

# CHEMKIN 4.1

## Enhancements since Release 4.0.2:

All new Graphical Post-processor with the following important features:

- a. 3-D, color Contour Plots
  - b. User interactive control of line types, symbols, thickness, and color
  - c. Extensive interactive control over plot formatting, including Undo capability, annotation, and drawing
  - d. Ability to create X-Y1-Y2 plots
  - e. Easy printing, copying & pasting, and exporting of plot graphics
  - f. Ability to save and re-apply plot styles
  - g. Ability to create and apply macros for plot modifications
  - h. Easy method to add data to an existing plot
  - i. Option to save and re-apply variable selections associated with a solution data set
2. Greatly extended reactor-network capabilities that include the following features:
- a. Ability to have flows split into two or more parallel streams
  - b. Linking of PaSRs with other, non-PaSR reactors in a reactor diagram
  - c. Initialization by an external stream of more than one inlet entering a reactor
  - d. Initialization of reactors and inlet streams from a stored (previously run) solution file, where the file path and name are stored with the project
3. Enhancements of the reactor diagramming functions and visualizations, including:
- a. Explicit toggling of the type of lines being drawn to distinguish between mass flow, heat flow, and initialization connections
  - b. Removal of extraneous inlets that were required between clusters in CHEMKIN 4.0.x; Inter-cluster mass-flow connections are now indicated by a line connection only
  - c. Inclusion of a "product" icon to indicate the end of a flow stream
  - d. Improved manipulation of line positions and line joints

- e. Ability to use “rubber-band” selection of multiple icons and Ctrl-key multiple selections for move and delete operations
  - f. User control over line types and colors used to distinguish different types of connections, which are saved as user preferences.
  - g. Ability to rename inlet source, inlet streams, or reactors from the diagram panel
4. New (Optional)Parameter Study Facility available for use with all reactor models for both steady-state and transient simulations. This facility has the following features:
- a. Allows users to set up parameter studies with chemistry-set parameters as well as reactor or operating-condition parameters
  - b. Provides an easy way to specify runs with one or more parameters varying, using minimum/maximum/increment or minimum/maximum/number-of-points convention
  - c. Allows user the option of setting up runs that include all possible combinations of multiple varying parameters or a matrix of runs where more than one parameter varies for each run.
  - d. Automatically launches the Solution Harvester when post-processing a Parameter Study. The Harvester extracts data from each of the runs in a parameter study to allow building of 2-D or 3-D contour plots in the Graphical Post-processor, where the user can select which data is extracted.
  - e. Automatically launches a Run Monitor window, which allows the user to track which runs have been successfully completed and to monitor progress in real time
  - f. Allows running of some or all of the cases at once through user selection on the new Parameter Study panel. This allows users to return to a parameter study in a project and easily resume where they left off.
  - g. Enables parameter studies to be performed on projects that contain multiple-cluster diagrams
5. New (Optional)Particle Tracking Module available for use with Closed Homogeneous Reactors, PSRs, PFRs, and Shear-Flow Reactors, as well as reactor networks that consist of these elements. This module includes the following features:
- a. New nucleation reaction type that allows formation of a condensed phase that is dispersed in the gas flow. Such nucleation reactions would be included in the user's Surface Kinetics input file, within the chemistry set.
  - b. Ability to include nucleation from more than one particle precursor
  - c. Initiation of particle size tracking using a method that tracks the moments of the particle size-distribution function, when a dispersed condensed-phase material is encountered in the chemistry set. These moments provide statistical measures of the size distribution function, including mean value, standard deviation, and skewness.

- d. Ability to specify surface reactions for growth or reduction of particles due to condensation, deposition, oxidation, and any other surface reaction.
  - e. Calculation and inclusion of particle coagulation rates for continuum-flow, Knudsen-flow, and transition regimes
  - f. Strict mass balances that includes tracking of the particle surface state from nucleation through coagulation and growth
  - g. Tutorial with sample project and chemistry files for ethylene/air combustion with soot-particle growth in a PSR-PFR reactor network
6. New gas-phase and surface reaction-rate formulation options:
- a. Gas-phase reaction rate specified as a probability associated with the collision frequency between two molecules. The collision frequency can be calculated based on the fundamental gas-phase transport data supplied for the species involved in the collision.
  - b. Option to include transport data for species as a sub-section within the Gas-phase Kinetics input file.
  - c. User option to use transport data only for the purpose of calculating collision frequencies, reducing the data requirements for those cases
  - d. New Units options for surface reactions, which allow users to enter surface reaction data in units of partial-pressures for gas-phase reactants and in units of coverage fractions for surface species.
7. New option to specify the dependence of the heats of formation of surface species on the local coverage of one or more surface species, within the thermodynamic data. This new capability allows more rigorous enforcement of thermodynamic consistency and accuracy of reaction-rate calculations, particularly those based on bond-order-correction methods used in catalysis.
8. Enhancements to Shear-Flow Reactors, including:
- a. Options that greatly improve convergence and allow robust and efficient handling of problems that have very stiff surface chemistry or sudden changes of surface conditions
  - b. Ability for user to specify initial flow, temperature, and composition profiles at the entrance of the boundary-layer flow simulation via a user-subroutine option. This allows, for example, the introduction of annular jets of gas into a cylindrical reactor, or parallel-plane jets into a planar reactor.
  - c. Multiple-materials option, which allows users to specify different surface materials with different chemistry mechanisms on the top and bottom walls of a non-symmetric channel, or on the same wall through assignment of area fractions for each material, for symmetric channel options.
  - d. Optional use of the Particle Tracking Module (see details above)

9. Enhancements to Plug-flow Reactors (PFRs), including:
  - a. Distributed inlet option with a mass-flow-rate profile as a function of distance that can be specified in the CHEMKIN User Interface
  - b. Options that greatly improve convergence and allow robust and efficient handling problems that have very stiff surface chemistry or sudden changes of surface conditions
  - c. Optional use of the Particle Tracking Module (see details above)
10. Advanced options for calculating Ignition Delay have been incorporated into all 0-D Reactors and PFRs. The new options include determination based on peak concentration of a user-specified species, determination of the temperature inflection point, specification of a fixed increment above the initial temperature, specification of the ignition temperature directly, or the option to write a user-defined subroutine for the ignition calculation.
11. Added Equivalence Ratio option for specifying initial or inlet conditions for all reactors and extended documentation of this option
12. Added Normalize option for all species-composition input, to allow users to input such data using relative moles within each phase
13. Automatic printing of a warning when some species are not included in any reactions for the gas-phase or surface reaction mechanisms
14. Removed requirement of a surface-chemistry file in the chemistry sets used for the Shear Flow Reactors and the Mechanism Analyzer
15. Added continuation and "new run" capability options for Shear Flow Reactors, PSRs, PFRs, Shock-tube Reactors, and Closed Homogeneous Reactors.
16. Added "new run" capability for Partially Stirred Reactors
17. Added continuation capability for Opposed-Flow Diffusion Flame Simulators
18. The User Interface now automatically provides unique names to the project solution files, instead of using the default name of "XMLdata.zip"
19. Allow user to easily view and search through chemistry-set data after it has been pre-processed, using the new Mechanism Parameters tab of the Pre-processor panel
20. Enabled interactive use of the User Interface while simulations are still running in the background.
21. Added calculation and printing of heat- and species-transport Peclet numbers within diagnostic output of the Shear Flow Reactors, as well as a warning when the Peclet number is less than 10, which may indicate that the Shear Flow assumptions are not valid
22. Allow user to select units for initial and inlet species composition in mole or mass units
23. Added explicit printout of species units (mole or mass fraction) for Partially Stirred Reactor diagnostic output files

24. Improved convergence of stiff surface-chemistry problems for all steady-state PSRs by implementing the use of the Positive Value to Reset Species Fractions for all phases in the system
25. Added calculation of the mixture enthalpy and sensible enthalpy to post-processing options for the Graphical Post-processor and the GetSolution command-line utility
26. Improved the ability of users to navigate among folders or directories on their hard drive when selecting files from within the CHEMKIN User interface. New options include a set of "history" locations that allow users to jump quickly to recently accessed locations
27. Added a new Manage RD License Tool for UNIX and Linux platforms that can be run from a UNIX shell and that is documented in the new and improved Installation and Licensing manual
28. Improved the flexibility and consistency in setting inlet conditions for different reactors, including optional translation between mass flow rates, volumetric flow rates, and velocities where appropriate
29. Improved UNIX installers for CHEMKIN
30. Provided option for user to cancel generation of the input files before writing over existing files in the working directory on the Run panel
31. Improved error messages concerning errors related to duplicate reactions in gas-phase kinetics input files
32. Automated inclusion of bulk-species and bulk-phase growth rate during post-processing of Shear Flow Reactors
33. Added storage of derived, single-point solution values, such as flame speed and ignition delay to solution files where appropriate, allowing users to easily visualize these results during parameter studies
34. Improved ability of the user interface to detect when cluster and reactor panels have been closed to allow access to pre-processing functions
35. In the Cluster Properties panel for multiple-PSR clusters, added table option that allows easy entry of reactor properties as alternative to entry in each reactor panel
36. Added Run Licensing Diagnostics option to the User Interface Help menu, to facilitate diagnosing licensing issues
37. Added new license utilities, check\_license.bat and check\_license.sh for PC and UNIX/Linux platforms, respectively
38. Added new license utilities, manage\_license.sh and request\_license.sh for UNIX/Linux platforms
39. Added option in Post-processor selections menu to allow rendering of reaction strings in plot labels, rather than using reaction numbers. This option is enabled using a check box in the data selections panel, when the Post-processor is first launched.
40. Improved labeling and bubble help on Equivalence Ratio panels to clarify input requirements.

41. Provide mole fractions for each phase, as well as fractions of total moles in the solution output from a multi-phase Equilibrium calculation. Also provide specific volume and average molecular weight in solution file for post-processing.

## Bug Fixes since Release 4.0.2:

1. Corrected problem that occurred in transient PSRs with a user-specified flow-rate profile, where the reactor was treated as closed when the start of the first inlet to the reactor had a zero flow rate
2. Fixed problem where data entered and later deleted in a profile in a project persisted in the saved project file, causing unexpected results
3. Fixed Opposed-Flow Diffusion Flame Simulator to correctly detect the maximum number of points located on a multiple-run solution file being used in a restart operation and to prompt the user with an error if that number exceeds the maximum number of points specified for that reactor simulation.
4. Eliminated interdependence of user-specified transient-solver time or distance intervals and the corresponding default values, to reduce confusion about the default values being used for a given simulation
5. Corrected Bubble Help description and user-manual documentation of default tolerances used by solvers for all reactors
6. Fixed implementation of the gas-phase auxiliary rate parameter, PLOG, where input was incorrectly processed when there were more than 4 pressure entries
7. Discontinued deletion of XMLdata.zip file in working directory when the project does not need to create this filename
8. Modified transport utilities to enforce physical limit of 0 to 1 for species fractions prior to using in transport-property calculations
9. Added protections in chemistry-rate utilities to avoid overflows introduced when user-supplied reaction orders are negative or when species fractions become small negative numbers during solution iterations
10. Fixed ability of user to override the inlet temperature during a restart or continuation of a plug-flow reactor
11. Corrected the Bubble Help for 'Positive Value to Reset Species Fractions' in the Advanced Solver Panel of the PSR model (steady state) to say that by default there is no resetting of the negative species fractions during solver iterations
12. Corrected the sign of deposition rates printed in the diagnostic output file of the Shear Flow Reactors for deposition on the upper wall
13. Eliminated issue with Chemistry Pre-processor ignoring species that have '.' in the symbolic name during processing of transport properties

14. Added missing documentation for the Fitdat Utility about the "NO298" option that allows users to override the constraint of the fit to the T=298.15 value
15. Fixed reaction-string printing in diagnostic output files, such that ion yield reactions and long reaction strings are presented correctly
16. Corrected problem in solution processing for CVD Reactors that occurred when no bulk species were included in the chemistry set
17. Corrected labels of rate-of-production print intervals in the diagnostic output files of Plug-flow Reactors, which were incorrectly reported as time rather than distance
18. When an Equilibrium Reactor is initialized by the output of another reactor, corrected the handling of bulk species, which should be neglected in this case.
19. Corrected handling of surface chemistry calculations when the surface area for a particular material is zero in 0-D Closed Homogeneous, PSR, and Plug Flow Reactors
20. Added error-handling to trigger an error during Pre-processing when user-specified transport-property data values include a molecular linearity that is less than zero or greater than 2
21. Fixed error propagation to the User Interface for errors encountered during transport-property Pre-processing, when the transport-data values cause the collision-integral table lookups to be out of range
22. Added error condition and handling when the gas-phase kinetics input file does not include any gas-phase species or elements
23. Corrected omission of surface site fractions in the initialization of reactor conditions from a stored solution, for all 0-D Closed Homogeneous, PSR, and Plug Flow Reactors
24. Corrected problem with the Manage RD License Tool on PCs inadvertently updating daemon paths that were not associated with the Reaction Design license daemon, which caused issues with licenses that had been merged with those of 3<sup>rd</sup>-party software vendors.
25. Discontinued use of the redundant ADIA keyword in Plug Flow Reactors when the energy equation is being solved, to eliminate extraneous warnings in the diagnostic output file.
26. Removed fatal-error condition when solution for an initial guess for the surface site-fractions in a Plug Flow Reactor fails, allowing the simulation to continue to attempt to solve the simultaneous system of equations without the improved initial guess.
27. For Opposed Flow Flames, corrected the implementation of the "plateau" profile method for introducing an initial guess for the temperature profile and improved the presentation of initial-temperature options in the reactor input panel
28. Fixed problem with typed values for some input in the CHEMKIN User Interface, where it was not being registered correctly in the project unless the user explicitly pressed the Enter key
29. Corrected enforcement of constraint that surface site fractions must be between 0 and 1 during solution for Shear Flow Reactors

30. Corrected problem when PSRs are initialized from a stored solution, where the saved-solution data was over-writing the inlet conditions of the first inlet
31. Removed restriction that disallowed restarting of a PSR when there was more than one inlet stream defined
32. Corrected initialization of engine parameters in an Internal Combustion Engine simulation when initialized from a stored solution file
33. Corrected grouping of equilibrium constraints on the input panel for the Equilibrium Calculator
34. Removed restriction requiring positive heat loss for heat-loss and heat-loss profile options for all Closed Homogeneous Reactors, PSRs, and Plug Flow Reactors
35. Added requirement that the user specify the pressure for Opposed Flow Flames, to avoid unexpected results with an assumed pressure value
36. Corrected treatment of chemistry files during unarchive operation, where file paths were not being set to the working directory in some cases
37. Corrected misspellings in error messages from Shear Flow Reactors
38. Corrected initial temperature in sample ic\_engine\_\_nbutane project to be 500 K
39. Changed default editor on UNIX and LINUX platforms to vi, to avoid problems with Java-based editor when working with large text files
40. Added pop-up warning during pre-processing of the chemistry set, when the user has specified non-existent file paths
41. Provide explicit file types for all file export options from the User Interface
42. Removed extraneous items from solution files for reactor models where those items are not relevant