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Djamel Hamiroune, Mohamad Metghalchi
Mechanical, Industrial and Manufacturing Engineering
Northeastern University
Boston, MA 02115

James C. Keck
Mechanical Engineering Department
Massachusetts Institute of Technology
Cambridge, MA 02139

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Djamel Hamiroune, Mohamed Metghalchi,
Mechanical, Industrial and Manufacturing Engineering
Northeastern University
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James C. Keck
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Massachusetts Institute of Technology
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Abstract

The Rate-Controlled Constrained-Equilibrium method (RCCE) is a powerful technique for simplifying the treatment of chemical reactions in complex systems. The method is based on the assumption that slow chemical reactions impose constraints on the allowed composition of such systems. Since the number of constraints can be very much smaller than the number of species, the number of rate equations to be integrated can be considerably reduced. In the present work, C1 chemistry with 33 species has been used to investigate stoichiometric formaldehyde-oxygen mixture in a constant energy constant volume chamber. The state of the system was determined by three elemental constraints: elemental carbon, elemental oxygen and elemental hydrogen and five variable constraints: total number of moles, moles of fuel, moles of active valence, moles of free oxygen, and moles of carbon dioxide. The eight rate equations for the constraint potentials were integrated for a wide range of initial temperatures and pressures. The RCCE calculations were in acceptable agreement with detailed calculations and were faster than the detailed calculations which required integration of 33 species rate equations. The saving in CPU time ranged from 15% to 50% depending on the initial conditions.

Introduction

The development of models describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. Although the rate equations describing the evolution of such systems are well known, for large systems containing hundreds or more species and thousands of possible reactions, their integration can be extremely difficult due to the large number of differential equations involved.

Numerous approaches for simplifying this problem have been made, some involving reduction of reaction mechanisms[1] and truncations of the species list[2] and others involving mathematical approximations that convert differential equations into algebraic equations such as partial equilibrium approximation and quasi-steady state approximation[3]. Another approach discussed in refs.[4] consists of method identifying the fast time scales of the chemical reaction systems based on eigenvalue analysis, assuming that fast relaxation processes are in local equilibrium. This work is to study the RCCE method which was proposed originally by Keck and Gillespie and later developed by Keck and co-worker [5]. In this method instead of a full set of rate equations for the species, only the rate equations for the constraints are needed to determine the state of the system. Since the number of constraints required is expected to be very much smaller than the number of species, the task of integrating these equations should be very much simplified. In addition if a reaction does not change any constraint, it will not affect the evolution of the system thus only reaction rates of those reactions which change the constraints are required. The RCCE method has been used on hydrogen/oxygen system [5].

The purpose of this work is to use RCCE method for systems with a large number of species and to compare results using RCCE with results obtained from a complete model. A C1 system, including 33 species and 88 reactions has been developed and used, as shown in table 1.

Detailed Treatment Of Chemical Reactions

Species Rate Equations

The most accurate method of describing the evolution of the system is the integration of the full set of rate equations for the species. For a given reaction mechanism the rate equation for an individual species j is given in terms of all reactions rates involved by

$$\dot{N}_j = V\sum_{k=1}^{nr} \nu_{jk} r_k \qquad j=1,\ldots,ns \tag{1}$$

where N_j is the number of moles of species j, V is the volume of the system, nr is the number of reactions, ns is the number of species, ν_{jk}^{+} *and* ν_{jk}^{-} are the forward and reverse stoichiometric coefficient of species j for reaction k, $\nu_{jk} = \nu_{jk}^{-} - \nu_{jk}^{+}$ is the net change in moles of species j due to reaction k, $r_k = r_k^{+} - r_k^{-}$ is the net reaction rate per unit volume, and r_k^{+} and r_k^{-} are the forward and reverse reaction rates.

In the case where the energy and volume are prescribed, and additional equation for the temperature can be obtained by differentiating the expression for the energy of the system with respect to time:

$$\dot{T} = (\dot{E} - \sum_{j=1}^{ns} \dot{N}_j e_j(T)) / \sum_{j=1}^{ns} N_j c_{vj}(T) \tag{2}$$

where e_j is the specific internal energy of species j, $c_{vj} = de_j / dT$ is the specific heat at constant volume for species j. Equation (1) can be integrated in conjunction with equation (2) to obtain the temperature and species composition. The pressure is determined using the ideal gas equation.

Rate-Controlled Constrained-Equilibrium (RCCE)

Since only the rate equations for the constraints are needed to determine the state of the system and the number of constraints required is expected to be very much smaller than the number of species, the task of integrating these equations should be very much simplified for large systems.

Rate equations for constraints

The constraints imposed on the reacting system are assumed to be a linear combinations of species composition present in a given system, the rate equations for the constraints are given by:

$$\dot{C}_i = \sum_{j=1}^{ns} a_{ij} \dot{N}_j \qquad i=1,\ldots,nc \tag{3}$$

where a_{ij} is the value of the constraint i for the species j and nc is the number of constraints.
Using the species rate equations (1) these rate equations are written in the following form:

$$\dot{C}_i = V\sum_{k=1}^{nr} b_{ik} r_k \qquad i=1,\ldots,nc \tag{4}$$

where $b_{ik} = \sum_{j=1}^{ns} a_{ij} \nu_{jk}$ is the change of constraint i due to the reaction k and nr is the number of reactions.

Note that since elements are conserved their corresponding constraints are constant then for elements, $b_{ik} = 0$ and $\dot{C}_i = 0$ for i=$1,\ldots ne$, where ne is the number of elements in the system. This ensures conservation of elements and reduces the number of rate equations to be integrated by ne.

Rate equations for Constraint Potentials

The constrained-equilibrium composition is found by maximizing the entropy or minimizing the Gibbs free energy of the mixture subject to a set of constraints using Lagrange multipliers method. For each constraint there is a corresponding Lagrange multipliers (constraint-potential). The species composition is then determined as a function of those multipliers:

$$N_j = Q_j \exp(-\sum_{i=1}^{nc} a_{ij} \gamma_i) \qquad j=1,\ldots,ns \tag{5}$$

where $Q_j = \frac{p_o V}{RT} \exp(-\mu_j^o)$ is the partition function for species j, and $\mu_j^o = F_j^o / RT$ is the dimensionless standard Gibbs free energy and γ_i is the Lagrange multiplier (constraint potential) conjugate to i^{th} constraint. The system is described by nc constraint potentials instead of ns species, thus the order of the system is reduced by ns-nc which results in reduction of number of rate equations to be integrated. Once the constraint potentials γ_i have been determined the constrained composition can easily be calculated using the equation (5). In the case where the independent thermodynamic variables are T and V, the rate equations for the constraints potentials can be easily

found combining equations (1), (3) and (5)

$$\sum_{n=1}^{nc} D_{in}\dot{\gamma}_n + D_{iT}\dot{T} + D_{iV}\dot{V} - V\sum_{k=1}^{nr} b_{ik}r_k = 0, \quad n=1,...,nc, \qquad i=1,...,nc \tag{6}$$

where $D_{in} = \partial C_i / \partial \gamma_n = \sum_{j=1}^{ns} a_{ij}a_{nj}N_j$, $D_{iT} = \partial C_i / \partial T = \sum_{j=1}^{ns} a_{ij}E_j(T)N_j / RT^2$ and $D_{iV} = \partial C_i / \partial V = \sum_{j}^{ns} a_{ij}N_j / V$

For the case where E and V are the independent variables, an additional equation for T is obtained by substituting equations (5) in equation (2)

$$\sum_{n=1}^{nc} D_{En}\dot{\gamma}_n + D_{ET}\dot{T} + D_{EV}\dot{V} - \dot{E} = 0 \tag{7}$$

where $D_{ET} = \partial E / \partial T = \sum_{j}^{ns}\left[c_{vj}(T)T + E_j^2(T)/RT\right]N_j / T$ and $D_{EV} = \partial E / \partial V = \sum_{j=1}^{ns} N_j E_j(T) / V$

In equations (6) and (7), the unknowns are the constraints potentials themselves. The number of unknowns is reduced from the full set calculations by *(ns-nc)*. The final set of differential equations to be integrated is a nonlinear system of first order differential equations in the form:

$$\begin{bmatrix} D_{in}(\gamma,T) & D_{iT} \\ D_{En} & D_{ET} \end{bmatrix}\begin{bmatrix} \dot{\gamma} \\ \dot{T} \end{bmatrix} = \begin{bmatrix} F(\gamma,t) \\ 0 \end{bmatrix} \tag{8}$$

The Constraints

The most obvious constraints are those imposed by the conservation of elements. These are time independent and must be included in all kinetic calculations. Among the most important time dependent constraints are those imposed by slow dissociation/recombination reactions, which control the total moles, slow branching reactions which control the total valence of the system, the fuel and free oxygen. There are also a number of conditions, which must be carefully observed in choosing constraints. The method of Lagrange multipliers requires that these constraints are linearly independent otherwise the matrix D_{in} is singular. The constraints must be capable of holding the system in the specified initial state within reasonable accuracy and the matrix D_{in} in equation (8) must be non-singular to permit inversion.

Premixed formaldehyde-oxygen mixtures in an adiabatic constant volume chamber have been studied. A full set of rate equations with 88 reactions and 33 species were integrated to obtain exact solutions for comparison with RCCE calculations. Calculations were carried out for a range of pressures between 0.01 atm to 1000 atm and a range of temperatures between 900 K and 1500 K using DASSL. The calculations using the constraint potentials method included up to eight constraints. The constraints used are three fixed constraints elemental carbon (EC), elemental oxygen (EO), elemental hydrogen (EH), and five variable constraints: total number of moles (M), moles of fuel (FU), moles of active valence (AV), moles of free oxygen (FO), and moles of carbon dioxide (CO_2). These constraints are shown in matrix form in terms of the 33 species in table 1.

Discussion

Figure 1 shows a plot of temperature as a function of time for the case with initial conditions of 1500 K and 1 atm. The solid curves represent the detail calculations, the dotted curves are the RCCE calculations. The curves show the behavior typical of the low and high pressure regimes.

Figures 2 to 4 show the number of moles for the individual species as a function of time. The solid curves represent the detail calculations, where the curves with symbols represent the RCCE calculations.

Summary

Rate equations for the constraint factors associated with the Rate-Controlled Constrained-Equilibrium (RCCE) method have been developed and successfully integrated for a stoichiometric mixture of formaldehyde-oxygen system over a wide range of initial temperatures and pressures. RCCE calculation using variable constraints on the total moles, fuel, active valence, free oxygen and CO_2 in additions to the three elemental constraints were in good agreement with detailed calculations. For this system including 33 species, there was a gain of 15 % in the high temperature case and a gain of 50 % in the low temperature case in running times.

References

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TABLE 1

Aij Matrix for CH_4/O_2 System

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
	CH2O	CH3	CH3O	CH4	CO	CO2	H	CHO	HO2	H2	H2O	H2O2	O	OH	O2	CH2OH	CH3OH	CH2	CHOH	HOCO	HOCHO	OCHO	HOCH2OH	CH3OOH	OCH2OH	CH2OOH	CH3OO	HOHOCO	HOOCHO	OHOCO	HOOCO	OOCHO	OCH2OOH
M	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
EH	2	3	3	4	0	0	1	1	1	2	2	2	0	1	0	3	4	2	2	1	2	1	4	4	3	3	3	2	2	1	1	1	3
E0	1	0	1	0	1	2	0	1	2	0	1	2	1	1	2	1	1		1	2	2	2	2	2	2	2	2	3	3	3	3	3	3
EC	1	1	1	1	1	1	0	1	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
AV	0	1	1	0	0	0	1	1	0	0	0	0	2	1	0	1	0	2	2	1	0	1	0	0	1	1	1	0	0	1	1	1	1
FU	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
FO	0	0	1	0	0	0	0	0	0	0	1	0	1	1	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

FIGURES

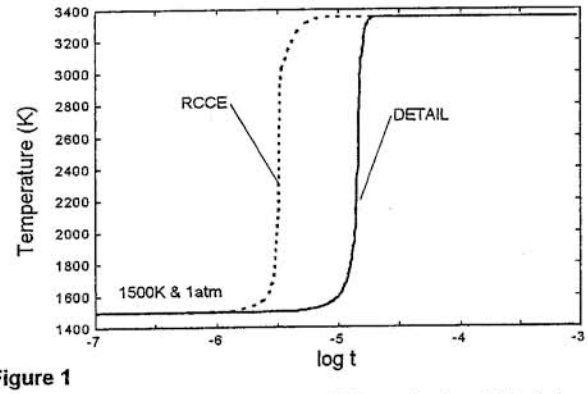

Figure 1

Temperature vs. time for constant E and V case for formaldehyde/oxygen system. Initial temperature and pressure are 1500K and 1atm

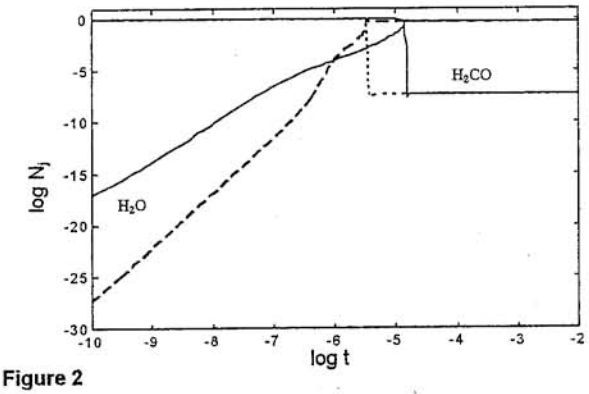

Figure 2

H_2CO and H_2O number of moles vs. time for constant E and V case the solid curves represent the detail calculations, where the dotted curves represent RCCE calculations with (M+FUEL+AV+FO+CO2) constraints.

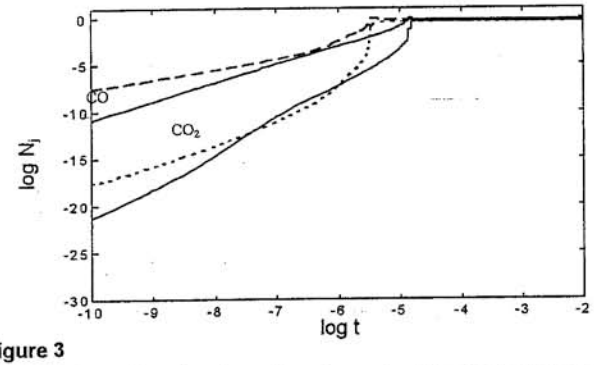

Figure 3

CO and CO_2 number of moles vs. time for constant E and V case the solid curves represent the detail calculations, where the dotted curves represent RCCE calculations with (M+FUEL+AV+FO+CO_2) constraints.

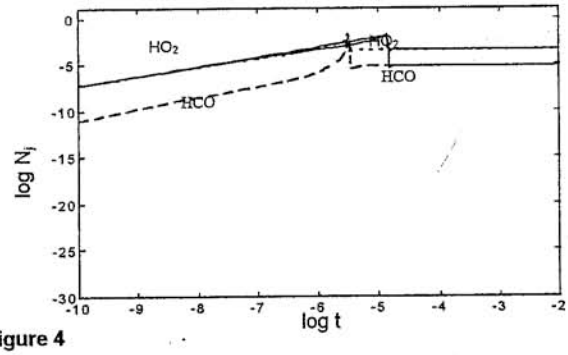

Figure 4

HO_2 and HCO number of moles vs. time for constant E and V case the solid curves represent the detail calculations, where the dotted curves represent RCCE calculations with (M+FUEL+AV+FO+CO_2) constraints.