

Introducing CHEMKIN 4.1

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**CHEMKIN in Combustion
Workshop
August 6, 2006**

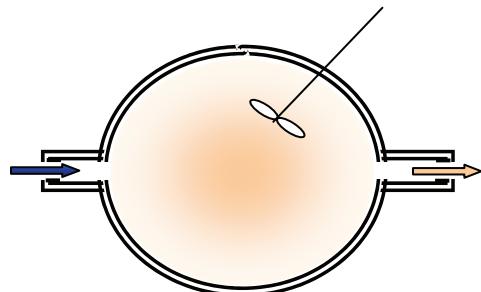


Outline

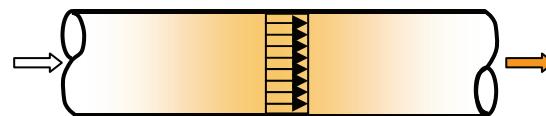
- Brief Introduction – What is CHEMKIN?
- CHEMKIN 4.1 – released July 2006
 - All New Graphical Post-processing
 - Parameter-study Facility
 - Particle Tracking Module (optional)
 - More Complex Reactor Networks
 - New Chemistry Formulations
 - Reactor Model Enhancements
- Future projects underway

Introduction

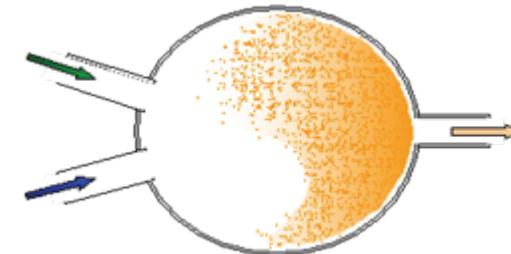
CHEMKIN® software allows focus on chemistry using engineering approximations



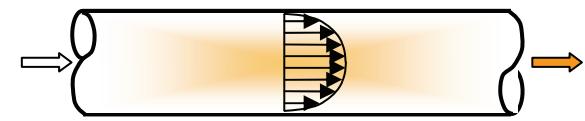
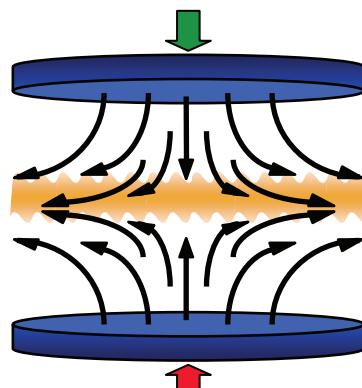
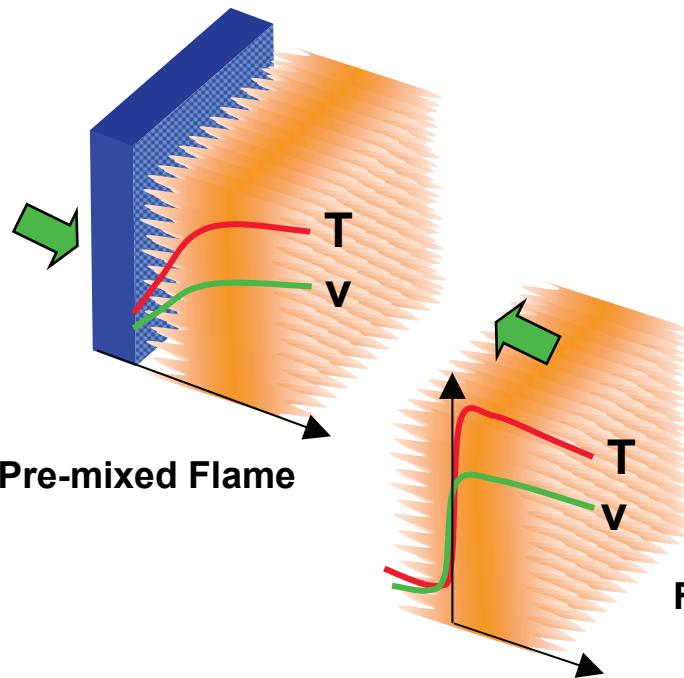
Perfectly Stirred Reactor (PSR)



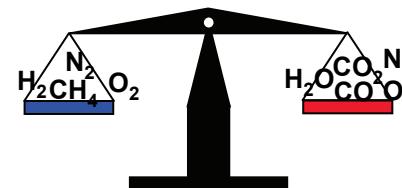
Plug-flow Reactor (PFR)



Partially Stirred Reactor



Shear-layer Channel-flow Reactor



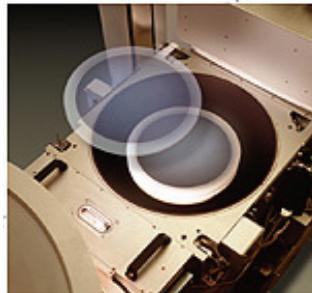
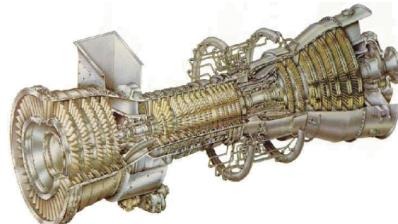
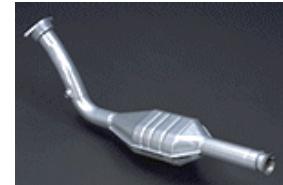
Equilibrium Calculator

The CHEMKIN approach provides efficient solutions with very short set-up time

- Supports large chemical kinetic mechanisms
 - 100s of species
 - 1000s of reactions
- Provides accurate information about reacting system
 - Trace species emissions
 - » (parts per billion or smaller)
 - Accurate handling of kinetics time and length scales
 - Complex dependency between major & minor species
 - Dominant reaction paths
 - Sensitivity of results to reaction parameters
 - *de facto* standard for describing elementary kinetics
- Computational time for single reactor ~ seconds-minutes
 - PC , Linux, UNIX

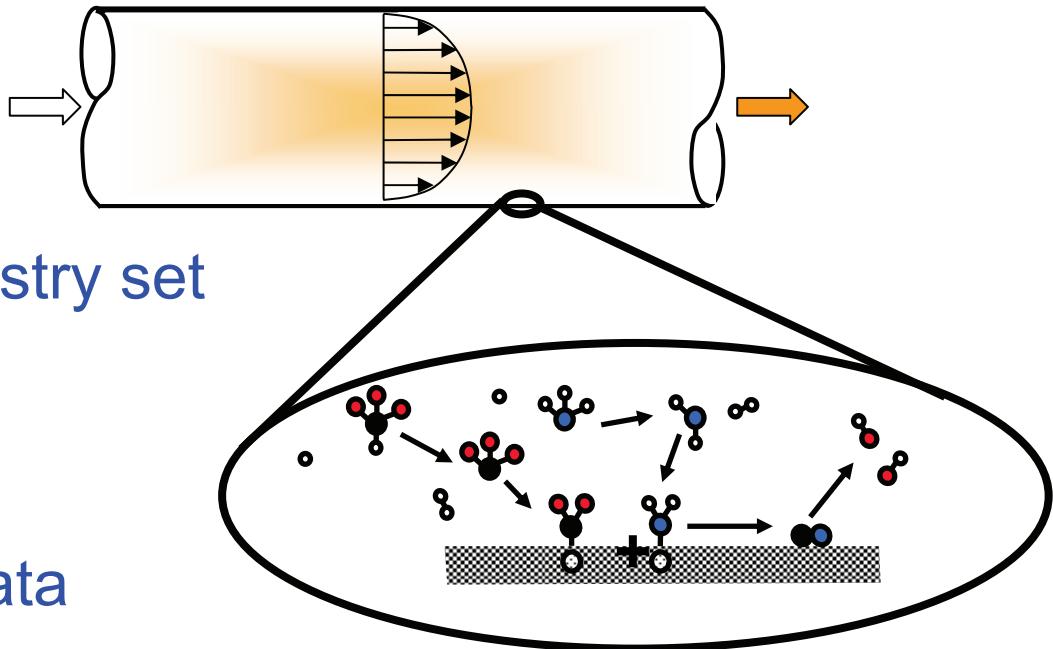
Detailed kinetics are critical for accurately modeling chemical systems

- Exhaust-gas emissions
- Ignition phenomena
- Engine knock
- Flame-speed
- Flammability limits
- Catalytic lightoff
- Chemical conversion
- Fuel reforming
- Material deposition
- Plasma processing



Using CHEMKIN requires a chemistry set, reactor definition, and operating conditions

- ▶ Choose a reactor model
- ▶ Define the geometry
- ▶ Specify operating conditions



- ▶ Define or select a chemistry set
 - Thermodynamic data
 - Gas-phase reactions
 - Surface reactions
 - Transport-property data

Reactor models predict the varying state of the gas and/or surface

- Thermodynamic state of the gas
 - Temperature / Enthalpy / Entropy
 - Pressure / Density
 - Rate of heat transfer to the environment
- Chemical state of gas / surface / solid
 - Gas-phase composition
 - Surface site coverage
 - Instantaneous deposition or etch rates
 - Species production rates
 - Rate of progress of individual reactions
- Flow state
 - Convective velocities
 - Diffusive velocities
 - Stefan velocity due to deposition
- Solution sensitivity to parameters

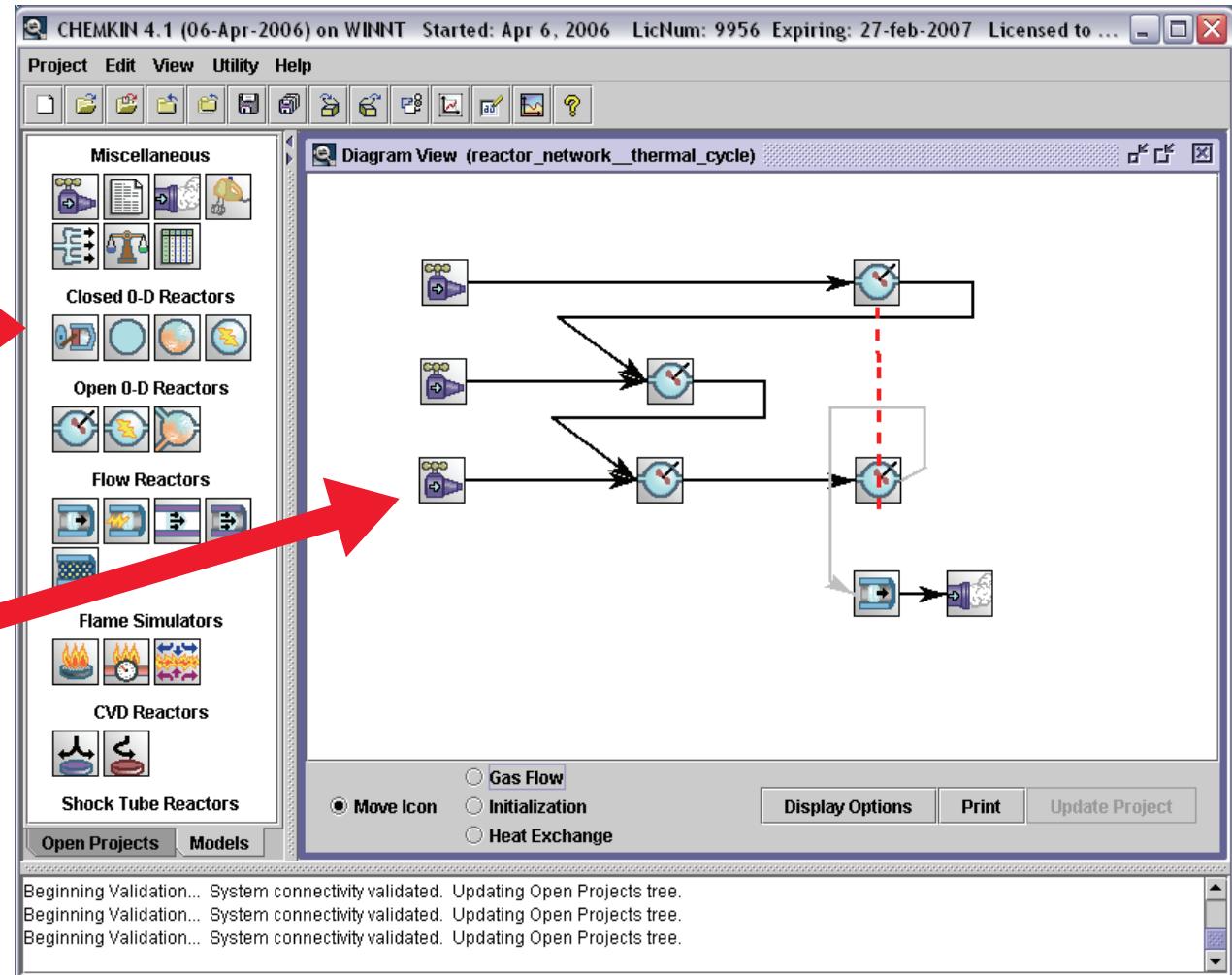
Predicted as a function of

- Time
- Distance
- Zone
- Parameter

Reactor networks are easily constructed using a visual diagram tool

Customizable palette of reactor modules

Drag and drop diagrams for reactor networks and series simulations



Reactor templates guide user inputs for problem-specific applications

- Reactor Models include:

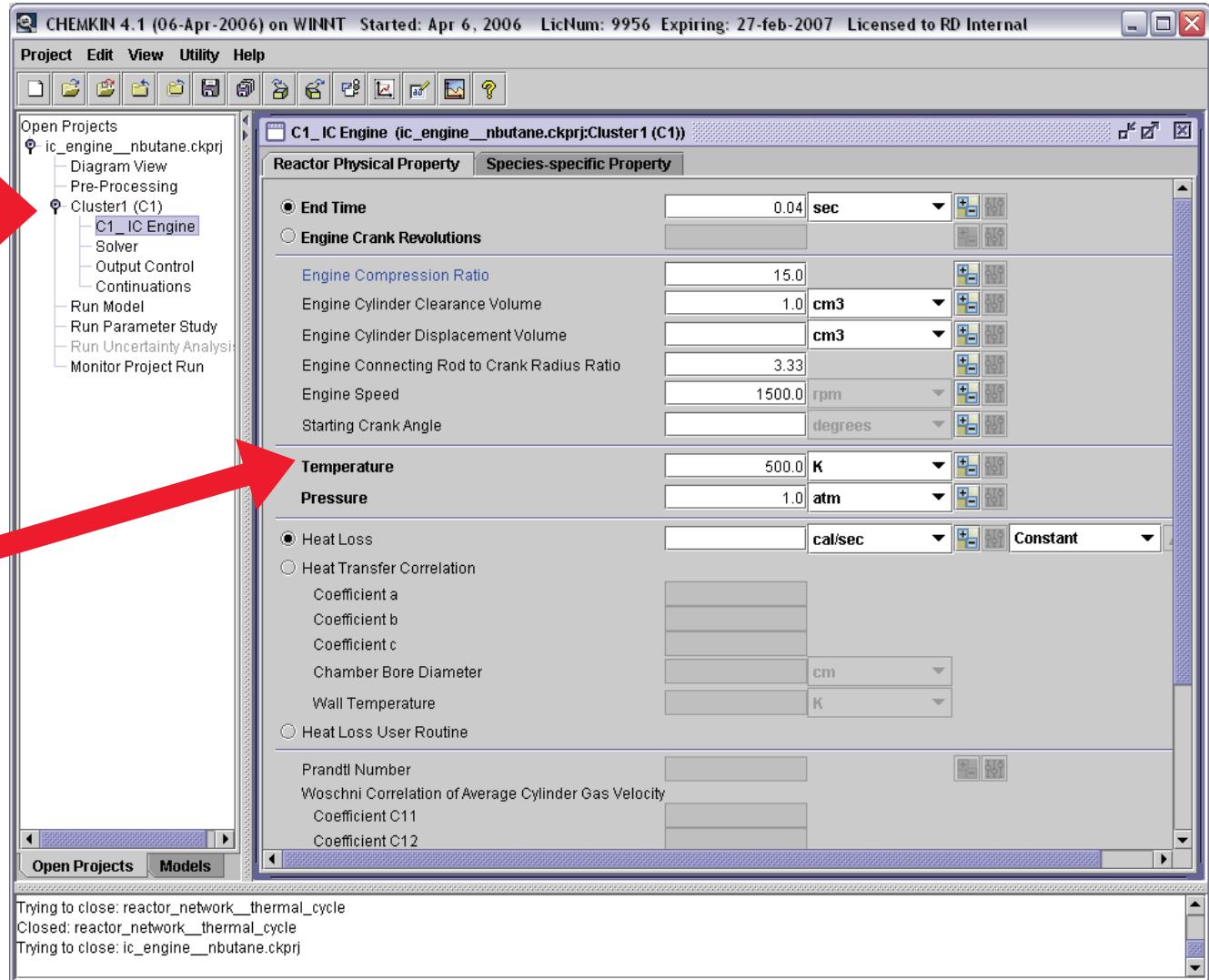
| | |
|---|---|
|  | Non-reactive Gas Mixer |
|  | Chemical and Phase Equilibrium Calculations |
|  | Mechanism Analyzer |
|  | Closed Internal Combustion Engine Simulator |
|  | Closed Homogeneous Batch Reactor |
|  | Closed Partially Stirred Reactor |
|  | Closed Plasma Reactor |
|  | Perfectly Stirred Reactor (PSR) |
|  | Plasma PSR |
|  | Partially Stirred Reactor (PaSR) |
|  | Plug Flow Reactor |

| | |
|--|--|
|  | Honeycomb Plug Flow Reactor |
|  | Plasma Plug Flow Reactor |
|  | Planar Shear Flow Reactor |
|  | Cylindrical Shear Flow Reactor |
|  | Premixed Laminar Burner-stabilized Flame |
|  | Premixed Laminar Flame-speed Calculation |
|  | Diffusion or Premixed Opposed-flow Flame |
|  | Stagnation Flow CVD Reactor |
|  | Rotating Disk CVD Reactor |
|  | Normal Incident Shock |

Descriptions of reactor configurations are through context-specific panels

Project tree with links to input panels

Input panels guide problem set-up and execution



Users can also create their own Applications through use of the CHEMKIN/API

- Subroutine Libraries are called from user programs
 - C/C++ or Fortran interfaces
 - Functions for determining chemical terms and properties
 - » Thermodynamic properties
 - » Gas-phase kinetics
 - » Surface kinetics
 - » Transport properties
 - Numerical solvers for transient and steady-state
- Detailed examples provided in standard install
 - C++ and Fortran programs and makefiles
 - Command-line / Scripting examples
 - Extracting data from XML solution data file

Summary of CHEMKIN Introduction

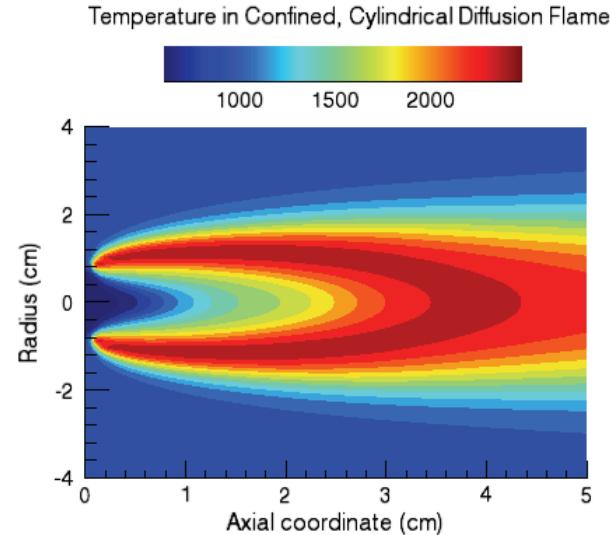
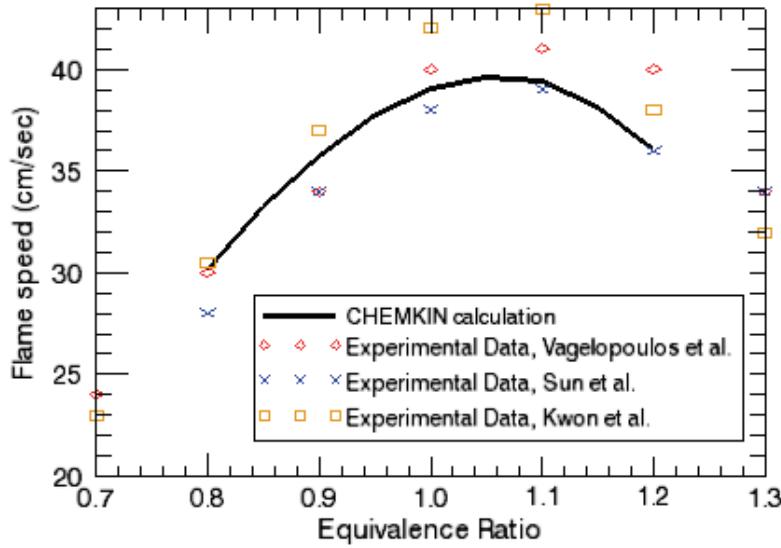
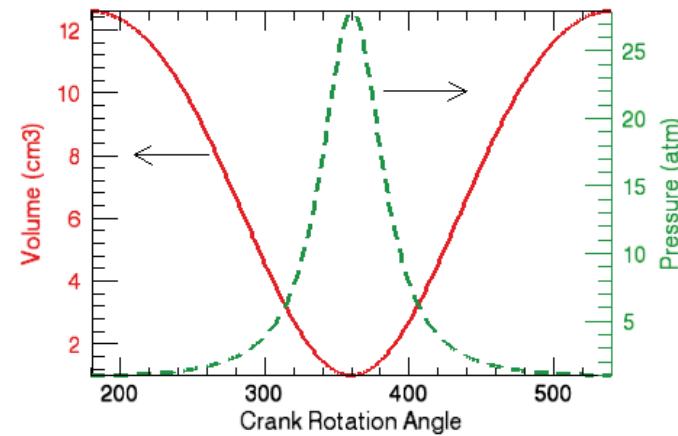
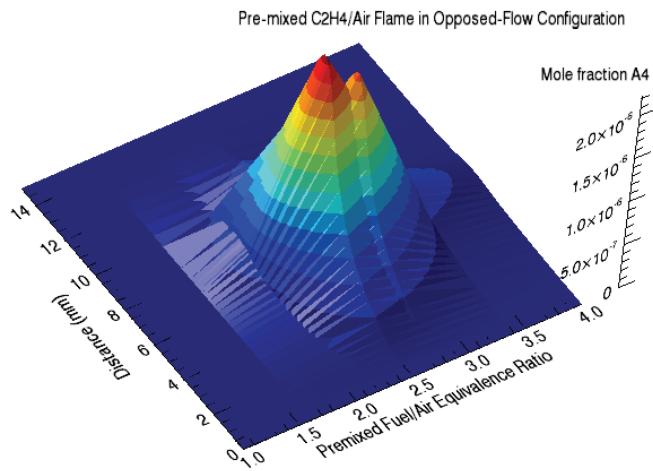
- Chemistry simulation is increasingly a key to design
- CHEMKIN's unique capabilities allow accurate kinetics
 - State-of-the art reaction-rate formulations
 - Advanced surface chemistry treatment
 - Elementary or global kinetics expressions
 - Multicomponent transport properties
 - Solution algorithms designed to dynamically adapt to stiff chemistry
- CHEMKIN provides flexible, easy-to-use interfaces
 - Fast set-up and run time
 - Visual diagramming of reactor networks
 - Extensive graphical presentation of results
 - Problem-oriented reactor models
 - Application-oriented tutorials and sample projects
 - API for advanced programming and command-line operation

CHEMKIN 4.1 Release – Important New Capabilities

Several all-new capabilities are available with the release of CHEMKIN 4.1

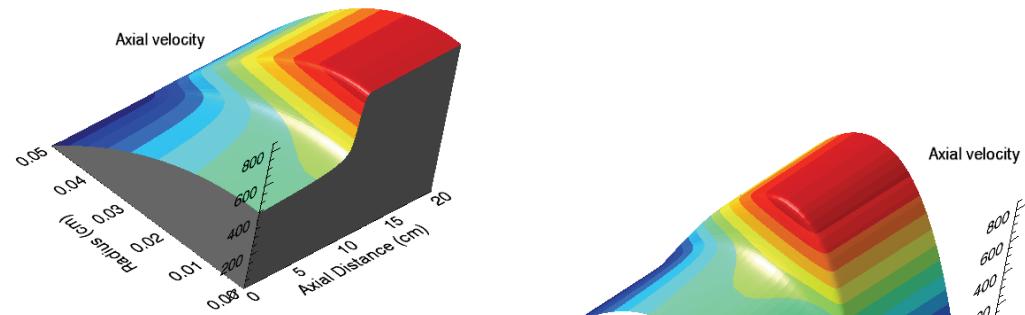
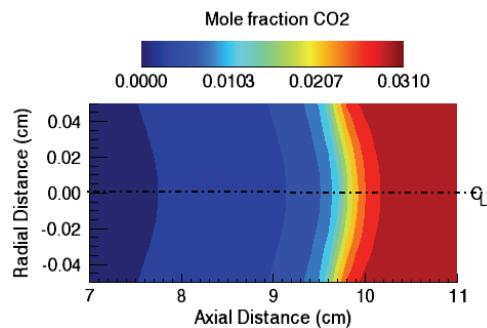
- New Visualizer / Post-processor
- New Parameter Study Facility
- New, advanced Particle Tracking Module (option)

The new Graphical Post-processor takes CHEMKIN visualization to the next level

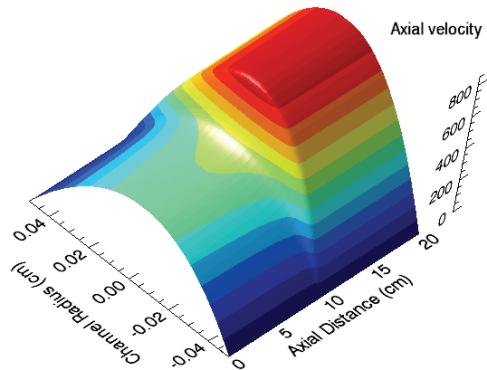


New plot types expand visualization options

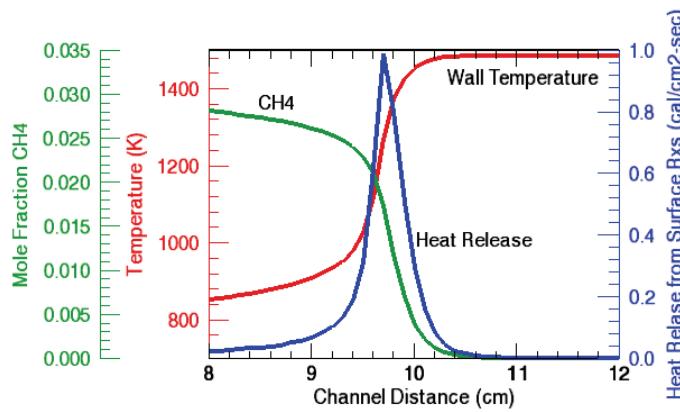
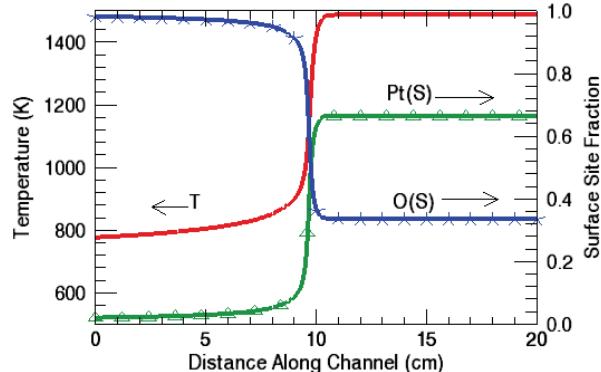
- 3-D Contour Plots
 - Interactive rotation



- Mirrored Plots
 - Axes of symmetry



- Multiple Y-axes



Users have full interactive control over formatting and presentation

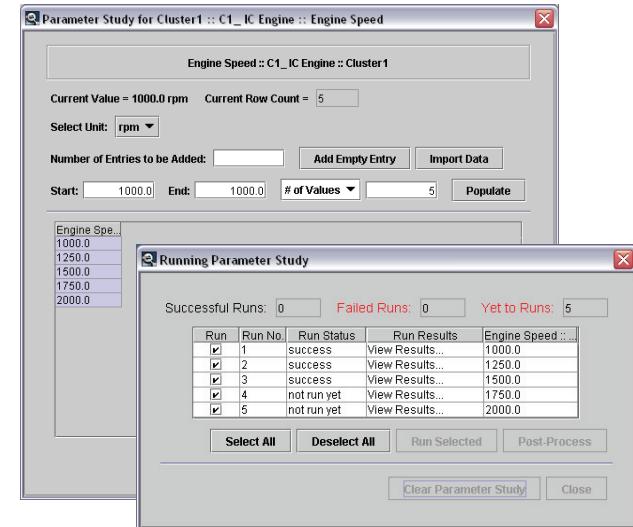
- Plot format
 - Color, line type, thickness
 - Symbol on/off, shape, size, color
 - Axis line, label, text font, ticks
 - Legend text font, spacing, outline
 - Background color, transparency
- Annotation insertions
 - Text boxes
 - Drawing, shapes, arrows
- Easy scaling of axes
- Sequential Undo (Cntrl-Z), for all operations!

Extensive save / reapply options reduce time needed for repetitive tasks

- Save / Reapply plot-set selections
 - Selections can be saved on a project-by-project basis
- Save and apply user-defined plot styles
- Record and apply “macros” for other operations
 - Mouse clicks and key strokes can be recorded

The Parameter-Study Facility automates a series of simulations

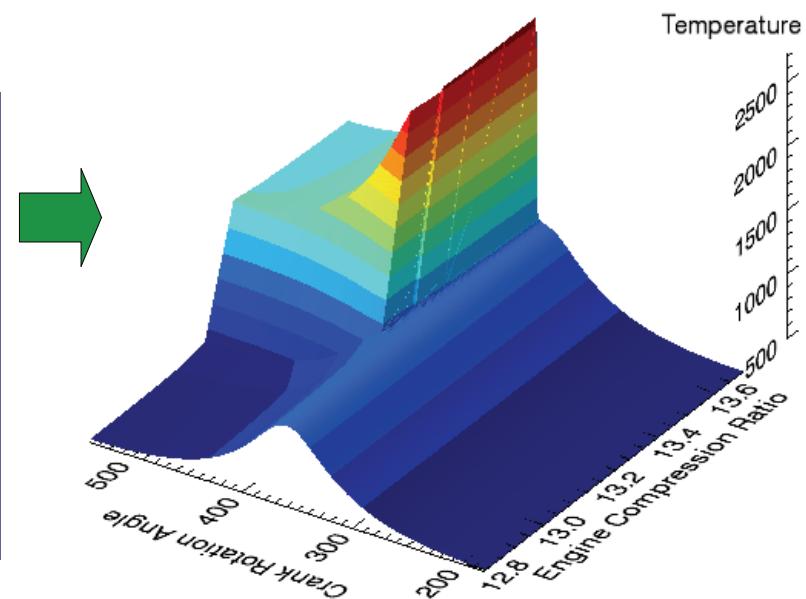
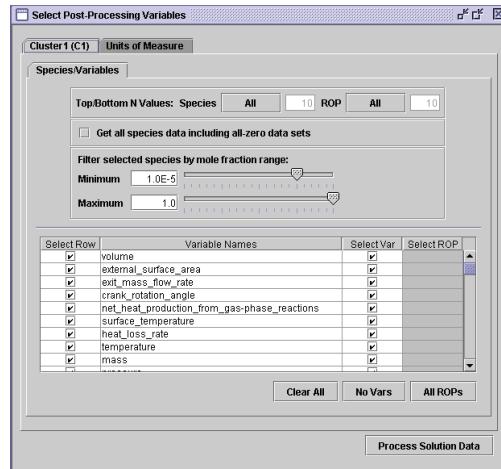
- Choose one or more user-specified input(s) to vary
 - User-interface panel inputs
 - Chemistry-set parameters
- Variations are controlled by:
 - Tables of discrete values
 - Specification of Min, Max, Increment
 - Specification of Min, Max, # of runs
 - Linear or Logarithmic interpolation
- Available for multiple-cluster reactor networks
 - Allows system studies
 - Shows effects of upstream variation on downstream results
- Complements existing “continuation” capability
 - Each cluster model can contain continuations
 - Each run starts from user-specified initial conditions and generates a separate solution file



Visualization of parameter-study results includes added “parametric” dimension

- Solutions are “harvested” from multiple runs
 - User selects variables for post-processing
 - Data is extracted out of multiple solution files
 - 2-D plot sets automatically constructed

Vary engine compression ratio



Multiphase CHEMKIN: the new Particle Tracking Module (PTM)

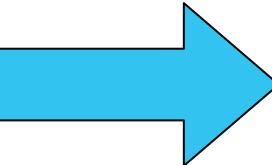
- Nucleation of particles from gas-phase species
 - e.g., poly-aromatic hydrocarbons (PAHs) for soot
 - Rates controlled by collision frequencies
- Growth by coagulation of particles
 - Collision-regime options
- Growth and reduction by general surface reactions
 - Vapor-deposition type reactions
 - Condensation of large species
- Tracking of particles
 - Moment Method calculates moments of size distribution
 - Provides particle mean diameter, mass & volume fractions
 - Average surface state and total surface area

The PTM can be used with any mechanism for particle growth and reduction

Coagulation

Nucleation reactions

Precursor collision frequency



$$\frac{DM_r}{Dt} =$$

$$R_0 + R_1 + \vdots + R_r$$

$$G_0 + G_1 + \vdots + G_r$$

$$S_0 + S_1 + \vdots + S_r$$

Surface reactions

- Oxidation
- Growth
- Condensation

Moment Equations

Particle nucleation and growth/reduction are described within the surface chemistry input

```
MATERIAL SOOT_PARTICLE
DISPERSED ←
END

SITE/PolyC/ SDEN/3.341E-9/
    H(se) open(se)
! se indicates edge or active site.
END

BULK C(B) /1.8/
END

REACTIONS
! nucleation from PAH
2A4 => 32C(B)+20H(se)+28.72open(se) 6.0E10 0.5 0.0
    NUCL ←
! HACA growth
H+H(se) => open(se)+H2          4.2E13 0.0 13000.0
open(se)+H2 => H(se)+H           3.9E12 0.0 9320.0
open(se)+H => H(se)              2.0E13 0.0 0.0
H(se)+OH => H2O+open(se)        1.0E10 0.734 1430.0
H2O+open(se) => OH + H(se)      3.68E8 1.139 17100.0
open(se)+C2H2 => H(se)+2C(B)+H  8.0E7 1.56 3800.0
! PAH condensation
C6H6+open(se) => H(se)+6C(B)+5H 0.1   0.0 0.0
    STICK ←
FORD/open(se) 2.0/
DCOL/4.E-8 ←
...

```

Indicate a dispersed phase and activates the soot module

Precursors for nucleation

Inception particle class

Particle bulk composition

Nucleation reaction

Grow particle by 2 classes

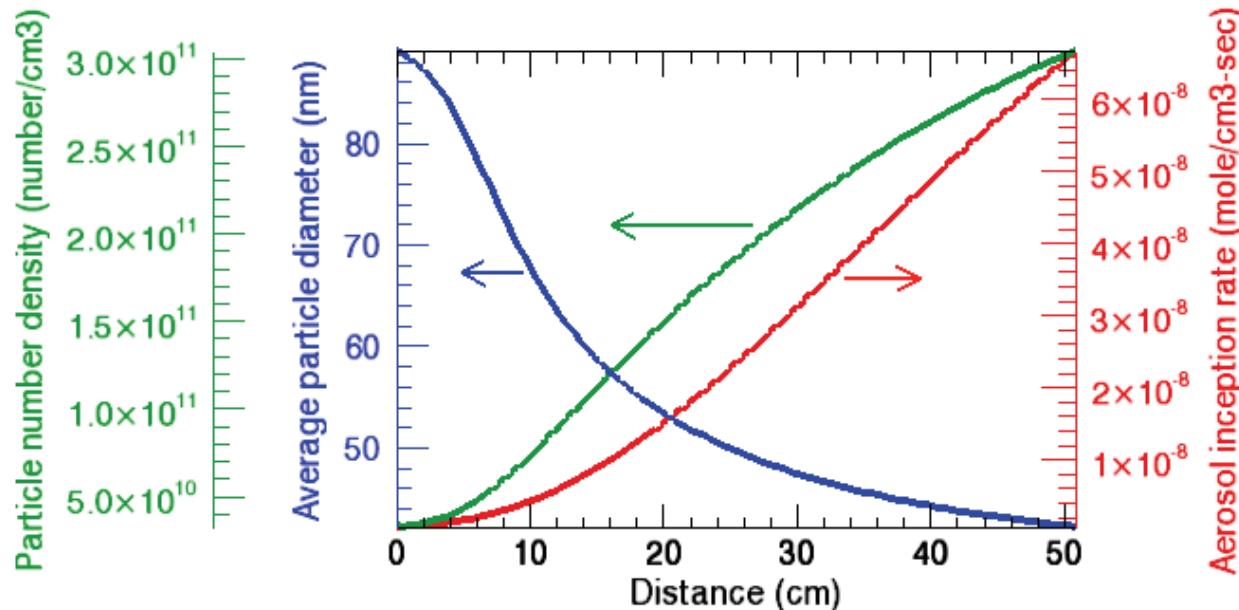
Grow particle by 6 classes

Sticking coefficient

Collision diameter for benzene

The PTM is available for use with All Homogeneous 0-D and Flow Reactors

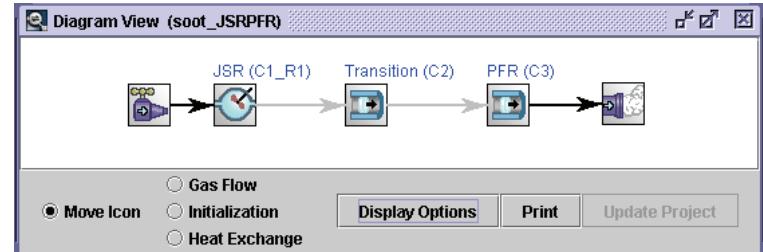
- Closed Homogeneous Reactors
- Perfectly Stirred Reactors
- Plug Flow Reactors
- Shear Layer Flow Reactors



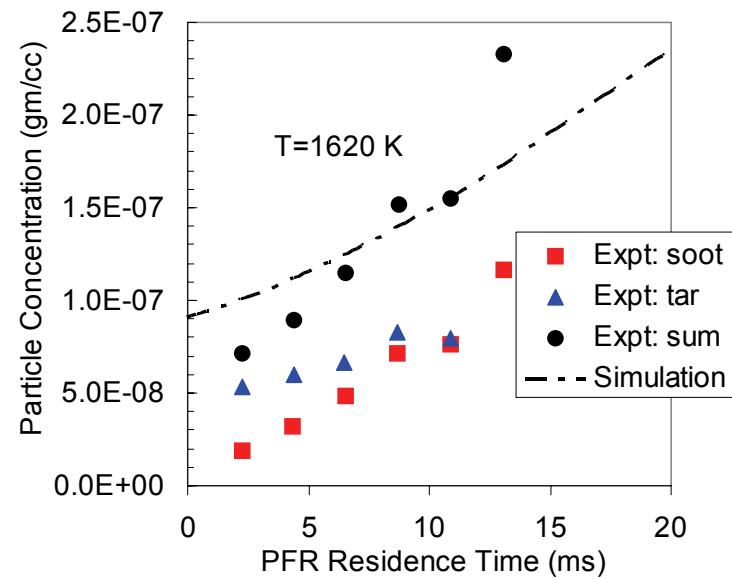
We have applied the new PTM in soot particle formation studies

Reaction Mechanisms Tested:

- Ethylene combustion, which determines PAH precursors
 - From *Appel, Bockhorn, Frenklach*
- Nucleation by single path
 - Pyrene (A4) dimerization
 - From *Frenklach*
- “HACA” growth by C_2H_2 addition
 - From *Frenklach and Wang*
- PAH condensation
- Particle coagulation
- Soot oxidation

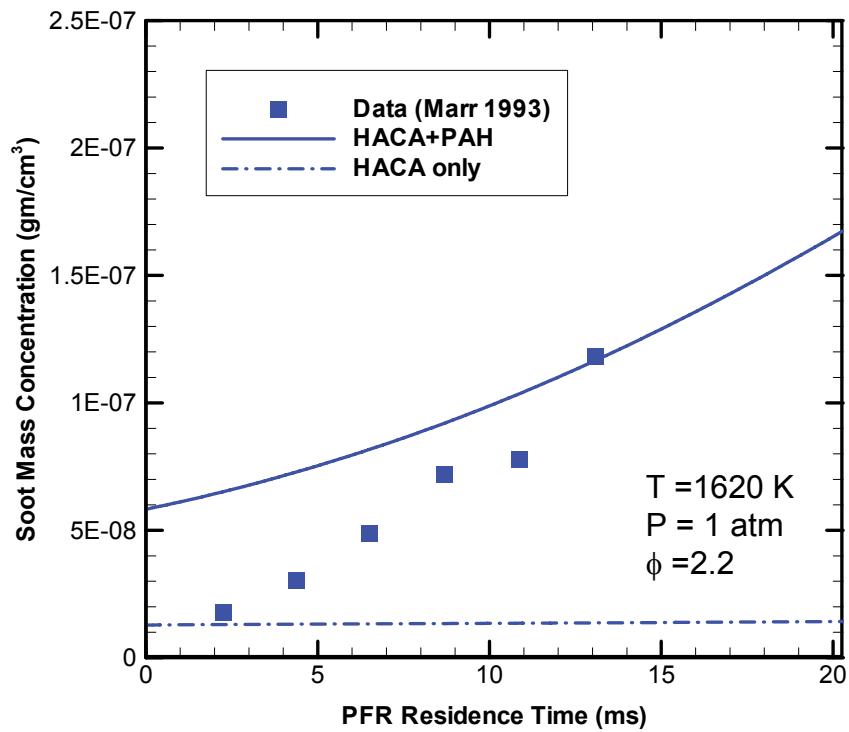
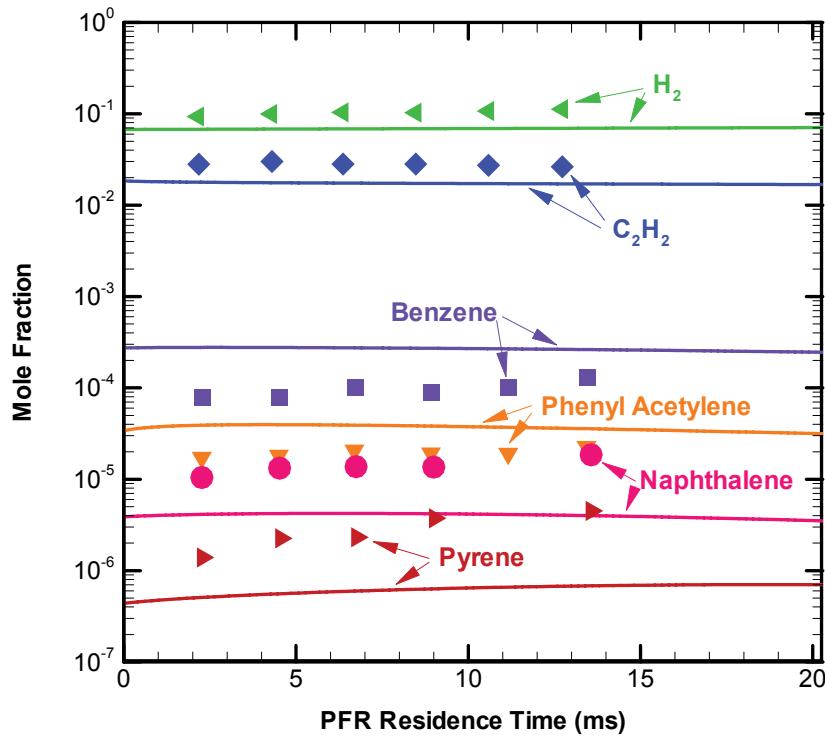


MIT JSR/PFR
Experiments with
Ethylene (Marr, 1993)



The model allows differentiation of contributions from mechanism components

- HACA cannot account for observed growth
- PAH condensation important for growth
- Large PAHs are under-predicted by gas mechanism

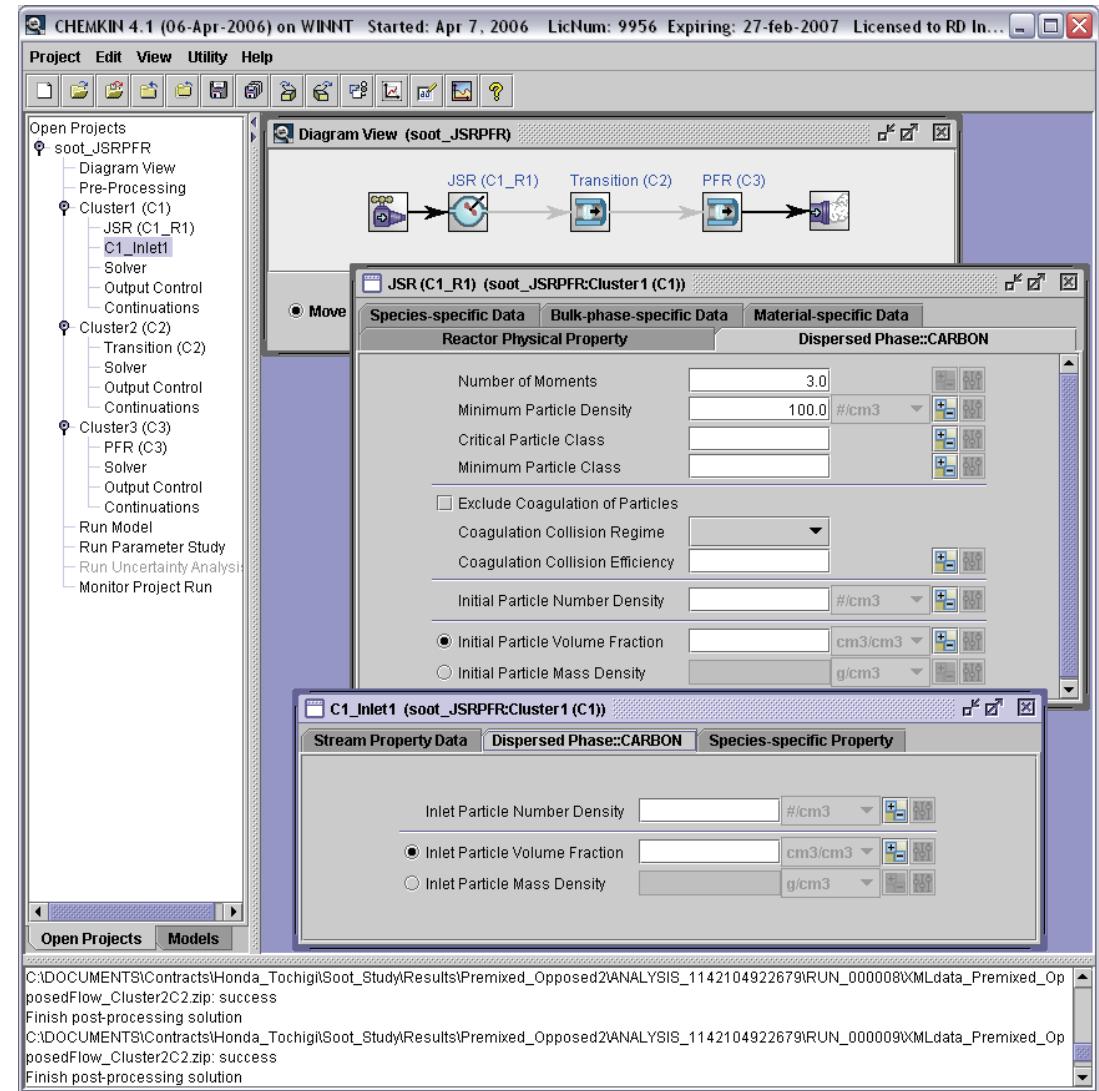


Users have full control over the particle-tracking simulation from the user interface

- Dispersed phases are identified in the Surface Kinetics Input file

- User options include

- Initial particle density
- Coagulation parameters
- Solver controls



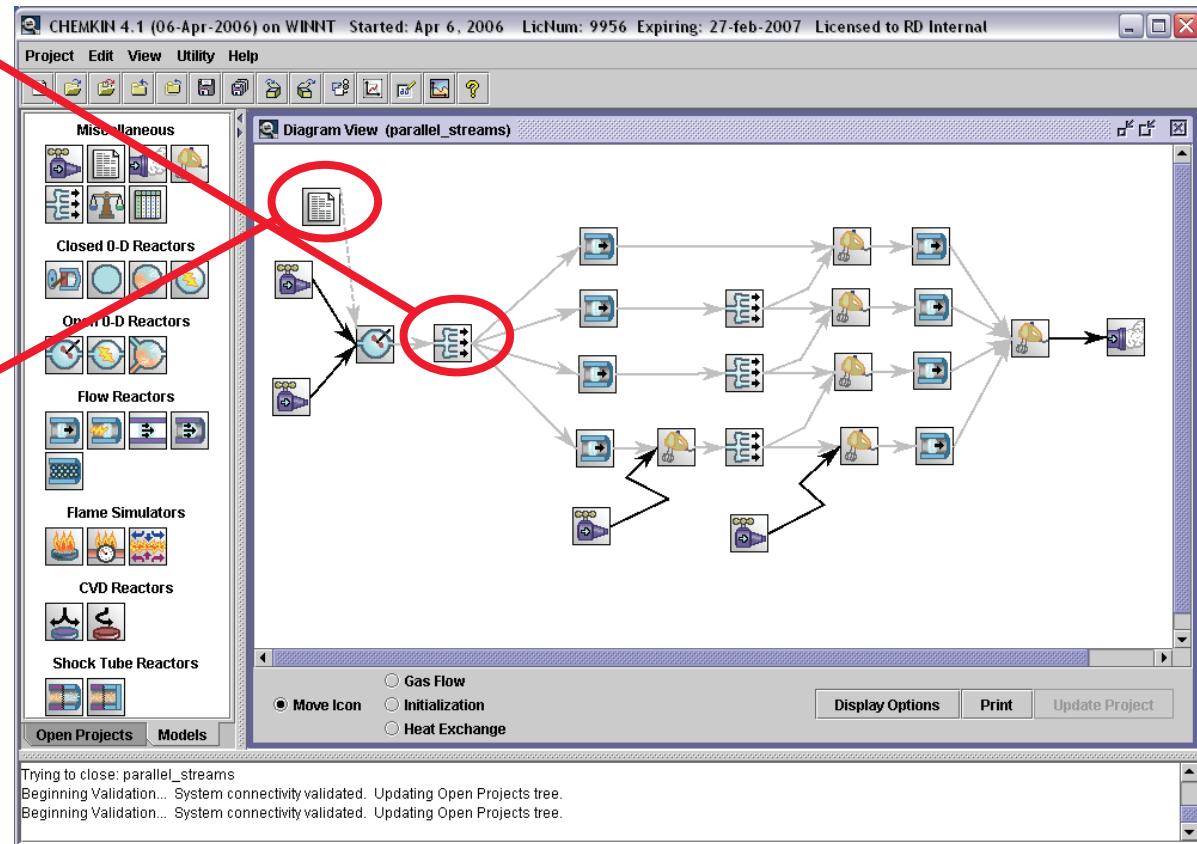
Many other important enhancements are introduced in CHEMKIN 4.1

Some Highlights:

- Expansion of reactor-networking capability
- New reaction-rate formulations
- Improved solver convergence
- Advanced ignition-delay calculations
- Entrainment flow-rate profile for Plug Flow
- Multiple materials option for Shear Layer Flow
- Improved consistency between input panels
- Easier-to-use diagramming and file browsing
- Ability to plot ignition delay & flame-speed in parameter studies

Enhancements to reactor networking add flexibility in describing complex systems

- “Splitter” allows flow splits to multiple reactors
- Parallel streams enabled
- Stored file icon allows initialization from previously saved solution
- Visual emphasis on flow streams

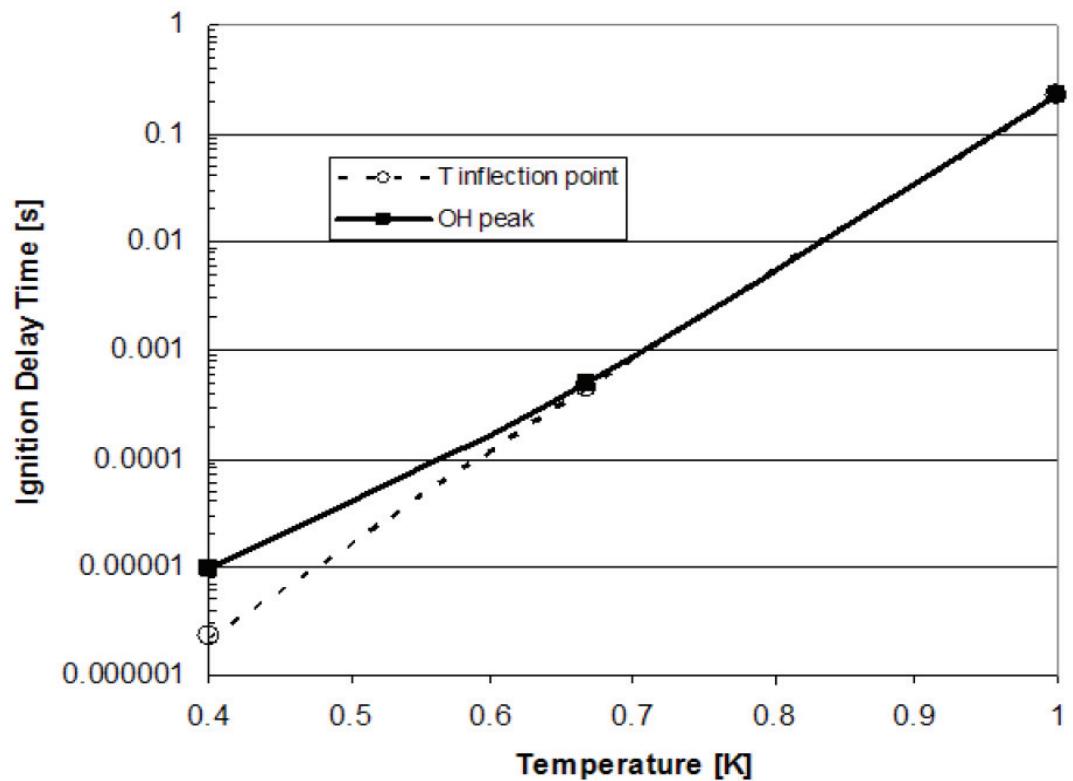


New chemistry formulations make it easier to transcribe and estimate rates

- Collision probability for gas-phase reactions
 - Rate based on collision frequency
 - User specifies reaction probability between 0 and 1
- New surface-reaction UNITS options
 - Facilitates direct use of published catalysis data
 - Partial-pressure units for gas-phase species
 - Site-fraction (coverage) units for surface species
- Dependence of surface species heats of formation on local coverage
 - Facilitates estimation of catalysis rates using Bond-Order-Conservation methods
 - Improved thermodynamic consistency

Several options allow more accurate prediction of ignition delay

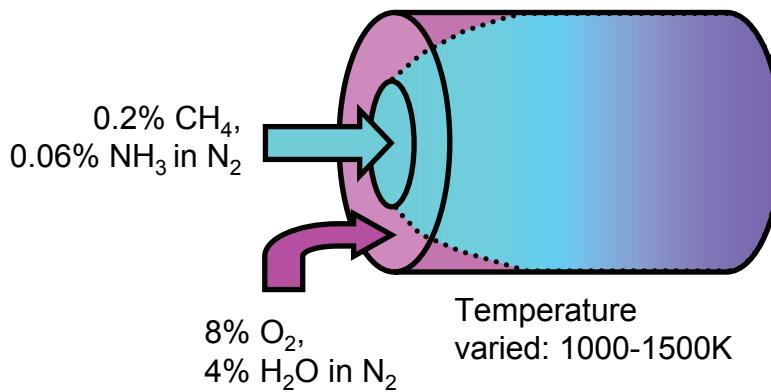
- Choices for ignition criteria:
 - Specified temperature threshold for ignition
 - Specified ΔT above initial temperature
 - Peak dT/dt (inflection point)
 - Peak concentration of any species (e.g., OH)
 - User-defined criteria in user subroutine



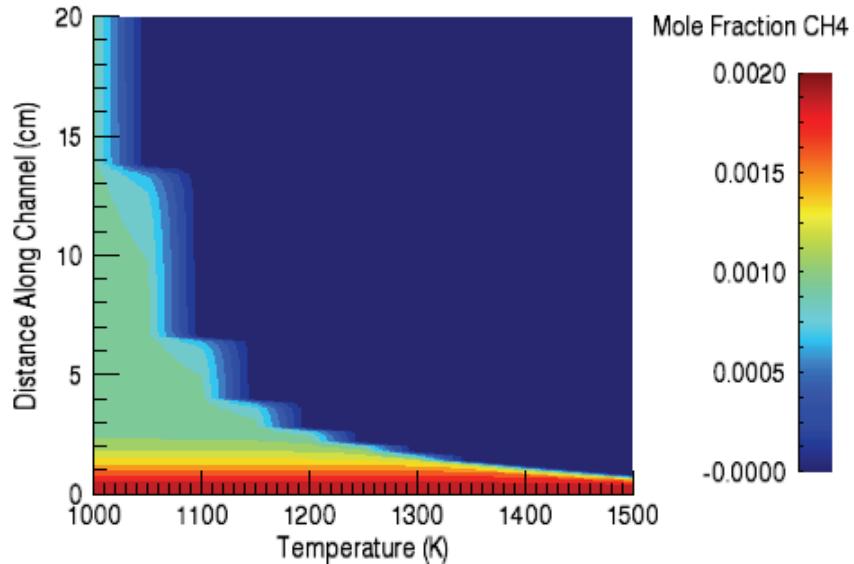
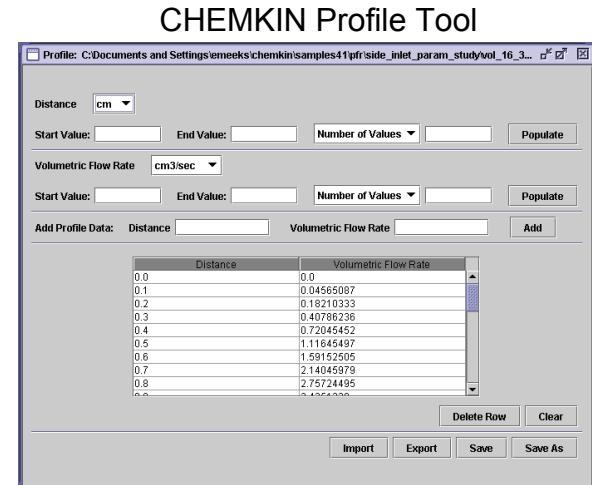
Propane / air ignition delay

Flow-rate profile option for PFRs allows gradual entrainment of gases

- Additional inlets in PFR allow varying of flow rate vs. distance
- Example for CH₄/NH₃ oxidation



Based on Experiments by Grcar,J.F., Glarborg, P., Bella, J.B., Day, M.S., Loren, A., Jensen, A.D.
Proceedings of the Combustion Institute, 30 (2004)



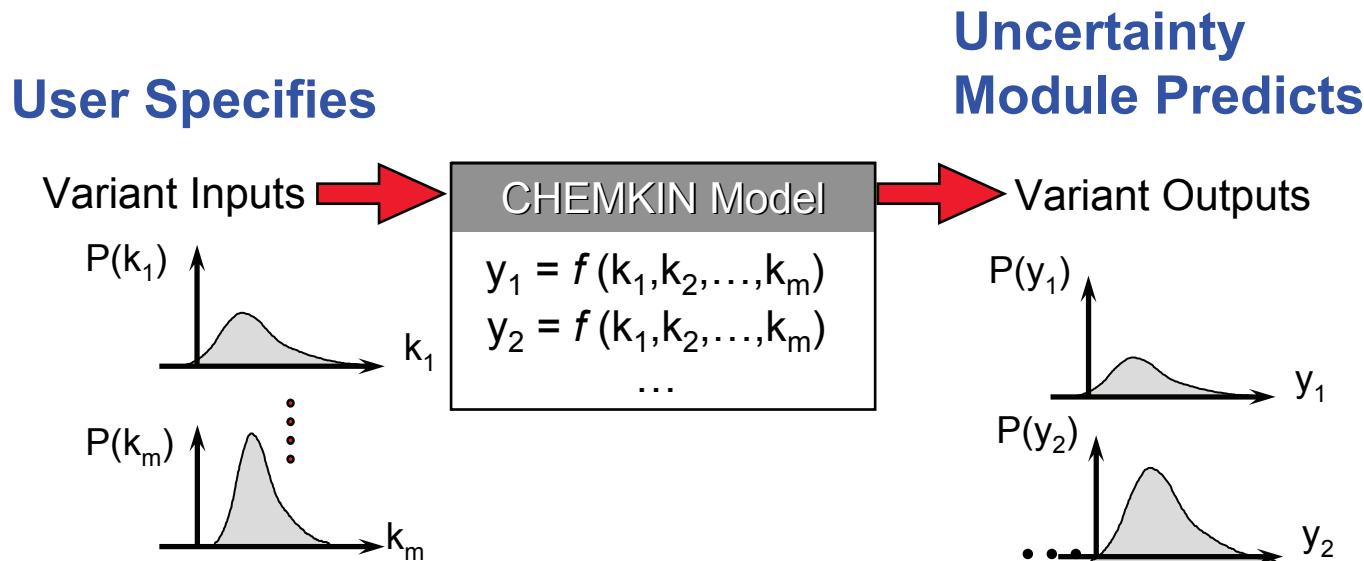
Summary – CHEMKIN 4.1 saves you time

- Parameter study
- More robust solutions
- Save/restore & macros for plotting
- Advanced visualization
- Easily plot single values from parameter study of 1-D simulations (e.g., flame speed, ignition)
- Improved diagramming
- 64-bit LINUX now available for AMD/Intel chips

Projects underway for future releases

A new Uncertainty Module is under development for use with CHEMKIN

- Currently in Alpha Testing
- Scheduled for release in Q1 2007
- Plug-in module to CHEMKIN (4.1 or Later)
- Based on polynomial chaos expansion theory
 - 10-1000 X faster than Monte Carlo approaches



Other major projects

- Implementation of tear-stream algorithm for heterogeneous reactor networks
- Extraction of reactor network from CFD solutions
- Particle Tracking Module option added to Flame Simulations
- Advanced mechanism-analysis tools
- Further improvements in solver speed and robustness

Discussion ...

Two years ago, we launched the Teaching Forum on our website

- How many have used accessed the information there?
- Is the site useful?
- Do you plan to contribute a problem to the site?
- What would you like to see improved or changed?

What technology enhancements would you find helpful to your work?

- New reactor models?
- New reaction rate formulations?
- More user-routine capabilities?
- Extended reactor connectivity options?
- Optimization or other add-on capability?
- Other thoughts or comments?

What aspects of CHEMKIN do you find the most difficult?

- Flame-code convergence?
- Finding / accessing chemistry data?
- Manipulating solution data?
- Linking to the API?
- Other thoughts / comments?

Of the recent enhancements, what do you find to be the most valuable?

- ?

CHEMKIN 4.1 Demo...