New Methods for Predictive Chemical Kinetics

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Introduction

In most reactive fuel chemistry problems, there are far too many species and reactions for there to be any hope of experimentally determining the thermochemistry of each species and the rate constants of each reaction. Historically, modelers have modeled these systems empirically, constructing a small kinetic model with a few effective parameters which could be regressed from experiment. However, these small kinetic models usually do not capture the real chemistry/physics of the system, and so these models are typically only useful for interpolation, not for extrapolation or predictive design of new systems.

Recently, quantum chemistry has advanced so much that it can provide reliable values of missing rate and thermochemical parameters, at considerably less cost than determining the same values experimentally. However, these calculations are still rather difficult and unreliable, each requiring considerable care and attention. So it is not practical to compute every rate constant and thermochemical parameter that might conceivably be important in a fuel chemistry system.

Even if accurate values of all the rate constants and thermochemical parameters were available, it is still very challenging to construct and solve the appropriate kinetic models. Solving the models is particularly difficult in systems which are spatially inhomogeneous, where the chemistry is significantly coupled to transport.

Many researchers [1] have attempted to move forward in this way:
1) use the computer to construct an approximate kinetic model using approximate rate parameters
2) use this approximate model to identify the most important reactions and species
3) refine the rate parameters for the most important reactions using experiment or quantum chemistry
4) construct smaller kinetic models faithful to the original
5) use the small models in the coupled chemistry-transport simulations.

However, although this concept has been pursued by several research groups in both industry and academia, progress has been rather slow, since each step in the process involves several difficult issues, both from the point of view of chemistry, and from the point of view of computer science/numerics. This preprint reports significant progress we have made on all fronts, based on a radically different software design of the mechanism generation software, a new approach to estimating the reaction rates, and recent advances in numerical algorithms.

Results

A new software paradigm for automated mechanism generation has been developed, which cleanly separates the computer science and chemistry aspects of automated mechanism generation. The key idea is that all of the chemical detail is represented by functional group and reaction template structures and associated parameters. The computer then compares these functional group structures with each molecule in the system, to determine which molecules can react in which ways. The rate and thermochemical parameters are also based on these functional groups. The new approach has the major advantage that chemists can extend and update functional group definitions and reaction rate or thermochemistry estimates without ever touching the source code. This is very important, since our understanding of chemistry is far from complete, and it will be many years before accurate estimates will be available for all the types of reactions important in fuel chemistry. The computer science and numerical aspects of the problem are handled by a robust black box code, while the assumptions made about the chemistry are clearly visible, unambiguous, and easy to document.

Known reaction rates and thermochemistry are stored in an extensible library, and unknown reaction rates and thermochemistry are estimated based on functional group additivity. Classic Benson-type group additivity has been extended to include transition states (to predict rates).[2] This requires the use of larger functional group templates than the simple atom-centered Benson groups. This more flexible group concept is also found to be very useful for estimating the thermochemistry of polycyclic aromatics – using bond-centered groups rather than traditional atom-centered groups doubles the accuracy of the estimation procedure. Several hundred new group values have been determined using quantum chemical methods, some reported elsewhere[3,4,5] and carefully organized into tree structures to avoid ambiguity and to speed computation times. We plan to make these tree structures and the associated parameters publicly accessible over the internet, so that chemists anywhere on the globe can easily improve the estimates.

The new Java software package that implements this new concept, RMG, includes several state-of-the-art features, including on-the-fly computation of k(T,P) using the efficient and accurate algorithm developed by D.M. Matheu et al..[6,7] The software architecture of RMG is considerably different than previous reaction mechanism generation programs, being completely object-oriented, and documented structured using UML.

The large kinetic models generated by RMG can be automatically and optimally reduced to any desired size using the algorithm of Bhattacharjee et al..[8] Valid ranges of the both the large and the reduced models are automatically estimated using a new rigorous method. The reduced models are very useful in reacting flow simulation and in other compute-intensive applications. Several numerical issues arise when using large kinetic models, particularly when coupling them into reacting flow simulations. In particular, it has been found very helpful to take advantage of the inherent sparsity of the Jacobians of large kinetic models [9], and to use operator-splitting methods which converge to the correct solution (rather than popular methods which have $O((\Delta t)^2)$ errors at convergence, since these errors can be very large if the chemistry is stiff).[10] Very recently, new global optimization algorithms have been developed which can guarantee error tolerances over a continuous range of reaction conditions [11], and these allow one to rigorously control the errors introduced by using reduced models rather than the full model.

In some situations, one does not want to simulate a specific known system, but rather to determine an upper bound on what is possible in any process of a particular type. We have run several examples of these upper bound calculations for catalytic oxidations, where the energetics of the surface intermediates are unknown.[12] This problem, the model reduction and range analysis problem, and a variety of safety/operability problems are mathematically related:

they all can be written as types of semi-infinite programs (i.e. optimization problems with an infinite number of constraints). Recent algorithmic advances using interval analysis [11] will allow significant advances in solving all these problems.

Conclusions

The new extensible modular design of mechanism generation software promises to greatly accelerate progress towards predictive chemical kinetics for problems in fuels chemistry. The computer-constructed kinetic models based on a library of small molecule reactions and group-additivity-based estimates of rate and thermochemistry of larger molecules are already quite accurate [7], and the accuracy can be refined by use of sensitivity analysis to identify which rate constants and thermochemical parameters merit further study. The extensible and unambiguous format should encourage community-wide efforts to improve the accuracy of the rate estimates, and to broaden the range of chemistry which can be modeled.

Advances in numerics and computer science are needed to parallel improved understanding of the chemistry. Recent improvements in optimization algorithms and in methods for handling large systems of stiff differential-algebraic equations are keeping pace with our ability to construct large accurate kinetic simulations. Although reacting flow simulations are still very challenging, effective algorithms are becoming available. In most cases the accuracy of the simulations are limited more by our ignorance of the chemistry than by the approximations introduced in order to solve the differential equations.

As the simulations become more complex, a variety of additional software tools are needed to help humans check the accuracy of the models and to correctly interpret the model predictions. Our 20+ year old paradigm of kinetics assumes that a single human can construct, solve, and interpret an entire simulation, doing most of the steps by hand. As the simulations become more detailed, we need to move to a new paradigm that encourages teamwork, and where all of the "well-understood" aspects of the problem are automated, to allow the scientists and engineers to focus on the aspects and issues that are really unresolved.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science Foundation, BP Chemical, and the Department of Energy.

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