



## **CHEMKIN 4.1 vs. Chemkin II**

By Reaction Design

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# The Maturing of CHEMKIN

In a world where everyone needs to maximize their resources - the longer it takes to accomplish a job, the more expensive it is. So when you look for tools to help your work, you look for the ones that get the work done in the fastest, most economical manner, with the highest return on your investment.

Time in the lab is expensive time, and some chemical kinetic questions can only be answered using simulation. When CHEMKIN was first introduced, it provided a flexible and powerful approach to implementing gas-phase kinetics simulations, allowing home-grown descriptions of the studied systems. However, working with Chemkin II required users to acquire an intimate understanding of programming and scripting languages, code compiling and debugging procedures on different computer operating systems, and to master the intricacies of problem-keyword syntax. It also required time-consuming manual manipulation of data to allow interpretation of the simulation results. Delving into material at this level of detail took quite a level of devotion, such that the typical researcher spent countless hours in preparing for, maintaining, and processing Chemkin II simulations.

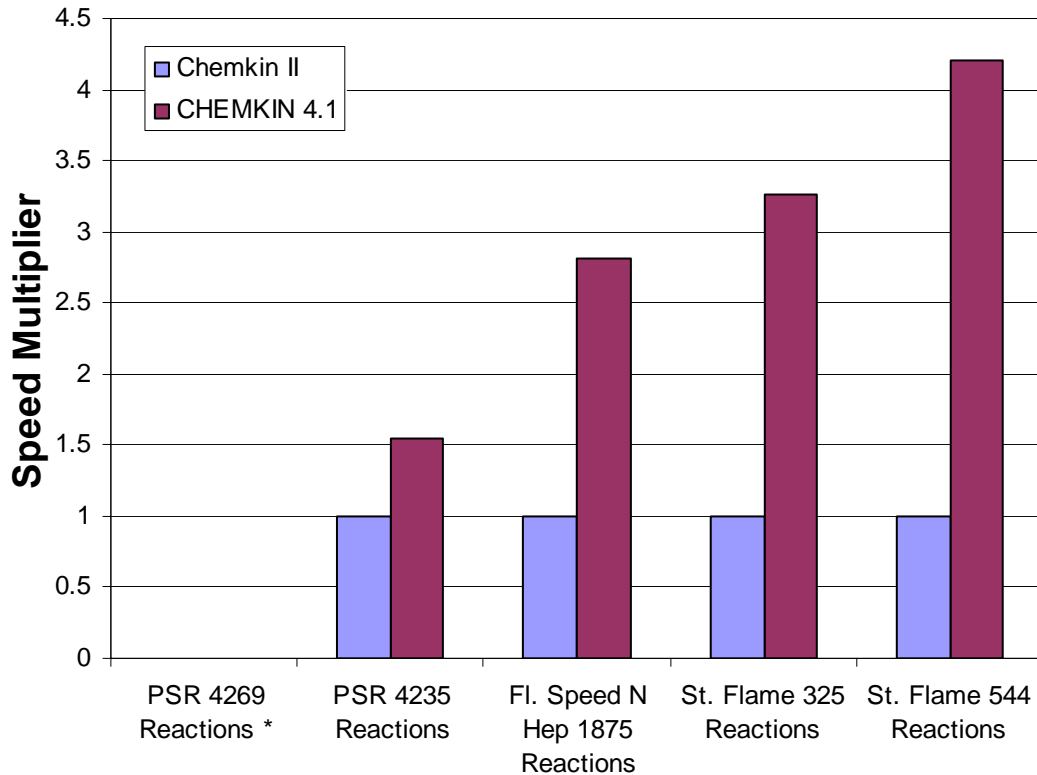
Commercial CHEMKIN provides you with flexible and easy application development and analysis avoiding the challenges associated with developing, maintaining, transferring and learning homegrown codes, at the same time keeping the modeling flexibility allowed by Chemkin II, while continuously improving performance, capability and flexibility of the software.

With officially improved speed and solver performance, numerous new reactor-model applications, a user interface that clarifies and speeds up user-software interactions, supported installers for multiple platforms, and professional technical support from a dedicated and expert staff, CHEMKIN 4.1 gives researchers the ability to focus on the problem and its solution, rather than the implementation of the tool..

## Chemkin II Overview

Chemkin originated out of Sandia National Laboratories as a software package, whose purpose was to facilitate formation, solution and interpretation of problems involving elementary gas-phase chemical kinetics. At the time of introduction to the combustion field, Chemkin represented an important advance in enabling the testing and interchange of different chemical mechanisms that were based on elementary kinetics, without the need to restructure code with each change in chemistry. The "Chemkin II" package consisted of several software components: a reaction-mechanism Interpreter, which parsed a symbolic description of an elementary, user-specified chemical reaction mechanism; a gas-phase subroutine library, which contained about 100 FORTRAN subroutines that could be called upon to return information on equations of state, thermodynamic properties and chemical production rates; a thermodynamic data file for many gaseous species; and four application codes that handled simulations of equilibrium, steady-state perfectly stirred reactors, transient closed systems with constant pressure or volume, and adiabatic, premixed laminar flames. For the flame calculations, a transport data file for selected species, a transport data-file interpreter, and a transport subroutine library were also included.

To apply Chemkin II to a problem, users often had to write their own FORTRAN programs that would include a set of governing equations to describe their particular system of interest, due to the limited number of application codes and options provided in the Sandia distribution. Writing such programs was facilitated by the use of the CHEMKIN subroutine libraries, which provide easy access to the terms in the governing equations of interest that relate to equations of state, chemical production, transport properties, and thermodynamic properties. (Kee, Rupley et al. 1989). In such cases the user would be responsible for setting up and solving a system of equations using numerical solver modules, compiling and linking code modules, executing pre-processor and application programs via command line, and extracting results from a separate set of machine-dependent binary solution files.



**Figure 1: Speed Comparison between CHEMKIN 4.1 and Chemkin II**  
 (\*Chemkin II did not converge for this case)

## Improved Performance

Along side the new features that came along with CHEMKIN 4.1, numerous improvements have been made to already existing features of Chemkin II. CHEMKIN 4.1 proves to provide superior solution speed over Chemkin II as seen in Figure 1. The speed increase is particularly noticeable for applications with large reaction mechanisms. Additionally, the CHEMKIN 4.1 solver is much more stable than the Chemkin II solver as is seen in Figure 1 where the first case (PSR with 4,269 reactions) did not converge for Chemkin II and CHEMKIN 4.1 produced a solution in 932 seconds.

- Improved speed (in some cases by a factor of 10) in transport-property evaluations
- Increased accuracy in conservation equations for flames that allows better convergence
- Automation of initial "guess" profiles for steady state reactors, including auto-calculation of equilibrium concentrations when initial guesses are not provided by the user and a simplified specification of initial dependent-variable profiles that can reliably provide convergence.
- Improved performance for running problems with and manipulating large mechanisms (1000s of species).
- Added facilities to easily import and export initial profiles (such as time profiles for transient problems or spatial profiles for initial guesses) that facilitates sharing or generating this information.

## Application Programming Interface (API)

One of the innovations of Chemkin II was the ease at which custom programs could be written, in which all chemistry-specific data was encapsulated through pre-processing of an input file, and transfer of that data to the application code through the use of chemistry-independent calls to the CHEMKIN subroutine library.









In the commercially supported CHEMKIN 4.1, the ability to call any of the routines in the subroutine libraries remains an important feature. This ability is part of the CHEMKIN/API, which is now thoroughly documented in the CHEMKIN/API manual. This documentation provides step-by-step instructions for building a user program. In addition, the subroutine libraries are continuously being expanded to return new types of information, including surface chemistry data. The API allows the user to write their own custom programs, or to modify or supplement the functionality of supported CHEMKIN application programs. The subroutine libraries may be accessed either from user-modified subroutines called by the supported CHEMKIN Reactor Models, or from entirely user-written application programs. User application programs may be written in C, C++, or FORTRAN computer languages. Extensive documentation of the API usage and examples is available as a part of CHEMKIN 4.1 install.















## Applications

### Reactor Models

While CHEMKIN 4.1 still allows user access to the CHEMKIN libraries, it also provides a great variety of pre-packaged, customizable Reactor Models, including all of Chemkin II application codes with additional improvements as well as various new Reactor Models. Table 1 summarizes the differences between availability of Chemkin II and CHEMKIN 4.1 reactor models.

**Table 1: Comparison of Chemkin II Application Codes and CHEMKIN 4.1 Reaction Models**

CHEMKIN 4.1		Chemkin II
	Non-reactive Gas Mixer (performs thermodynamic calculations)	none
	Chemical and Phase Equilibrium	Equil- Chemical Equilibrium
	Mechanism Analyzer	none
	Closed Internal Combustion Engine Simulator	none
	Closed Homogeneous Batch Reactor with advanced ignition delay calculations and options to constrain the problem using volume vs. time or pressure vs. time profiles)	Senkin - Closed Homogeneous Batch Reactor with constant volume or constant pressure
	Closed Partially Stirred Reactor	none
	Closed Plasma Reactor	none
	Perfectly Stirred Reactor (steady state or transient, where transient simulations can use a variety of time-profile constraint options)	PSR - Perfectly Stirred Reactor, steady state only

	Plasma Perfectly Stirred Reactor	none
	Partially Stirred Reactor (PaSR)	none
	Plug Flow Reactor	none
	Honeycomb Plug Flow Reactor	none
	Plasma Plug Flow Reactor	none
	Planar Shear Flow Reactor	none
	Cylindrical Shear Flow Reactor	none
	Premixed Laminar Burner-stabilized Flame with heat loss options	Premix - adiabatic Laminar Burner-stabilized Flame
	Premixed Laminar Flame-speed Calculation, with heat-loss options	Premix - adiabatic Laminar Flame-speed Calculation
	Diffusion or Premixed Opposed-flow Flame	none
	Stagnation Flow CVD Reactor	none
	Rotating Disk CVD Reactor	none
	Normal Incident Shock	Shock
	Normal Reflected Shock	Shock
	Low Pressure CVD (LPCVD) Furnace Model	none
	Low Pressure CVD (LPCVD) Thermal Analyzer	none

### Enhancements to the Original Chemkin Reactor Models

In addition to expanding the types of reactor models available, CHEMKIN 4.1 reactor models include many enhancements compared to their Chemkin II counterparts. Such enhancements include additional capabilities as well as improved convergence and performance. Specific examples include:

- The Equilibrium Reactor was expanded to include the ability to perform phase equilibrium as well as chemical equilibrium calculations, with consideration of gas, liquid, and solid phases.
- Closed Homogeneous Reactors (including the IC Engine Model) have additional capabilities of calculating ignition delay times based on temperature inflection and peak species concentrations
- All transient 0-D simulations (e.g. all closed reactor models, PSRs and PaSRs) include the ability to specify input profiles that vary as a function of time for such constraints as temperature, pressure, volume, heat loss and power (plasmas).
- PSRs can be run in transient or steady-state mode. The transient capability includes integrated sensitivity analysis for both gas and surface reactions.

- The Freely Propagating and Burner Stabilized Flame Reactors include improved performance, easier set up of initial conditions to reach efficient convergence, as well as several heat-loss specification options and a user-programmable radiant-heat-exchange routine.

## New Reactors in CHEMKIN 4.1

There are many new reactor models in commercially supported CHEMKIN, which are run via user customizable templates. Examples of new reactor models include:

- The Internal Combustion Engine (ICE) model simulates a combustion cylinder in an internal combustion engine under auto-ignition conditions, which is most relevant to the study of fuel auto-ignition behavior, engine knock, and homogeneous charge compression ignition (HCCI) engines. A variety of heat-transfer correlation options are included.
- Plasma reactors (PSR, Plug-flow, and Closed systems) are designed to handle non-equilibrium plasma processes where the electrons are not in thermal equilibrium with the background gas. This has particular value in the modeling of plasma chemical-vapor-deposition or etching processes in microelectronics manufacturing and other areas of materials processing.
- Partially Stirred Reactors (Open and Closed) allow users to explore turbulent-kinetic interactions by simulating both the mixing process and the detailed kinetics. These reactors use a Monte-Carlo based stochastic model of mixing controlled by a mixing time coupled to detailed kinetics controlled by a specified residence time. Equilibrium conditions can also be assumed.
- The Plug Flow Reactor is designed to model the non-dispersive one-dimensional flow of a chemically reacting gas mixture. With full surface chemistry, the PFR allows simulation of fixed bed reactors in which the user can specify area per length for surface chemistry independent of the hydraulic diameter of the flow.
- The Honeycomb Monolith Reactor is a special case of the PFR, which allows direct simulation of honeycomb geometry and catalyst loading for automatic calculation of active surface areas for catalyst heterogeneous chemistry.
- The Opposed Flow Flame model is designed to model one-dimensional, axisymmetric or planar diffusion flames between two opposing nozzles, using a similarity transformation that reduces the three-dimensional flow field to a one-dimensional problem.
- The CHEMKIN LPCVD Furnace Model and Thermal Analyzer provide accurate simulation of multi-wafer LPCVD reactors, allowing users to specify the process chemistry, reactor dimensions, flow rates, pressures, temperatures, wafer quantities and wafer sizes.
- Finally, the Mechanism Analyzer presents, in tabular and graphical form, detailed information about the temperature and pressure dependence of chemical reaction rate constants and their reverse rate constants, reaction equilibrium constants, reaction thermochemistry, chemical species thermochemistry and transport properties without requiring the user to do any programming.

## **Reactor Networks**

Not available with Chemkin II, the CHEMKIN 4.1 visual building and execution of reactor networks allows users to route the flow out of one reactor into an inlet of another reactor, providing representation of more complex reacting flow systems. When the reactors connected in this way are all PSRs, they can form a “cluster” with special capabilities and options. Clusters can include “recycling” flows, where the flow out of one reactor can flow upstream to become an inlet of an upstream reactor. Clusters can also include heat exchange (convection, conduction and/or radiation) between PSRs. The reactors in a cluster are solved simultaneously to provide full coupling of the dependent flows. They can be run in both transient and steady-state modes. A Reactor Network can consist of a mixture of any open reactors as well as PSR clusters. In addition to flow networks, CHEMKIN 4.1 users can take advantage of the reactor-networking diagramming options to link simulations for purposes of initialization, restart, and information-transfer. These capabilities are facilitated by the use of a unified solution-file structure for all reactor models, based in XML (eXtensible Markup Language).

## Surface Chemistry

With Chemkin II, access to surface chemistry capability was restricted, due to export controls and licensing restrictions in place at the time of the initial "Surface Chemkin" release from Sandia. However, in CHEMKIN 4.1, all 0-D (closed homogeneous and PSR; steady-state and transient), as well as all plug-flow, shear-flow, and CVD reactors provide ready access to the latest surface chemistry capabilities. These capabilities have been greatly expanded since the initial Surface Chemkin report (Kee, Rupley et al. 1989). For example, global reaction mechanisms were enabled, allowing non-elementary kinetics where reactions may be written with non-integer stoichiometric coefficients and arbitrary reaction orders for any species in the system. This facilitates use of semi-empirical reaction mechanisms for catalytic and chemical vapor deposition systems. Another example is the inclusion of a wide range of new reaction formulations to describe plasma-surface interactions, as well as Langmuir-Hinshelwood and Eley-Riedel rate expressions. In addition, several of the reactor models make use of the multiple materials option, which allows 4.1 users to specify separate chemistry mechanisms for different materials within the same reactor and to control relative surface areas of those materials. Sensitivity and Rate-of-production analyses are available for all surface species and reactions, in both transient and steady-state reactor models.

### ***Particle Tracking Module***

The most recent capability built on the detailed surface chemistry capability of CHEMKIN 4.1, is the Particle Tracking Module (PTM). This module tracks particle growth and size distributions, including detailed chemical production terms from particle-gas interactions. The module is available for use with all 0-D Closed Homogeneous Reactors, PSRs, PFRs and Shear Flow reactors. Particle nucleation reactions are defined and included in the surface chemistry input file, thus allowing multiple nucleation pathways. The user is able to specify surface reactions for growth, reduction, condensation, and deposition on the particle surface. The coagulation of particles is accounted for using built-in coagulation models for various flow regimes. The particle size distributions are determined using the Method of Moments (Appel, Bockhorn et al. 2001).

## Usability

### ***Problem Setup***

Chemkin II required that users compile, link, and run, FORTRAN files from the command line of a UNIX shell. In order to set up a problem, users had to first become familiar with a lexicon of keywords that varied from application to application. In order to make any modifications to application-program behavior, users had to be experts in FORTRAN programming, be able to create their own "make" files and build scripts, and work with code debuggers to diagnose any difficulties encountered. Code modification was required every time the problem size changed to accommodate a larger chemistry set or computational grid.

These limitations are eliminated with CHEMKIN 4.1. There is no longer need to memorize keywords or their usage rules. Memory is allocated dynamically and automatically for each problem, without the need of code recompiling. Problems are defined through panels with mouse-over help for each parameter, including default values and usage guidelines. Although some programming may be required to customize applications and to work with the CHEMKIN/API, the API manual provides step-by-step instructions for both Windows and UNIX/LINUX platforms along with sample code and an integrated build environment. The CHEMKIN User Interface manages the execution of CHEMKIN programs, as well as the organization and specification of input and output files used in the calculations. This point-and-click interface guides users through the pre-processing of chemistry data, reactor-model set-up, and results analysis, verifying user input along the way.

The CHEMKIN 4.1 User Interface (UI) was designed to reduce setup time for new problems, to speed the learning required for new users, and to enhance retention of knowledge for experienced users. The UI includes visual diagramming options that make it easy to build reactor networks and to perform a series of calculations to represent complex flows. For example, stirred reactors can have multiple inlet flows with mass flow rates that may vary as a function of time. Outlet flow from reactors can be split into two or more

parallel streams, where each stream can be fed into different reactors downstream. Multiple flows from different reactors can also be thermodynamically mixed to form a single stream. Within the interactive diagramming facility, inlet streams, and reactors can be easily added, deleted or moved.

## Reaction Rate Formulations

Many new reaction-rate formulations have been added to those that were originally handled in Chemkin II. The list of differences is shown in Table 2.

**Table 2: Comparison of CHEMKIN 4.1 and Chemkin II Reaction Rate Formulations**

CHEMKIN 4.1 Reactions	Chemkin II
Pressure dependant reactions with neutral third body efficiency	same
Reverse Rate Parameters - supersedes the reverse rates that would normally be computed through the equilibrium constant	same
Troe fall-off for pressure-dependant reactions	same
Chebyshev Polynomial Rate Expressions	none
Ability to superseded Chebyshev polynomial temperature and pressure limits	none
Efficiency of Collision Frequency Expression - If a reaction is bimolecular and the approximate collision diameters are known- the collision frequency efficiency expression can be used to calculate the reaction rate constant.	none
Duplicate Reactions – when two or more reactions involve the same set of reactants and products, but proceed through distinctly different processes.	same
Ability to specify reactions that depend on a specific species temperature; e.g., the electron temperature for non-equilibrium plasmas.	none
Energy Loss Parameter -overrides the calculation of energy loss from the change in enthalpy determined by the reaction description and the thermodynamic data of the reactants and products. Useful in describing electron-impact excitation reactions.	none
Ability to use non-integer stoichiometric coefficients to describe non-elementary reactions	none
Forward Reaction Order Parameter - supersedes the forward reaction order for any species in the mechanism (with respect to species concentration), regardless of whether the species appears as a reactant or a product in the reaction	none
Optional Rate Fit Expressions - Supersedes the default reaction rate expression by a Janev-Langer reaction rate (plasma reactions)	none
Landau-Teller Rate expressions	same
Pressure Dependence Through Logarithmic Interpolation - Provides a general-purpose way of describing pressure-dependent reaction rates	none
SRI pressure-dependent reaction rate	same
UNITS option allows specification of different units on a reaction-	One unit system must be used all reaction-rate

by-reaction basis.	parameters in the system
Limited to 16 characters for species names.	Limited to 10 characters for species names
Reactions allow up to 6 reactants and 6 products per reaction	Reactions limited to 3 reactants and 3 products per reaction
In addition to NASA format, extensions allow inclusion of any number of temperature ranges; species can have more than 5 elements and unlimited number of each element per molecule.	Thermodynamic properties must strictly adhere to NASA 14-coefficient, two-temperature-range format
Optional User Rate Subroutines – user can define a custom rate-of-progress expression for an individual reaction or net rates of production for all species in user routines designed to be called during any CHEMKIN application run	none

## ***Parameter Study***

In order to perform a parametric study in Chemkin II, users had two choices: Use of “continuation” keywords within a keyword input file, or writing complex scripts to manage input and output through manipulation of keyword files. Continuation options were limited to certain reactor parameters and were only available for steady-state simulations. To do any kind of parameter variation that involved chemistry parameters, users had to write their own programs or scripts that parsed and modified keyword-input files, managed file naming and organization, executed programs, and extracted data from binary FORTRAN solution files.

The Parameter Study Facility in CHEMKIN 4.1 allows users to perform complex parametric studies without having to write programs or scripts and without running from the command line. The Parameter Study can be used with all reactor models and reactor networks, for both steady-state and transient simulations. This capability automates conducting multiple runs to consider the effects of varying one or more input variables. Parameter Studies can be set up with chemistry-set parameters (such as reaction-rate constants or Lennard-Jones potentials) as well as with reactor, inlet, or operating-condition parameters. All or a selection of the Parameter Study cases can be run within a given session, thus allowing the user to return later to the project to continue running additional cases. The Continuation option (which was also available in Chemkin II) can easily be used alongside with Parameter Study to provide an added dimension for model refinement.

An important aspect of the parameter-study option is the harvesting of solution data from each of the model runs to provide compound solution sets that may be plotted using line or contour plots, giving quick visualization of parameter-variation effects.

## ***Visualization and Analysis of Results***

### **Graphical Post-Processing**

No visualization or post-processing capabilities were built into Chemkin II. CHEMKIN 4.1 allows users to quickly view CHEMKIN results vs. time, distance, and varied parameter, including ignition times, flame speeds, rates of production, and sensitivity coefficients. Data can be viewed using line plots, or as 2 or 3-D contour plots. CHEMKIN 4.1 gives the user interactive control over numerous plot-formatting options as well as allows for easy exporting of all or selected data in comma, space or tab-delimited formats. Figure 2 Figures 1 through 3 below demonstrate various abilities of the 4.1 post-processor.

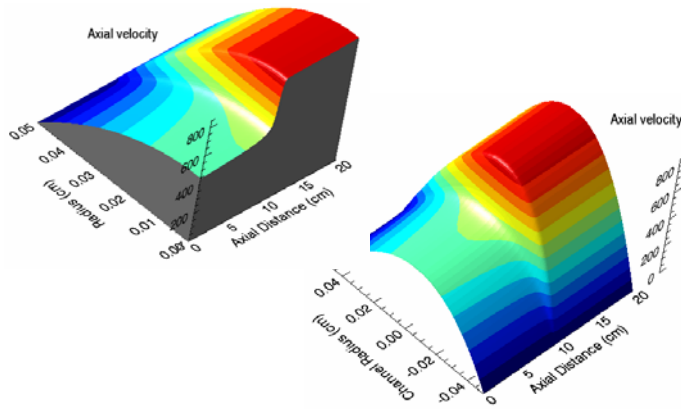


Figure 2: Ability to mirror 3-D contour plots about symmetric axis

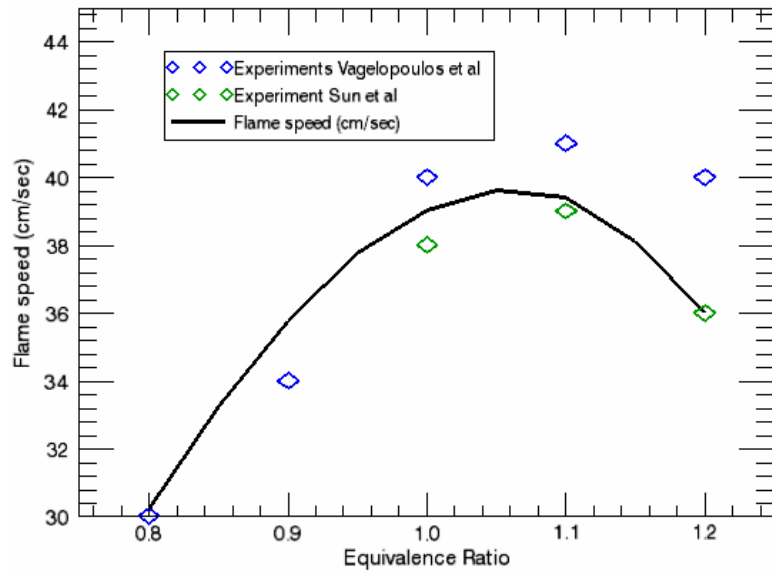
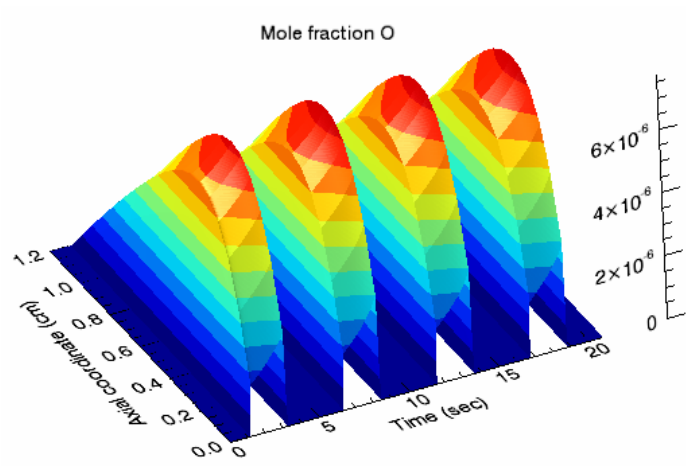


Figure 3: Ability to import experimental data in a variety of delimited formats directly into the same plot as simulations



**Figure 4: Ability to create plots of variables vs. a parameter varied in the Parameter Study**  
*(Mole Fraction of O species was varied in Parameter Study)*

***Input consistency***

Units

Chemkin II application codes had inconsistent unit requirements for user input and code output, often causing confusion when moving from one application to another. In addition, the required units were often inconvenient for certain systems, requiring the user to manually convert “natural” units to the required units system. CHEMKIN 4.1 offers a variety of unit options for both user-input values and for solution output during post-processing. Input and output variable units can be controlled separately through stored, user-defined preferences or through interactive control during input/output of data. For example the user can provide his/her initial pressure in psi units, but choose to plot the resulting pressure in atmosphere (atm) units. Table 3 lists all current units systems available for CHEMKIN 4.1 users to choose from.

**Table 3: Unit Options Comparison**

Chemkin II	CHEMKIN 4.1
Mixed “Chemkin” units	Mixed “Chemkin” units
none	cgs
none	SI
none	British Units
none	custom (defined by user)

## Support/Maintenance Documentation

The original Chemkin II functionality is described in static Sandia reports (Kee, Rupley et al. 1989) that were not maintained, as new versions of code were distributed. Since the software was open-source code, there was no formal tracking or documentation of changes made to the software, and only limited examples of capabilities were provided.

The commercially supported CHEMKIN is frequently updated and maintained by Reaction Design. Formal documentation is available with every CHEMKIN install and includes detailed examples pertaining to combustion, materials and microelectronic industries, as well as descriptions of all input parameters and problem set-up procedures. This documentation is updated with every maintenance and major CHEMKIN release.

Because there was no version control for Sandia distributions of Chemkin, modifications or improvements to the software were often lost during upgrades to later versions, forcing users to continuously re-apply their local modifications. Version control of the commercially supported CHEMKIN allows users to track and inform customers of all of software updates, new capabilities, enhancements and bug fixes included in each version of CHEMKIN. This standardizes results obtained with supported CHEMKIN, assures backwards compatibility, and allows highly-reproducible results among different researchers.

No formal technical support was available for Chemkin II. In contrast, Reaction Design quickly responds to all emailed or phoned-in tech support questions for all supported versions of CHEMKIN. Reaction Design also maintains an on-line user group and frequently asked questions (FAQ) forum. Professional support addresses a wide range of problems, ranging from installation issues to problem-specific applications. In addition, frequent training classes and web-based seminars are available

## The History of Chemkin

In the early 1980s, Sandia National Laboratories developed CHEMKIN and CHEMKIN II. Sandia had and maintained copyright and ownership of the CHEMKIN programs and the CHEMKIN name, although it distributed this code widely to collaborators around the world. Until 1997, the only organizations authorized to distribute versions of CHEMKIN were Sandia and Department of Energy Office of Scientific and Technical Information (OSTI). In 1995, Sandia initiated a fee-based license program for the current version of CHEMKIN II and the initial version of CHEMKIN III.

In February 1997, Sandia contracted with Reaction Design to become the exclusive worldwide CHEMKIN distributor. Currently, Reaction Design is the sole distributor of CHEMKIN software, although parties that originally obtained their Chemkin II license directly from Sandia National Laboratories maintain the ability and rights to run and modify their original Chemkin codes.

Since Reaction Design took over all of development, support and distribution of Chemkin (currently entitled CHEMKIN) software, six major release versions have been created and distributed by Reaction Design. The latest version, CHEMKIN 4.1, was released in July of 2006.

## References

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- Kee, R. J., F. M. Rupley, et al. (1989). Chemkin-II: A FORTRAN chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics, SAND89-8009, Sandia National Labs.