CHEMKIN Study – Computing Package for Thermal Gas-Phase Chemical Reactions

Summary

A validated computer code was created that performs the basic functions of the CHEMKIN chemical kinetics software.

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Full Description

This is a software package programmed in 3 different styles:
(1) Pure Matlab (which stands for "matrix laboratory" and is the industry standard for scientific, engineering, and economic calculations) (Note: meaning of "Pure" in this context means "entirely in")
(2) Pure GNU Octave (a free-software Matlab alternative part of the GNU project)
(3) A hybrid of GNU Octave and Fortran (Fortran code requires f95 compiler or equivalent)

This chemical kinetics package has been fully validated against the CHEMKIN package using the GRI 3.0 methane (CH4) mechanism, and any difference in output can be attributed to numerical error. One of the issues that arises when using the CHEMKIN chemical kinetics package, which is written entirely in Fortran, is that the source code is very hard to understand. No one has yet written a CHEMKIN-like package purely in Matlab. There is an open source chemical kinetics package called Cantera written in C++, but it is also very hard to understand, which stagnates collaboration.

The advantage of programming a chemical kinetics package entirely in Matlab is that it is a high level programming language. What might take many lines in Fortran, can be done in one line in Matlab. For a scientific person who is more of a chemist than a computer scientist, this makes the code much easier to read, allowing one to focus on the problem

at hand instead of a computer science problem. Of course some scientists prefer Fortran over Matlab either because it is what they know (and don't want to learn anything else) or they like the way every array/matrix has to be allocated at the top of each function. This is really annoying in that it adds many extra lines, but makes it easier to know what every variable is doing. Although even the most hardcore Fortran-fan will still use Matlab's plotting functions. (GNU Octave also has great plotting functions)

When doing a task such as reading in a chemical mechanism, due to the tedious nature of Fortran, Matlab and its free-software cousin GNU Octave make this task much easier and the code much more readable. This allows the user to play around with the problem at hand. With my code it is clear exactly how you get from the chemical mechanism file to the functions that are needed to solve the system, and it is done in significantly fewer lines of code.

Issues arise dealing with programming language speeds and licenses:
(1) Matlab solves the chemical kinetics problem fast for a high level language, but a corporate Matlab license is very expensive (upwards of $50,000/year for a major company), which is why a GNU Octave version was created.
(2) GNU Octave can run most Matlab code with no modification but is much slower than Matlab; therefore, after GNU Octave read the chemical mechanism, I decided to print the functions that are constantly called from the ODE solver (reaction rates, specific heat, internal energy, etc) in Fortran.

Therefore, the third version of the package is a GNU Octave-Fortran hybrid, which uses the DASSL (Differential Algebraic System Solver) ODE solver written in Fortran and available in the public domain. This version is competitive with the CHEMKIN package. If you have a very large chemical mechanism, this might be the only feasible way to converge your problem with my package. The hybrid code is still relatively easy to understand, because complex reading and printing of hard coded functions is done in GNU Octave and only the heavy lifting is done in Fortran. (Note: when finding chemical equilibrium a root finder is used, not DASSL, because you are not solving a time dependent ODE)

Currently this is not a package that fully represents every aspect of CHEMKIN (all sorts of reactors and equilibrium solvers), but I do provide a zero dimensional volume as a function of time adiabatic reactor (equivalent to the Senkin program in CHEMKIN), an time dependent perfectly stirred reactor (equivalent to PSR program in CHEMKIN) and a constant pressure adiabatic equilibrium solver (equivalent to the Equil program in CHEMKIN). Also included are derivations that are much easier to understand, allowing for more collaboration (including an excellent step-by-step derivation of the equilibrium constant used for calculating reverse reaction rates). There is no mystery as to what unit any variable is, or how something is calculated, nor do you need to open any textbooks to understand my code. Although I do not go as far to explain how Troe form reactions or the Arrhenius form were invented. Mechanism reduction (which requires use of large scale parallel computing) using the GNU Octave parallel package could be easily implemented on Amazon's cloud. I provide directions on how to install GNU Octave and

its parallel package and how to implement a simple parallel example on Amazon's Cloud servers.

The format for reading chemical mechanisms is the CHEMKIN-II input format, this includes NASA polynomials for thermodynamic data, where 7 numbers are used to calculate quantities such as specific heat, enthalpy, entropy, etc. Currently this code reads the following type of chemical reactions: standard A-B-E style Arrhenius reactions, 3rd body reactions, pressure dependent reactions (Lindeman form), and Troe form reactions. It can handle 4 elements per chemical but can be easily modified to allow many more (current CHEMKIN package allows 5 elements per chemical). Also, some chemical mechanisms calculate reverse reaction rates using an extra set of "reverse" Arrhenius coefficients instead of the equilibrium constant (Kc), this is not implemented in my code. You could easily add this functionality by modifying your chemical input file, making your reaction only a forward reaction (this option is in my code) and then writing the reaction again, but in reverse (again as a forward only reaction) and then writing in your reverse Arrhenius coefficients as normal/forward Arrhenius coefficients. When you run the program you create hard-coded functions that can be read and understood very easily, and can be used without the code that created them. This style can be useful to get a feel for what is really going on in the problem at hand. For me personally, I don't fully understand any equation until I see it solved computationally and all the units are clearly indicated.

This software may need to be completely overhauled to suit another's purpose. For example, a user might want to take the hybrid version, convert it to pure Fortran, and then integrate it into their computational fluid dynamics package. The Ansys Corporation did exactly this when they integrated CHEMKIN style chemical mechanisms into their Fluent CFD program.

In its current form, it would work great to experiment with: new chemical reactions (by easily modifying the code), NTC (negative temperature coefficient) behavior of reactions, or to examine the effects of clean-burning biofuels (ignition delay, maximum temperature, pollutants, etc). Whatever you can imagine to help you analyze gas-phase chemical reactors can be easily added to this code. This code could serve as an excellent foundation for a modern CHEMKIN alternative. It could be very useful for researchers who don't want to be bogged down with the high cost of Matlab and CHEMKIN licensing.

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