Rate-Controlled Constrained-Equilibrium Theory of Chemical Reactions

James C. Keck

MIT, Cambridge, MA 02139

Abstract. The Rate-Controlled Constrained-Equilibrium (RCCE) method for simplifying the treatment of reactions in complex systems is summarized and the selection of constraints for both close-to and far-from equilibrium systems is discussed. Illustrative examples of RCCE calculations of carbon monoxide concentrations in the exhaust products of an internal combustion engine and ignition delays for methane-oxygen mixtures in a constant volume adiabatic chamber are given and compared with "detailed" calculations. The advantages of RCCE calculations over "detailed" calculations are discussed.

INTRODUCTION

Improving the efficiency and reducing the emissions of automobile engines and power plant burners requires a fundamental understanding of hydrocarbon oxidation. This is an extremely complex process involving thousands of chemical species and millions of possible chemical reactions [1]. Clearly, greatly simplified chemical kinetic models are needed for practical applications.

The most popular approach to this problem is to start with "detailed" models involving as many differential rate equations for the species as can be handled by available computers, then simplify the model using various mathematical approximations that convert differential rate-equations to nonlinear algebraic equations, but leave the total number of equations unchanged [2]. A major problem with this approach is that less than fifty of the millions of possible reaction rates involved are known to better than a factor of two and including those with larger uncertainties is unlikely to improve the accuracy of the results and makes little or no sense.

RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM

A more rational approach, firmly based on the Second Law of Thermodynamics, is the Rate-Controlled Constrained-Equilibrium (RCCE) theory of chemical reactions in complex systems [3]. All the possible species and reactions for a system with specified elements and state-variables are included implicitly in this model, but the number of chemical rate-equations required to describe the evolution of the system can be zero if the only constraints are the thermodynamic state variables. The assumptions of the

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model are:

1. Slow reactions impose slowly changing constraints on the allowed state of a complex system.
2. Fast reactions relax the system to the constrained-equilibrium state determined by the instantaneous values of the constraints.
3. The system evolves through a sequence of constrained-equilibrium states at a rate controlled by the rate-equations for the constraints alone.

For the case where the state variables are the temperature, T, and the pressure, p, the constrained-equilibrium state is obtained by minimizing the Gibbs free energy function

$$F = RT \sum_{j=1}^{ns} N_j \ln(N_j/Q_j) \tag{1}$$

subject to the constraints

$$C_i = \sum_{j=1}^{ns} a_{i,j} N_j \qquad i = 1, \ldots, nc \tag{2}$$

where ns is the number of species, N_j is the mole number for the species j, Q_j is the corresponding Partition Function, nc is the number of constraints, and $a_{i,j}$ is the value of the constraint i for the species j.

Using the method of Lagrange multipliers, one obtains the species mole numbers for the constrained-equilibrium state

$$N_j^{ce} = Q_j \exp\left(- \sum_{i=1}^{nc} a_{i,j} \gamma_i / RT \right) \tag{3}$$

where γ_i is the constraint potential conjugated to the constraint i. The constraint potentials, in conjunction with the rate-equations for the constraints fully determine the composition and evolution of the system.

SELECTION OF CONSTRAINTS

Any linearly independent property of a system can be used as a constraint. The most fundamental are the state variables and the number of moles of the individual elements of which the system is composed. At the temperatures of interest for gas-phase chemistry, the rates of nuclear and ionization reactions are negligible and the elements are conserved. The state variables, however, may change as a result of work interactions with the environment. If these are the only constraints, the system will evolve through a sequence of constrained-equilibrium states at a rate controlled by the rate-equations for the state variables. This is the well-known case of “shifting equilibrium.” At the other extreme is the case of “detailed” modeling where all possible species in the system are included as additional time-dependent constraints and the evolution of the system is controlled by the rate-equations for both the species and the state variables.

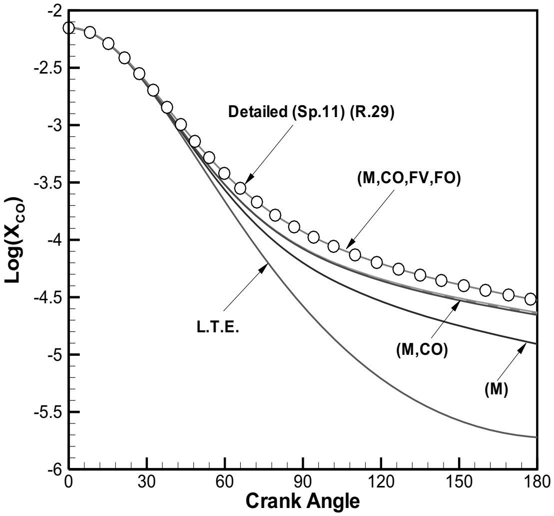

FIGURE 1. CO mole fractions as a function crank angle during the expansion stroke of an internal combustion engine.

In RCCE calculations, constraints which are linear combinations of species are also considered. Such constraints are imposed by classes of slow reactions associated with the making and breaking of valence bonds or changes in electronic state due to collisions. Among the most basic constraints of this type are:

1. M, the total number of moles of gas in the system: controlled by slow dissociation/recombination reactions.
2. FV, the free valence = number of unpaired electrons in the system: controlled by slow branching reactions.
3. FO, free oxygen = any O-atom not directly bound to another O-atom: controlled by slow OO bond breaking reactions.
4. CO, carbon monoxide: controlled by slow electron spin changing reactions.

CLOSE-TO-EQUILIBRIUM SYSTEMS

These four constraints are particularly useful for modeling systems driven away from an initial equilibrium by fast expansions and compressions. An example of this is shown in Fig. 1 where RCCE calculations of the CO mole fraction during the expansion of combustion products in an internal combustion engine are compared with detailed calculations [4].

RCCE calculations involving only energy and volume constraints are shown by the curve labeled L.T.E. This is the case of "shifting" equilibrium. "Detailed" calculations including 11 species and 29 reactions abstracted from the GRI-3 mechanism [5] are shown by the circles. It can be seen that the L.T.E. results at the end of the expansion stroke are lower than the "detailed" results by more than an order of magnitude. Adding

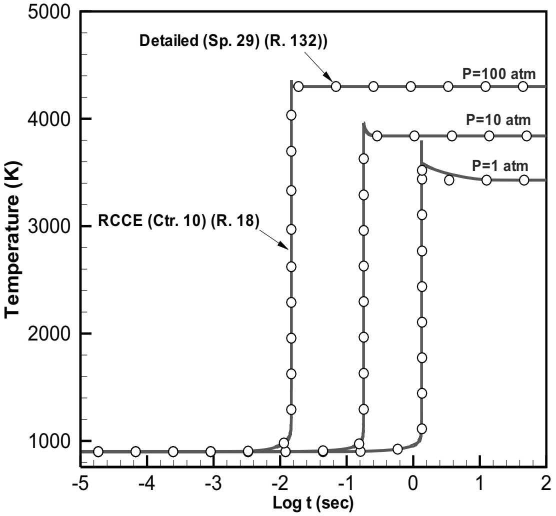

FIGURE 2. Temperature as a function of time during the oxidation of stoichiometric methane-oxygen mixtures at various initial pressures in a constant volume adiabatic chamber.

additional time-dependent constraints, first on the moles of gas, M, alone and then on both M and the moles of carbon monoxide, CO, significantly improves the agreement. Finally, adding two more constraints on the free valence, FV, and the free oxygen, FO, gives virtually perfect agreement between RCCE and "detailed" calculations. It should be noted that the constraint-potentials obtained from the RCCE calculations can be used to obtain mole fractions not only for the 10 species in the "detailed" model but for any species for which the thermodynamic properties are known.

FAR-FROM-EQUILIBRIUM SYSTEMS

For far-from-equilibrium systems, such as a reacting fuel/oxygen mixture, it is necessary to use the fuel as a constraint to fix the initial state of the system. The fuel constraint alone plus the fixed elemental constraints are sufficient to guarantee the system will go to the correct final equilibrium state. However, to obtain the correct time evolution of the system, additional constraints may be needed and the accuracy of the results depends on the careful selection of these added constraints.

This case is illustrated in Fig. 2 which shows temperature as a function of time curves for stoichiometric CH_4/O_2 mixtures in a constant volume adiabatic chamber at an initial temperature of 900 K and initial pressures of 1, 10 and 100 atmospheres [6].

The circles show the results of "detailed" calculations including 132 reactions and 29 species based on the GRI-3 mechanism previously cited. The lines show the results of RCCE calculations for 18 reactions and 10 constraints including 3 fixed elemental constraints, the 4 basic time-dependent constraints and 3 additional time-dependent constraints on fuel radicals, alcohols and aldehydes. The agreement is within 2 percent over the entire range of conditions studied. Calculations with the first 8 constraints give agreement within 10 percent.

In general, the accuracy of RCCE calculations improves as the number of constraints increases and, in the limit where the number of constraints equals the number of species in the "detailed" model, the RCCE and "detailed" calculations are equivalent. However, given the large uncertainties in most of the reaction rates involved in the "detailed" calculations, it is not unreasonable to anticipate that RCCE calculations using a limited number of constraints based only on reliable rate data may be more accurate than "detailed" calculations including a large number of estimated reaction rates. In this connection, it should be noted that for large systems, it is impossible to "back out" accurate reaction rates due to the large amount of data required and the limited accuracy of the experimental measurements.

SUMMARY AND CONCLUSIONS

The RCCE model based on the Second Law of Thermodynamics has the potential to greatly simplify the treatment of complex reacting systems for which incomplete information is available without truncation of the species list or the introduction of *ad-hoc* global reactions. Moreover, within the framework of Bayesian inference, this model gives the most reliable results consistent with the information that is available. Among the advantages of the RCCE model are:

1. By focusing attention on the rate-limiting reactions, it leads a better understanding of the important mechanisms and reaction paths involved in the evolution of a complex system.
2. Since the number of constraints required for RCCE calculations is very much smaller than the number of species required for "detailed" calculations, the total number of differential + algebraic equations required will be very much smaller than that for other models.
3. Since only reactions that change a constraint are needed, the number of reaction rates and the level of effort required to tabulate and input them is greatly reduced.
4. RCCE calculations can be initiated with only the constraints on the state variables and systematically improved by adding constraints on the internal variables one at a time until an acceptable level of accuracy is reached. When the number of constraints equals the number of species in a "detailed" model the result agree perfectly.
5. The Entropy production in RCCE calculations will always be positive and the correct final equilibrium state for the fixed elemental constraints will always be reached regardless of the number of constraints employed.
6. The method can be applied to any thermodynamic system: classical, quantum mechanical, or relativistic, including the Universe as a whole.

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