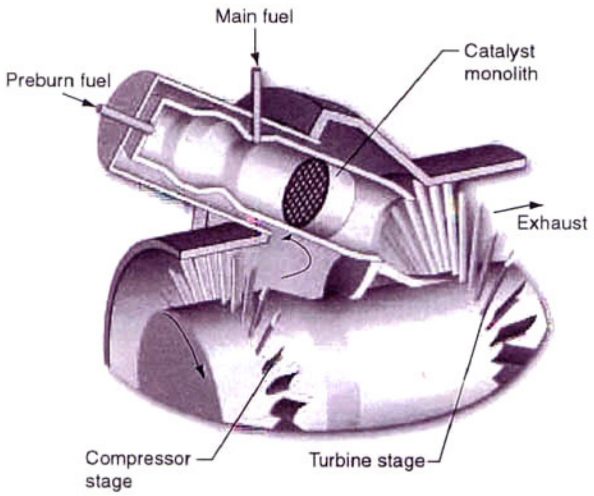
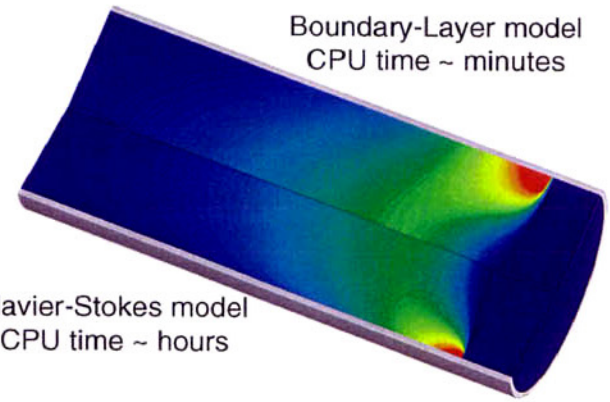


Predicted CO mass fractions in a single channel



L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, Catal. Today 59 (2000) 47

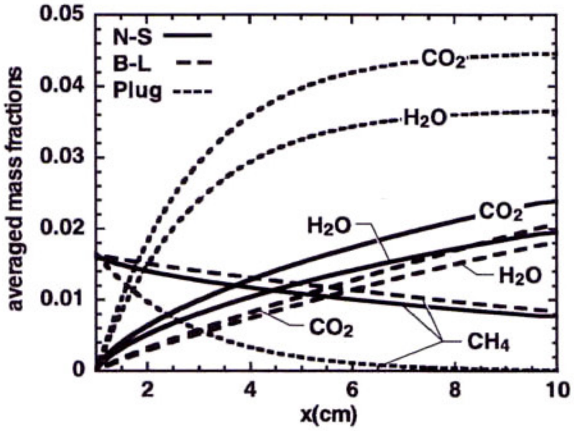
Picture: Courtesy of R.J. Kee, Colorado School of Mines

Olaf Deutschmann, Second International Workshop on CHEMKIN in Combustion, Edinburgh/Scotland, July 30, 2000

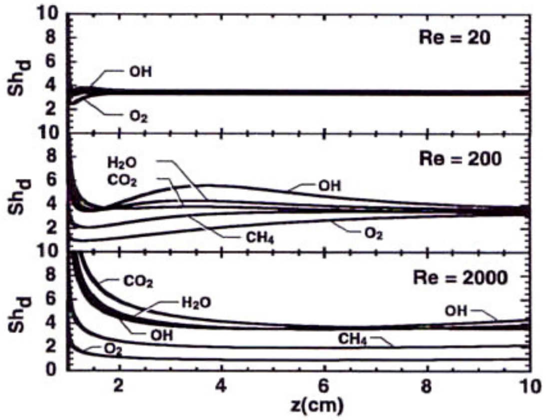
OD_00_084

Mass transport limitation in a single channel of a catalytic monolith: Caution when using the Plug-Flow model

Averaged mass fraction species profiles from the Navier-Stokes, Boundary-Layer and Plug-Flow model



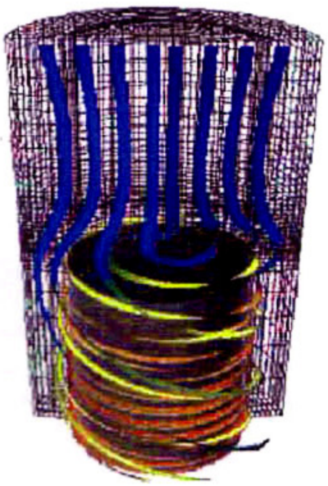
Mass-transfer coefficients for Plug-Flow model can be derived from full models

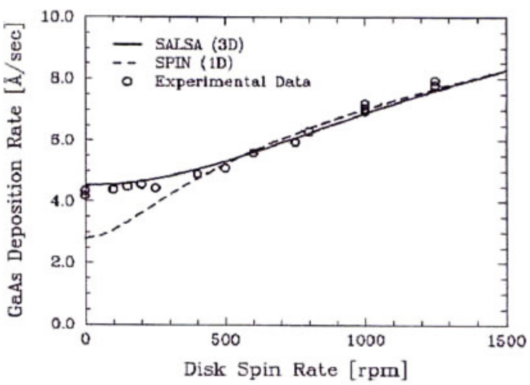


L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, Catal. Today 59 (2000) 47

Modeling CVD in a rotating disk reactor: Caution when using simplified models

Comparison of 3D (MPSalsa) and 1D (SPIN) simulation reveals weakness of the 1D model at low disk spin rates. Both codes use CHEMKIN software.

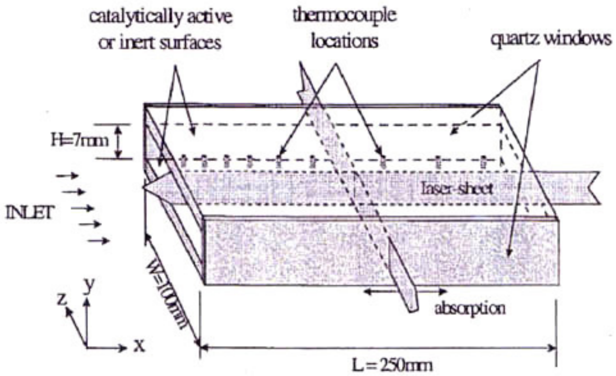


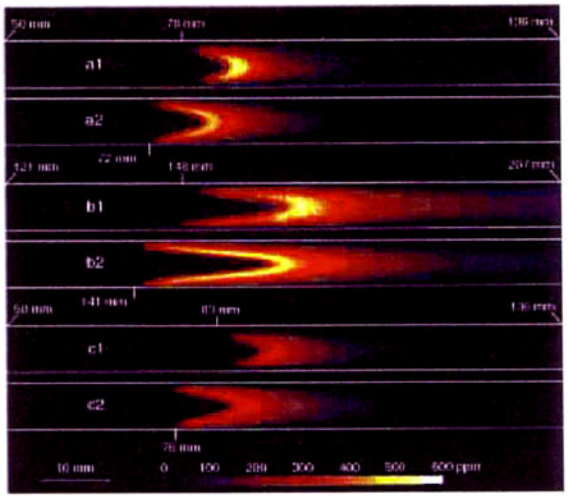


K.D. Devine, G.L. Hennigan, S.A. Hutchinson, A.G. Salinger, J.N. Shadid, R.S. Tuminaro: High Performance MP Unstructured Finite Element Simulation of Chemically Reacting Flows. Proc. of SC97, San Jose, CA, Nov. 15-21, 1997

Homogeneous ignition in catalytic combustion of methane/air mixtures over platinum

Comparison of experimentally observed (PLIF) and numerically predicted (2D NS model with detailed gas phase and surface kinetics using CHEMKIN) OH profiles in a laminar plane channel flow



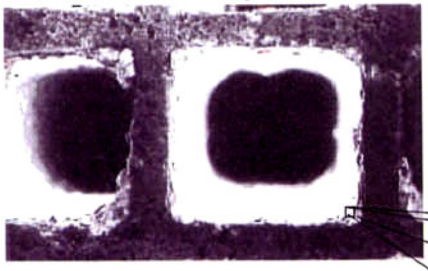


U. Dogwiler, J. Mantzaras, C. Appel, P. Benz, B. Kaeppeli, R. Bombach, A. Arnold. Proc. Combust. Inst. 27 (1998) 2275

* * *

Washcoat pore diffusion in catalytic monoliths: Potential source of transport limitation

Monolith channel: Diffusion and convection (gas phase)



Molecular diffusion

$$D_{eff} = \frac{\varepsilon_P}{\tau} D_{mol,i}$$

Knudsen-diffusion

$$D_{eff} = \frac{\varepsilon_P}{\tau} \frac{d_P}{3} \sqrt{\frac{8RT}{\pi M_i}}$$

Boundary condition at gas-surface interface

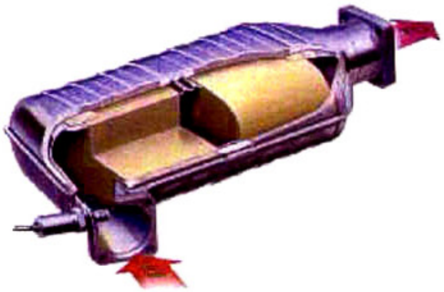
$$\eta F \dot{s}_i M_i = (j_{ir} + \rho Y_i v_{st})$$

$$\eta = \frac{tanh\,(\phi)}{\phi} \qquad \phi = L\sqrt{\frac{s_i \gamma}{D_{eff} c_{i,0}}}$$

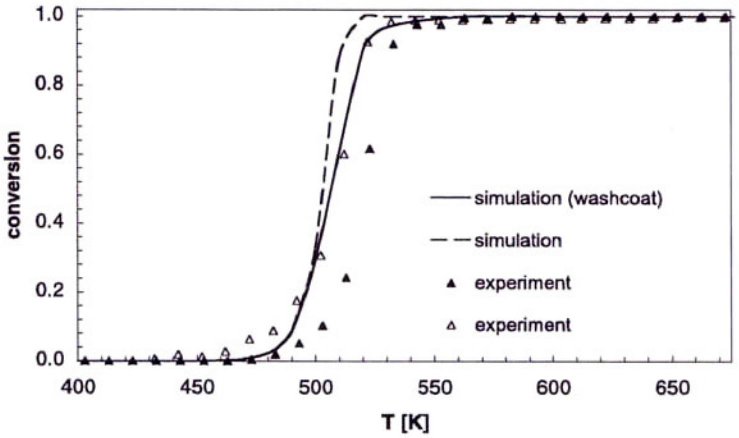
Washcoat: Diffusion in porous media

Washcoat in a single channel of an automotive catalytic converter: Impact of pore diffusion on conversion

HC-SCR on Pt/Al_2O_3: Conversion of propane as a function of temperature, simulation vs. experiment

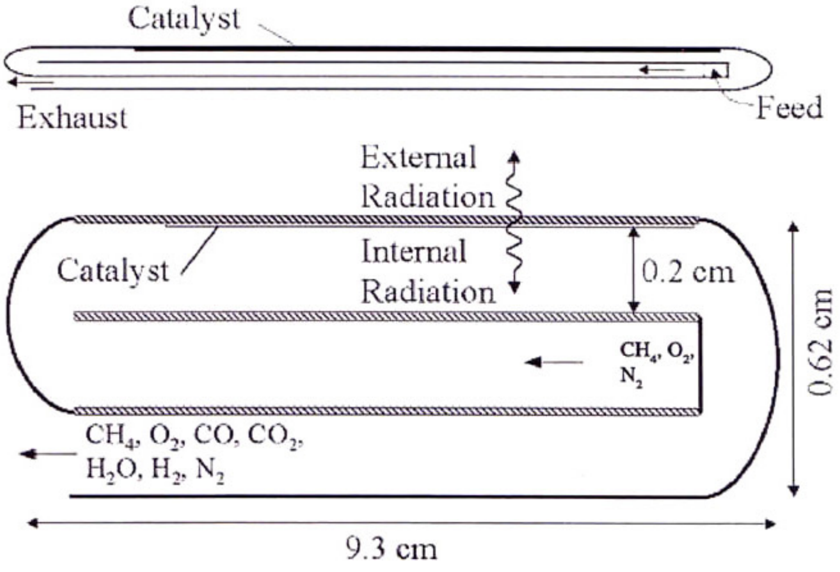


Picture: Courtesy of J. Eberspächer GmbH&Co.



(Chatterjee / Deutschmann / Warnatz, 2000)

Catalytic radiant burner with energy recuperation: Experimental setup



J. Redenius, L.D. Schmidt, O. Deutschmann, AIChE J. (submitted)

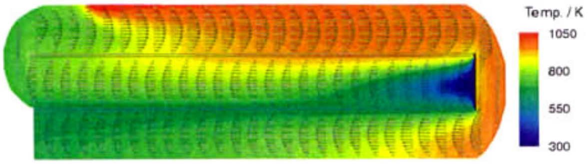
Catalytic radiant burner with energy recuperation: Simulation uses FLUENT and DETCHEM

IWR **Universität Heidelberg**

Methane

Carbon dioxide

Temperature



Water

J. Redenius, L.D. Schmidt, O. Deutschmann: AIChE J. (submitted)

FLUENT:http://www .fluent.com DETCHEM:http://www .reactiveflows.com

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Modeling surface reactions in catalytic combustion: Kinetics depends on coverage and catalyst structure

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Assumptions mostly made:

- Adsorbates are assumed to be randomly distributed on the surface (mean field approximation)
- Surface is viewed as being uniform, the local environment is not taken into account (edges, defects, terraces, different structures)

Reaction rate:

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{f_k} \prod_{i=1}^{N_g+N_s+N_b} [X_i]^{\nu'_{ik}}$$

Sticking coefficient:

$$k_{f_i}^{\text{ads}} = S_i^0 \frac{1}{\Gamma^\tau} \sqrt{\frac{RT}{2\,\pi M_i}}$$

Rate coefficient:

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] f(\theta_1, \theta_2 \ldots)$$

$$f(\theta_1,\theta_2\ldots) = \prod_i 10^{\eta_i[\theta_i]} [\theta_i]^{\mu_i} \exp\left(\frac{\varepsilon_i \theta_i}{RT}\right)$$

$$k_{r_k}(T) = \frac{k_{f_k}(T)}{K_{c_k}(T)}$$

Binding states of adsorption on the surface vary with the surface coverage of all adsorbed species.

Catalytic combustion of methane over platinum: Proposed scheme of surface reactions

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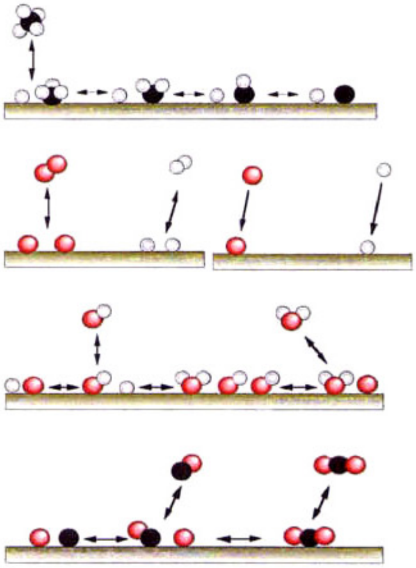

D. A. Hickman, L. D. Schmidt, AIChE J. 39 (1993), 1164.
O. Deutschmann, F. Behrendt, and J. Warnatz: Catal. Today 21 (1994), 461.

Reaction scheme for modeling catalytic ignition of H_2, CO, CH_4 on Pt in SURFACE CHEMKIN format

Reaction	A	b	E(J/mol)	Comment
H2 + 2PT(S) => 2H(S)	0.046	0.0	0	STICK, FORD /PT(S) 1/
2H(S) => H2 + 2PT(S)	3.70E+21	0.0	67400	COV /H(S) 0 0 -6000/
H + PT(S) => H(S)	1.00	0.0	0	STICK
O2+ 2PT(S) => 2O(S)	1.80E+21	-0.5	0	DUP
O2+ 2PT(S) => 2O(S)	0.023	0.0	0	STICK, DUP
2O(S) => O2 + 2PT(S)	3.70E+21	0.0	213200	COV /O(S) 0 0 -60000/
O + PT(S) => O(S)	1.00	0.0	0	STICK
H2O + PT(S) => H2O(S)	0.75	0.0	0	STICK
H2O(S) => H2O + PT(S)	1.0E13	0.0	40300	
OH + PT(S) => OH(S)	1.00	0.0	0.0	STICK
OH(S) => OH + PT(S)	1.00E13	0.0	192800	
H(S) + O(S) = OH(S) + PT(S)	3.70E+21	0.0	11500	
H(S) + OH(S) = H2O(S) + PT(S)	3.70E+21	0.0	17400	
OH(S)+ OH(S) = H2O(S) + O(S)	3.70E+21	0.0	48200	
CO + PT(S) => CO(S)	0.84	0.0	0	STICK, FORD /PT(S) 2/
CO(S) => CO + PT(S)	1.00E+13	0.0	125500	
CO2(S) => CO2 + PT(S)	1.00E+13	0.0	20500	
CO(S) + O(S) => CO2(S) + PT(S)	3.70E+21	0.0	105000	
CH4 + 2PT(S) => CH3(S) + H(S)	0.01	0.0		STICK, FORD/ PT(S) 2.3/
CH3(S)+ PT(S) => CH2(S)s + H(S)	3.70E+21	0.0	20000	
CH2(S)s + PT(S) => CH(S) + H(S)	3.70E+21	0.0	20000	
CH(S) + PT(S) => C(S) + H(S)	3.70E+21	0.0	20000	
C(S) + O(S) => CO(S) + PT(S)	3.70E+21	0.0	62800	
CO(S) + PT(S) => C(S) + O(S)	1.00E+18	0.0	184000	

Courtesey of L.L. Raja, R.J. Kee, Colorad School of Mines
http://reaflow.iwr.uni-heidelberg.de/~dmann/sm_ch4_ox_1.2_SURFACECHEMKIN

O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnatz: Proc. Comb. Inst. 26 (1996), 1747

Different kinetics proposed for CH_4 combustion on Pt: Mechansisms are often based on few experimental data

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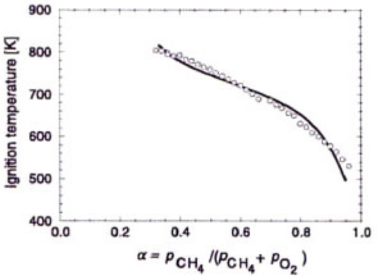
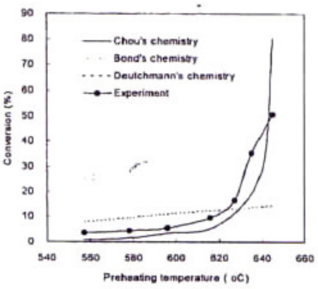
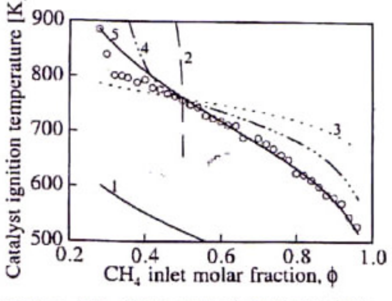


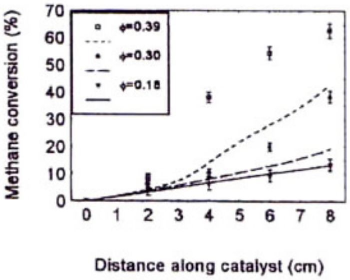
O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnatz: Proc. Comb. Inst. 26 (1996), 1747



Y.S. Seo, S.J. Cho, S.K. Kang, H.D. Shin, Catal. Today 59 (2000) 75.

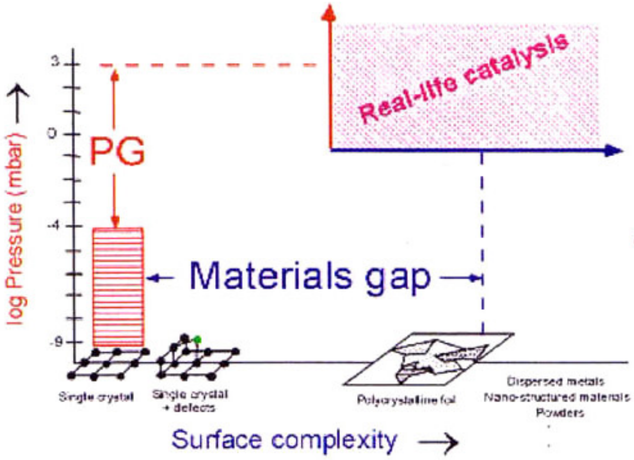


P.-A. Bui, D.G. Vlachos, P.R. Westmoreland, Surf. Sci. 385 (1997) L1029

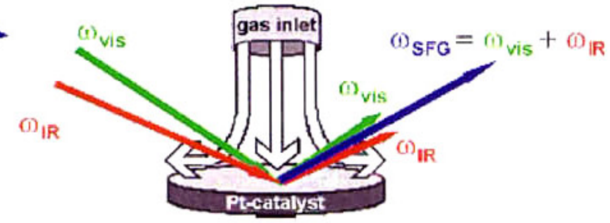


T.C. Bond, R.A. Noguchi, C.-P. Chou, R.K. Mongia, J.-Y. Chen, R.W. Dibble, Proc. Comb. Inst. 26 (1996) 1771

Kinetic data for surface reactions at practically relevant conditions and technically used catalysts



Laser-spectroscopic methods such as SFG (Sum Frequency Generation) can bridge the pressure and materials gap

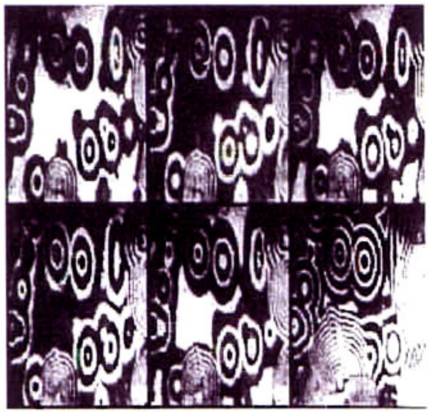


=> Quantitative determination of surface coverage with adsorbed species

R. Kissel-Osterrieder, F. Behrendt, J. Warnatz, U. Metka, H.-R. Volpp, J. Wolfrum. Proc. Combust. Inst. 28 (2000)

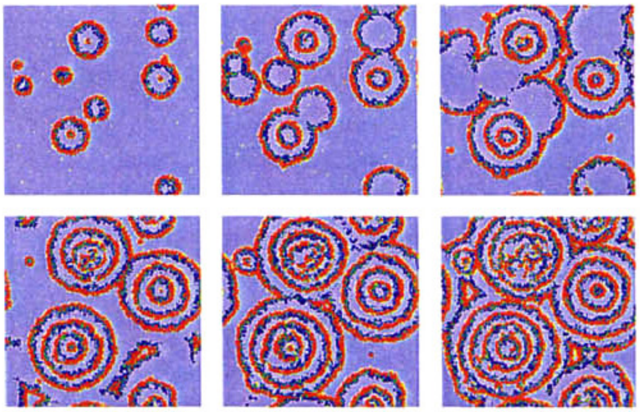
Coupling between surface structures and chemical reactions: Dynamic Monte-Carlo simulations

Catalytic oxidation of CO on platinum; 2D resolution of the non-homogeneous layers of adsorbed species; experiment vs. simulation



Pt(110), PEEM, 0.2 x 0.3 mm², T = 427 K, p_{O2}= $32 \cdot 10^{-3}$ mbar, p_{CO} $3 \cdot 10^{-3}$ mbar, Δt = 4.1/ 30 s

S. Jakubit, H.H. Rotermund, W. Engel, A. von Oertzen, G. Ertl. Phys. Rev. Lett. 65 (1990) 3013

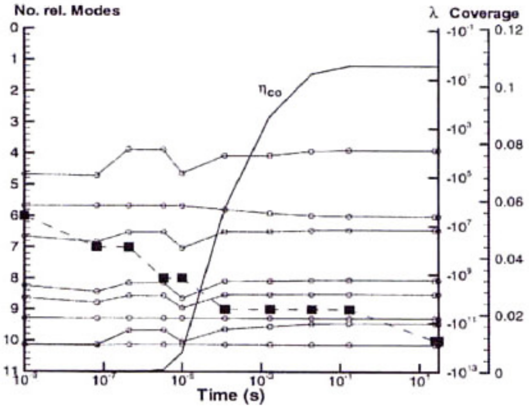


Target pattern on Pt(100), Δt = 10 s, 1000 x 1000 lattice, 0.25 x 0.25 mm², T = 490 K, p_{O2}= $50 \cdot 10^{-3}$ mbar, p_{CO} $1.5 \cdot 10^{-3}$ mbar

R. Kissel-Osterrieder, F. Behrendt, J. Warnatz. Proc. Combust. Inst. 28 (2000)

Intrinsic Low-Dimensional Manifolds of Heterogeneous Combustion Processes

Application of the ILDM approach for the reduction of a detailed reaction mechanism describing the oxidation of methane on platinum in a stagnation point flow configuration

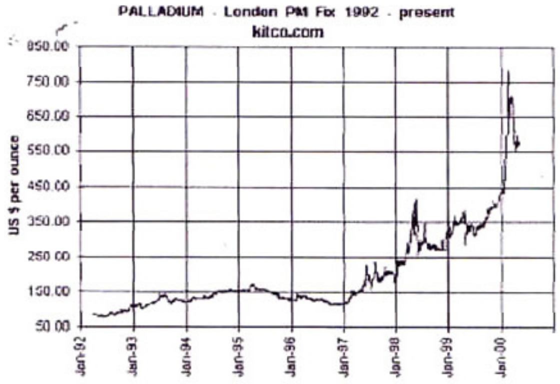


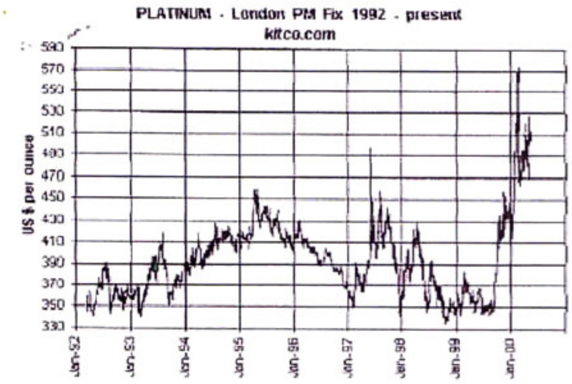
The number of relaxed modes (■) increases with time until all ten chemical time scales have relaxed (chemical equilibrium on the surface).

X. Yan, U. Maas. Proc. Comb. Inst. 28 (2000)

* * *

Catalyst materials for catalytic combustion: Variation of market prices of noble metals





Source: http://www.kitco.com, 20.07.2000

Palladium and metal-substituted hexaluminates: Catalyst materials for catalytic combustion

Palladium and metal-substituted hexaluminates are catalysts of great interest for gas turbine applications

Comparison of methane oxidation rate at 400°C, 2% CH_4 in air at 1 atm		
Material	Areal rate (10^{-7} mol m^{-2} s^{-2}	Surface area) m^2 g^{-1}) (
Pd/Al_2O_3	140	2
Pt/Al_2O_3	50	1
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	0.045	70

R.A. Dalla Betta. Catalysis Today 35 (1997) 129

Wide variety of studies on the complexity of Pd catalysts exists (phase transformation and activity of Pd/PdO, hydroxide formation, interaction with support, support sintering, vaporization, lightoff, aging)

but *no detailed reaction scheme has been established yet*

Catalytic combustion: Modeling needs

- Use of adequate flow field models for the simulation of catalytic combustion devices
- CFD tools including detailed chemistry models are meanwhile available
  but they are very time-consuming and still have problems solving very stiff systems
- Consideration of pore diffusion in washcoats
- More accurate development of heterogeneous reaction schemes needed
  (distribution of rxn mechanisms in electronic form, well-defined experiments, accurate description of flow field and potential homogeneous reactions)
- Studies of heterogeneous reaction kinetics at relevant conditions
  (pressure and materials gap)