Int.J. of Thermodynamics,
Vol.8, (No1), pp.43-53, March-2005

ISSN 1301-9724

Application of the Maximum Entropy Principle in the Analysis of a Non-Equilibrium Chemically Reacting Mixture

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Abstract

The Maximum Entropy Principle has been used to model complex chemical reaction processes. The maximum entropy principle has been employed by the Rate-Controlled Constrained-Equilibrium (RCCE) method to determine concentration of different species during non-equilibrium combustion process. In this model, it is assumed that the system evolves through constrained equilibrium states where entropy of the mixture is maximized subject to constraints. Mixture composition is determined by integrating set of differential equations of constraints rather than integration of differential equations for species as is done with detailed kinetics techniques. Since the number of constraints is much smaller than the number of species present, the number of rate equations required to describe the time evolution of the system is considerably reduced. This method has been used to model the stoichiometric mixture of the formaldehyde-oxygen combustion process. In this study 29 species and 139 reactions has been used, while keeping the energy and volume of the system constant. Calculations have been done at different sets of pressures and temperatures, ranging from 1 atm to 100 atm, and from 900 K to 1500 K respectively. Three fixed elemental constraints: conservation of elemental carbon, elemental oxygen and elemental hydrogen and from one to six variable constraints were used. The four to nine rate equations for the constraint potentials (Lagrange multipliers conjugate to the constraints) were integrated and as expected, RCCE calculations gave correct equilibrium values in all cases. Only 8 constraints were required to give very good agreement with detailed calculations. Ignition delay times and major species concentrations were within 0.5% to 5% of the values predicted by detailed chemistry calculations. Adding more constraints improved the accuracy of the mole fractions of minor species at early times, but had only a little effect on the ignition delay times. Rate-Controlled Constrained-Equilibrium calculations reduced the computation time by 50% when using eight constraints.

Keywords: Maximum entropy principle, combustion modeling, formaldehyde oxidation, ignition delay, rate-controlled constrained-equilibrium

1. Introduction

The development of models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. The conventional approach to this problem involves (1) specifying the state and species variables included in the model, (2) compiling a full set of rate-equations for these variables, and (3) integrating this set of equations to obtain the time-dependent behavior of the system. Such calculations are frequently referred to as comprehensive or fully detailed although, except for the hydrogen/oxygen system, they contain only a small fraction of the species and reactions possible, some of which have been developed by Westbrook (2000) and Davis et al. (1999). For complex systems, this approach can involve formidable computational tasks requiring the tabulation of a great many reaction rates and the integration of a large number of stiff differential equations. Indeed, for hydrocarbon systems involving the possibility of literally thousands of chemical species and isomers, and millions of reactions, a truly fully detailed solution is difficult, if not impossible to conceive.

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Over the past several decades, numerous methods for simplifying the kinetics of large chemical systems have been proposed. These can be roughly divided into two classes. The first involves reducing the number of rate equations and reactions required by truncation of the species list (Hautman et al., 1981, Frenklach, 1987, 1991, Paczko et al., 1986, Peters, 1988, Chen, 1988, Tam and Ludforrd, 1988a, 1988b, Wang and Frenklach, 1991); the second involves the use of various mathematical approximations to simplify the system by converting differential equations to algebraic equations without reducing the number of species (Benson, 1952, Rein, 1992, Turanyi et al., 1993, Blasco et al., 2000). The methods in the first class increase the speed of calculation but reduce the level of detail of the results. The methods in the second class maintain a reasonable level of detail but it is not clear that the speed of calculation increases. Important advances in model reduction and in the accuracy of the results have more recently been made with the method of intrinsic, low-dimensional manifolds (ILDM) (Mass and Pope, 1992a, 1992b, Eggels and de Goey, 1995, Skodje and Davis, 2001) and with the method of computational, singular perturbation (CSP) (Lam and Goussis, 1988, Lam, 1993)

Here, we investigate an alternative approach, the Rate-Controlled Constrained-Equilibrium (RCCE) method, originally proposed by Keck and Gillespie (1971) and later developed by Keck and co-workers (Keck, 1990, Law et al., 1987, 1988, Bishnu et al., 1997, 2001, Hamiroune et al., 1998, Gao, 2003, Ugarte et al., 2003) and Yousefian (1998). The method is based on the maximum entropy principle of thermodynamics and involves the fundamental assumption that slow reactions in a complex reacting system impose constraints on its composition, which retard its relaxation to chemical equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. The solution of the systems using RCCE always evolves to the correct equilibrium state.

A major advantage of the RCCE method is that it is unnecessary to start with a complete reaction model that must then be simplified by various approximations. Instead, one starts with a small number of constraints to which more can be added to improve the accuracy of the calculations if desired. In the limit where the number of constraints equals the number of species specified for a system, the method reduces to an exact calculation. However, as with all thermodynamic systems, the number of constraints necessary to describe the state of the system within measurable accuracy is in general very much smaller than the number of species in the system. In addition, reactions that do not change any constraint do not affect the evolution of the system. Thus, only the rates of slow reactions that change constraints are required and these are the ones most likely to be known.

In previous studies, the RCCE method has been applied to hydrogen/oxygen mixtures (Law et al., 1987, Bishnu et al., 1997, 2001, Hamiroune et al., 1998). In this paper we will discuss the rational for the formulation of this model, starting with detailed chemical kinetics, equilibrium calculations using Lagrange multipliers, constrained-equilibrium determination, and finally the non-equilibrium dynamic method of RCCE.

1.1 Modeling chemical reaction processes

A description of the conventional approach of detailed kinetics for modeling chemical reaction processes is given. Then, two techniques, Lagrange multipliers and constrained-equilibrium to calculate the final equilibrium composition using constraints are explained and discussed. The Lagrange multipliers method uses only the elemental constraints that reflect the conservation of elements. The constrained-equilibrium method also uses the elemental constraints as well as additional constraints that are imposed to better define the system subject to extremely slow rate-controlling reactions. Finally, time evolution through constrained shifting equilibrium is included in order to completely describe the processes. The maximum entropy principle is used in the last three methods.

2. Detailed Kinetics

To describe the detailed evolution of a specified chemically reacting system, a complete reaction mechanism including all species present in the system is required. For gas phase systems, obeying the ideal gas equation of state

$$PV = \sum_{j=1}^{ns} N_j RT \qquad (1)$$

changes in the chemical composition of the system are the result of reactions of the type

$$\sum_{j=1}^{ns} \nu^{+}_{jk} B_j \leftrightarrow \sum_{j=1}^{ns} \nu^{-}_{jk} B_j \quad k=1,\ldots,nr \qquad (2)$$

where V is the volume of the system, P is the pressure, T is the temperature, N_j is the number of moles of species j, B_j is the symbol for species j, nr is the number of reactions, ns is the number of species, and ν^{+}_{jk} and ν^{-}_{jk} are the forward and reverse stoichiometric coefficients of species j for reaction k. The corresponding rate-equations have the form

$$\dot{N}_j = V \sum_{k=1}^{nr} n_{jk} r_k \quad j=1,\ldots,ns \qquad (3)$$

where $\nu_{jk} = \nu^+_{jk} + \nu^-_{jk}$ 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. The forward and reverse reaction rates are given by

$$r_k^+ = k_k^+(T) \prod_{j=1}^{n_s} \left(N_j/V\right)^{v_{jk}^+} \qquad (4a)$$

$$r_k^- = k_k^-(T) \prod_{j=1}^{n_s} \left(N_j/V\right)^{v_{jk}^-} \qquad (4b)$$

where $k^+_k(T)$ and $k^-_k(T)$ are the forward and reverse rate constants for reaction k, for k=1,…nr. At equilibrium the species composition must be independent of time so that r_k must vanish. This leads to the detailed balancing condition

$$k_k^+(T)/k_k^-(T) = \prod_{j=1}^{ns} (N_j/V)^{n_{jk}} = K_{ck} \qquad (5)$$

where K_{ck} is the equilibrium constant for reaction *k* based on concentration. Given the initial conditions, the set of equations (3) can be integrated numerically using routines such as LSODI (Hindmarsh and Byrne, 1977) or DASSL (Petzold, 1982) to obtain the species composition as a function of time.

For the systems of interest in combustion, the number of species is of order 10^2 and the number of reactions is of order 10^4. Thus the tabulation of reaction rate constants and the integration of rate equations are extremely time consuming and difficult tasks. In addition, accurate rate constants are known only for a small fraction of the possible reactions.

3. Rate-Controlled Constrained-Equilibrium (RCCE)

3.1 Equilibrium calculation using Lagrange multipliers

This method for chemical equilibrium provides a superior means for solution of complicated problems, and it is used by the NASA and STANJAN programs. Its implementation in the interactive program STANJAN has been well described by W.C. Reynolds (1986). Equilibrium composition is calculated by maximizing the entropy of the mixture subject to elemental constraints of the form:

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j \quad i=1,\ldots,ne \qquad (6)$$

where N_j is the number of moles of the jth species in the system, a_{ij} is the number of atoms of the ith element in the jth species, *ns* is the number of species, C_i is the elemental constraint i, and *ne* is the number of elements, which is 3 in this study: H, C, and O. The elemental constraints are the sum of atoms present in the system and due to mass conservation, these constraints are always constant. The method relates the mole fractions of each species to quantities called element potentials γ_i (Lagrange multipliers conjugate to constraints). There is one element potential for each constraint in the system and these element potentials, plus the total number of moles in each phase, are the only variables for which one must solve. In a complex system, the total number of unknowns using the element potential method is much less than the number of species and this approach is a robust method of equilibrium calculation. The concentration of species can be calculated by

$$\frac{N_j}{V} = \left(\frac{1}{RT}\right) \exp\left(-\mu_j^0 - \sum_{i=1}^{nc} a_{ij} \gamma_i\right) \qquad (7)$$

where $\mu_j^0 = (h_j^0 - Ts_j^0)/RT$ is the standard Gibbs free energy for species j divided by RT and nc the number of constraints. The model assumes that the gas phase is a mixture of ideal gases and that condensed phases are ideal solutions.

3.2 Constrained-equilibrium calculation

Constraints in addition to the elemental ones can be imposed on any system. These are called generalized constraints and are of the same form as equation (6). These additional constraints are imposed to better define the system subject to extremely slow rate-controlling reactions. The GNASA and GSTANJAN codes (Bishnu et al,, 1997, 2001) (Generalized NASA and Generalized STANJAN respectively) were developed by our research group to find the constrained equilibrium composition of complex systems. For systems which include a large number of species, the number of constraints is much smaller than the number of species, therefore, solving for the constraint potentials is much easier than solving for the species concentrations using the method of equilibrium constants. The primary difference between GNASA and GSTANJAN is in the techniques used to solve these equations and the manner in which the calculations are initialized.

Two examples of constraints imposed by chemical reactions in gas-phase systems are the total moles of mixture (M), which is controlled by slow three-body association and dissociation reactions and the free valence (FV) number of unpaired electrons, which is controlled by slow branching and termination reactions. These additional constraints are required for dynamic calculations as we will also see in the RCCE method.

3.3 Rate-controlled constrained-equilibrium (RCCE)

The Rate-Controlled Constrained-equilibrium method can be used to reduce computation time in modeling combustion processes. The RCCE method only requires solving the rate equations for a few constraints to predict the time evolution of all species and to guarantee the right final equilibrium state. This method is based on the assumption that complex chemical systems evolve through a sequence of constrained equilibrium states determined by the instantaneous values of internal constraints on the system's composition. These constraints are imposed by slow rate-limiting reactions. The technique involves direct integration of either the rate equations for the constraints or the rate equations for the constraint potentials (Lagrange multipliers conjugate to the constraints).

3.3.1 Rate-equations for constraints

In the present work, as well as most previous applications of the RCCE method (Bishnu et al., 1997, 2001, Hamiroune et al., 1998, Gao, 2003, Ugarte et al., 2003), the constraints imposed on the system by the reactions have been assumed to be a linear combination of the mole number of the species present in the system. They can be written in the form

$$C_i = \sum_{j=1}^{ns} a_{ij} N_j \quad i=1,\ldots,nc \qquad (8)$$

where a_{ij} is the value of the constraint *i* for the species j and nc the number of constraints. The first ne constraints will be elemental constraints followed by additional constraints. Differentiating equation (8) with respect to time and substituting equation (3) in the result gives the rate-equation for the constraints, namely,

$$\dot{C}_i = \sum_{j=1}^{ns} a_{ij} \dot{N}_j = V \sum_{k=1}^{nb} b_{ik} r_k \qquad (9)$$

where

$$b_{ik} = \sum_{j=1}^{ns} a_{ij} v_{jk} \qquad (10)$$

is the change of constraint *i* due to the reaction *k* and nb is the number of reactions which change the constraints, i.e. for which $b_{ik} \neq 0$. Since elements are conserved, the corresponding $b_{ik}= 0$. This reduces the number of rate-equations to be integrated by ne, where ne is the number of elemental constraints.

Given the initial conditions, the nc - ne rate-equations (9) for the constraints can be integrated in stepwise fashion. At each step, the constrained-equilibrium composition

$$N_j(t) = N_j(V(t), T(t), C_1, \ldots C_{ne}, C_{ne+1}(t), \ldots C_{nc}(t)) \quad (11)$$

must be evaluated using a generalized equilibrium code such as GNASA or GSTANJAN (Bishnu et al., 1997, 2001). This method is very slow because of the time required by the generalized equilibrium code.

3.3.2 Rate-equations for constraint-potentials

The constrained-equilibrium composition of a system found by maximizing the entropy of the mixture subject to a set of constraints using the method of Lagrange multipliers is found by first rewriting equation (7) such that

$$N_j = \frac{V}{RT} \exp(-\mu_j^0 - \sum_{i=1}^{nc} a_{ij} g_i) \quad j=1,\ldots,ns \quad (12)$$

where γ_i is the constraint potential (Lagrange multiplier) conjugate to the constraint i. Thermodynamic species data is mainly taken from the tables given by Gordon and McBride (1994). Differentiating equation (12) with respect to time and substituting the result into equation (9) leads to the implicit rate-equation for the constraint-potentials, namely,

$$\dot{C}_i = C_{iV} \dot{V}/V + C_{iT} \dot{T}/T - \sum_{n=1}^{nc} C_{in} \dot{\gamma}_n \quad i=1,\ldots,nc \quad (13)$$

where;

$$C_{in} = \sum_{j=1}^{ns} a_{ij} a_{nj} N_j \qquad (14a)$$

$$C_{iV} = \sum_{j=1}^{ns} a_{ij} N_j \qquad (14b)$$

$$C_{iT} = \sum_{j=1}^{ns} a_{ij} \frac{e_j}{RT} N_j \qquad (14c)$$

where e_j is the specific (internal) energy of species j on a mole basis.

In cases where state variables other than T and V are used, additional equations for these other variables are required. For example, if the energy

$$E = \sum_{j=1}^{ns} e_j N_j \qquad (15)$$

is used to replace T, differentiating equation (15) provides the needed equation, i.e.

$$\dot{E} = C_v \dot{T} - V \sum_{k=1}^{nr} E_k\, r_k \qquad (16)$$

where,

$$C_v = \sum_{j=1}^{ns} c_{vj} N_j \qquad (17a)$$

$$E_k = \sum_{j=1}^{ns} (h_j - RT)\nu_{jk} \qquad (17b)$$

and $c_{vj} \equiv \partial e_j/\partial T$ is the constant volume specific heat for species j and $h_j=e_j+RT$ is the enthalpy of species j at temperature T. Note that only reactions that change constraints contribute to the sum in equation (16) since all others are in equilibrium and r_k is zero for those reactions. Combining equations (13) and (16) then gives,

$$\dot{C}_i = \frac{C_{iT}(E - V\sum_{k=1}^{nr} E_k r_k)}{C_v T} + \frac{C_{iV}\dot{V}}{V} - \sum_{n=1}^{nc} C_{in}\dot{\gamma}_n \qquad i=1,\ldots,nc \qquad (18)$$

Given E(t) and V(t) and initial values for γ_i, the implicit equations (18) for the Lagrange multipliers (γ's) can be integrated with respect to time using integration routines such as DASSL or LSODI to obtain the constraint-potentials. These can then be used in equation (12) to obtain the final composition as a function of time. The number of unknowns is reduced from the number of species ns included in the detailed calculations to the number of constraints nc used in the RCCE calculations. In addition, the rate-constants for those reactions that do not change any of the constraints are not needed.

3.3.3 Selection of constraints

The selection of appropriate constraints is the key to the successful application of the RCCE method. Among the general requirements for the constraints are that they (1) be linearly independent combinations of the species mole numbers, (2) include the elements, (3) determine the energy and entropy of the system within experimental accuracy, and (4) hold the system in the specified initial state. In addition, they should reflect whatever information is available about rate reactions controlling the time evolution of the system.

In the temperature range important for chemical reactions, extremely slow nuclear reactions imply strict conservation of the elements on any observable time scale. Among the rate-limiting reactions of interest for chemical kinetics are the following:

- Initiation reactions which hold the system in the specified initial state
- Dissociation/recombination reactions which determine the total number of particles
- Ionization reactions which determine the charge density in a system
- Branching reactions which control the total free valence of the radicals
- O-O bond breaking reactions which control the “fixed oxygen”
- Reactions that change fuel radicals
- Carbon dioxide forming reactions
- Reactions that form cyclic molecules.

In this work, there are three fixed elemental constraints: elemental carbon (EC), elemental oxygen (EO), and elemental hydrogen (EH) and from one to nine variable constraints: total number of moles (M), moles of free oxygen (FO), moles of free valence (FV), moles of fuel (FU), and moles of fuel radicals (FR), moles of CO_2 (CO_2) and moles of HO_2 (HO_2), moles of OH (OH) and moles of H_2 (H_2).

4. Results and Discussion

Illustrative calculations were carried out for premixed stoichiometric mixtures of formaldehyde-oxygen at constant energy in a constant volume chamber for initial pressures ranging from 1 atm to 100 atm and initial temperatures ranging from 900 K to 1500 K using 4 to 12 constraints. For comparison, corresponding rate-equations in a detailed model which includes 29 species and 139 reactions (20 species and 102 reactions from the GRI-Mech 3.0 model (Bowman et al., 2000) along with another 9 species and 38 additional reactions (Tsang and Hampson, 1986, 1987, Estimation by authors) were integrated using DASSL (Petzold, 1982) to obtain exact solutions.

The system was very well modeled with only 8 constraints. The constraints in the order in which they were introduced into the RCCE calculations are defined in TABLE I which forms the constraint matrix [A] in equation (8).

TABLE II shows all 139 reactions with their corresponding enthalpies of reaction, and reaction rate constants ($k = AT^n \exp(-E_a/RT)$) that are required in equation (9). In this table, the difference of stoichiometric coefficients for the five variable constraints (M, FV, FO, FU and FR) for each reaction are also shown. It should be noted that only the first 97 reactions change the constraints and the remainder do not; therefore, their rate information is not needed and equilibrium composition is reached without them.

TABLE I. MATRIX [A] FOR THE FORMALDEHYDE-OXYGEN MIXTURE

		Species																												
		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
N°	Constraint	CO2	O2	H2	H2O2	HO2	H2O	H2CO	HCO	CO	CH3OO	CH4	H	CH3OH	CH3OOH	HOCHO	HO	O	HOCO	OCHO	HOOCO	OOCHO	CH3	CH2	CH	C	CH2OH	CH3O	HOOCHO	CH2OOH
1	EC	1	0	0	0	0	0	1	1	1	1	1	0	1	1	1	0	0	1	1	1	1	1	1	1	1	1	1	1	1
2	EO	2	2	0	2	2	1	1	1	1	2	0	0	1	2	2	1	1	2	2	3	3	0	0	0	0	1	1	3	2
3	EH	0	0	2	2	1	2	2	1	0	3	4	1	4	4	2	1	0	1	1	1	1	3	2	1	0	3	3	2	3
4	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
5	FV	0	0	0	0	1	0	0	1	0	1	0	1	0	0	0	1	2	1	1	1	1	1	2	3	4	1	1	0	1
6	FO	2	0	0	0	0	1	1	1	1	0	0	0	1	0	2	1	1	2	2	1	1	0	0	0	0	1	1	1	0
7	FU	0	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
8	FR	0	0	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

TABLE II. REACTION SET MECHANISM FOR FORMALDEHYDE OXIDATION

N°	Reactions							ΔHTref kcal/mol	Constraints					Ref.	Reaction Rates		
									M	FV	FO	FU	FR		A	n	Ea (cal)
1	CO	O	M	=	CO2		M	-127.9	-1	-2	0	0	0	36	1.80E+10	0	2385
2	OH	H	M	=	H2O		M	-121.6	-1	-2	0	0	0	36	2.20E+22	-2	0
3	O	O	M	=	O2		M	-120.8	-1	-4	-2	0	0	36	1.20E+17	-1	0
4	CH2	H	M	=	CH3		M	-112.7	-1	-2	0	0	0	36	6.00E+14	0	0
5	CH	H2	M	=	CH3		M	-109.4	-1	-2	0	0	0	36	2.00E+12	0.4	-370
6	CH3	H	M	=	CH4		M	-107.6	-1	-2	0	0	0	36	1.40E+16	-0.5	536
7	H	H	H2	=	H2		H2	-106.2	-1	-2	0	0	0	36	9.00E+16	-0.6	0
8	H	H	H2O	=	H2		H2O	-106.2	-1	-2	0	0	0	36	6.00E+19	-1.3	0
9	H	H	M	=	H2		M	-106.2	-1	-2	0	0	0	36	1.00E+18	-1	0
10	H	H	CO2	=	H2		CO2	-106.2	-1	-2	0	0	0	36	5.50E+20	-2	0
11	CH3O	H	M	=	CH3OH		M	-106.0	-1	-2	0	0	0	36	2.40E+12	0.5	50
12	H	O	M	=	OH		M	-104.3	-1	-2	0	0	0	36	5.00E+17	-1	0
13	CH2OH	H	M	=	CH3OH		M	-99.4	-1	-2	0	0	0	36	1.10E+12	0.5	86
14	CH3	OH	M	=	CH3OH		M	-94.2	-1	-2	0	0	0	36	2.80E+18	-1.4	1330
15	HCO	H	M	=	H2CO		M	-90.3	-1	-2	0	1	-1	36	1.10E+12	0.5	-260
16	OH	OH	M	=	H2O2		M	-52.2	-1	-2	-2	0	0	36	7.40E+13	-0.4	0
17	H	O2	O2	=	HO2		O2	-51.0	-1	0	0	0	0	36	2.08E+19	-1.24	0
18	H	O2	H2O	=	HO2		H2O	-51.0	-1	0	0	0	0	36	1.10E+19	-0.8	0
19	H	O2	M	=	HO2		M	-51.0	-1	0	0	0	0	36	2.80E+18	-0.9	0
20	CH3O	OH		=	CH3OOH			-46.3	-1	-2	-2	0	0	39	6.00E+14	0	42300
21	HCO	O2	M	=	OOCHO		M	-41.5	-1	0	0	0	-1	39	2.00E+13	0	8000
22	OCHO	OH	M	=	HOOCHO		M	-38.5	-1	-2	-2	0	0	39	2.00E+13	0	0
23	H2CO	H	M	=	CH2OH		M	-30.6	-1	0	0	-1	0	36	5.40E+11	0.5	3600
24	CH3	O2	M	=	CH3OO		M	-28.1	-1	0	0	0	0	39	1.46E+37	-7.86	8975
25	H2CO	H	M	=	CH3O		M	-24.0	-1	0	0	-1	0	36	5.40E+11	0.5	2600
26	H2CO	OH	HO2	=	CH3OOH	O2		-19.3	-1	-2	-2	-1	0	39	1.00E+13	0	19306
27	CO	H	M	=	HCO		M	-17.3	-1	0	0	0	1	36	1.90E+17	-1	17000
28	CO	H	H2O	=	HCO		H2O	-17.3	-1	0	0	0	1	36	1.50E+18	-1	17000
29	CO	H2	M	=	H2CO		M	-1.3	-1	0	0	1	0	36	4.30E+07	1.5	79600
30	H2CO	OH	H2O2	=	CH3OOH	HO2		18.8	-1	0	-2	-1	0	39	1.00E+13	0	0
31	H2CO	OH	CH3OOH	=	CH3OOH	CH3OO		23.9	-1	0	-2	-1	0	39	1.00E+13	0	0
32	H2CO	CH4	OH	=	CH3OOH	CH3		37.3	-1	0	-2	-1	0	38	1.00E+13	0	0
33	CO	H	OH	=	CH2	O2		57.1	-1	0	-2	0	0	36	5.00E+12	0	1500
34	CO	H	H2	=	CH3	O		67.2	-1	2	0	0	0	36	3.40E+13	0	0
35	CO	H	H	=	CH2	O		73.6	-1	2	0	0	0	37	5.00E+13	0	0
36	CO2	H	H	=	CH2	O2		80.8	-1	0	-2	0	0	36	5.80E+12	0	1500
37	CH2	O2		=	CO2	H2		-187.0	0	-2	2	0	0	37	6.90E+11	0	500
38	CH2	O		=	CO	H2		-179.9	0	-4	0	0	0	37	3.00E+13	0	0
39	CH	O		=	CO	H		-176.6	0	-4	0	0	0	36	5.70E+13	0	0
40	C	OH		=	CO	H		-154.8	0	-4	0	0	0	36	5.00E+13	0	0
41	C	O2		=	CO	O		-138.3	0	-2	2	0	0	36	5.80E+13	0	576
42	OCHO	OH		=	CO2	H2O		-123.8	0	-2	0	0	0	39	5.00E+12	0	0
43	CH2	HO2		=	H2CO	OH		-113.8	0	-2	2	1	0	36	2.00E+13	0	0
44	HCO	O		=	CO2	H		-110.6	0	-2	0	0	-1	36	3.00E+13	0	0
45	HCO	OH		=	CO	H2O		-104.3	0	-2	0	0	-1	36	5.00E+13	0	0
46	CH3O	OH		=	H2CO	H2O		-97.6	0	-2	0	1	0	36	5.00E+12	0	0
47	CH2OH	OH		=	H2CO	H2O		-91.0	0	-2	0	1	0	36	5.00E+12	0	0
48	CH2	O		=	HCO	H		-91.0	0	-2	0	0	1	36	8.00E+13	0	0
49	CH3	HCO		=	CH4	CO		-90.2	0	-2	0	0	-1	36	2.60E+13	0	0
50	CH	OH		=	HCO	H		-89.6	0	-2	0	0	1	36	3.00E+13	0	0

TABLE II. (CONTINUATION)

N°	Reactions							ΔHTref kcal/mol	Constraints					Ref.	Reaction Rates		
									M	FV	FO	FU	FR		A	n	Ea (cal)
46	CH3O	OH		=	H2CO	H2O		-97.6	0	-2	0	1	0	36	5.00E+12	0	0
47	CH2OH	OH		=	H2CO	H2O		-91.0	0	-2	0	1	0	36	5.00E+12	0	0
48	CH2	O		=	HCO	H		-91.0	0	-2	0	0	1	36	8.00E+13	0	0
49	CH3	HCO		=	CH4	CO		-90.2	0	-2	0	0	-1	36	2.60E+13	0	0
50	CH	OH		=	HCO	H		-89.6	0	-2	0	0	1	36	3.00E+13	0	0
51	HCO	H		=	CO	H2		-88.9	0	-2	0	0	-1	36	7.30E+13	0	0
52	HCO	O		=	CO	OH		-87.0	0	-2	0	0	-1	36	3.00E+13	0	0
53	CH3O	H		=	H2CO	H2		-82.3	0	-2	0	1	0	36	2.00E+13	0	0
54	CH3O	CH3O		=	CH3OH	H2CO		-82.1	0	-2	0	1	0	37	3.00E+13	0	82100
55	CH3O	O		=	H2CO	OH		-80.3	0	-2	0	1	0	36	1.00E+13	0	0
56	CH2	OH		=	H2CO	H		-76.9	0	-2	0	1	0	36	2.00E+13	0	0
57	CH2OH	H		=	H2CO	H2		-75.6	0	-2	0	1	0	36	2.00E+13	0	0
58	CH2OH	O		=	H2CO	OH		-73.7	0	-2	0	1	0	36	1.00E+13	0	0
59	HCO	HO2		=	CO	H2O2		-71.8	0	-2	0	0	-1	39	2.00E+13	0	12000
60	HO2	OH		=	O2	H2O		-70.6	0	-2	0	0	0	36	1.40E+13	0	-500
61	CH3	OH		=	H2CO	H2		-70.5	0	-2	0	1	0	36	8.00E+09	0.5	-1755
62	CH3	O		=	H2CO	H		-68.5	0	-2	0	1	0	36	5.10E+13	0	0
63	CO2	CH		=	HCO	CO		-66.0	0	-2	0	0	1	36	1.90E+14	0	15792
64	CH	H2O		=	H2CO	H		-58.3	0	-2	0	1	0	36	5.70E+12	0	-755
65	CH3	HO2		=	CH4	O2		-56.6	0	-2	0	0	0	36	1.00E+12	0	0
66	HO2	H		=	O2	H2		-55.3	0	-2	0	0	0	36	4.50E+13	0	1068
67	CH3O	HO2		=	CH3OH	O2		-55.1	0	-2	0	0	0	39	1.00E+14	0	55100
68	HO2	O		=	OH	O2		-53.3	0	-2	0	0	0	36	2.00E+13	0	0
69	CH2	CO2		=	H2CO	CO		-53.3	0	-2	0	1	0	37	1.10E+11	0	1000
70	CH2OH	HO2		=	CH3OH	O2		-48.4	0	-2	0	0	0	39	1.50E+15	0	48400
71	HOCO	HO2		=	HOCHO	O2		-47.2	0	-2	0	0	0	39	1.00E+14	0	40000
72	CH3OO	HO2		=	CH3OOH	O2		-43.2	0	-2	0	0	0	37	4.64E+10	0	2582
73	HCO	HO2		=	H2CO	O2		-39.3	0	-2	0	1	-1	36	1.00E+14	0	40000
74	HO2	HO2		=	O2	H2O2		-38.1	0	-2	0	0	0	37	1.80E+12	0	0
75	CH3O	O		=	CH3	O2		-28.3	0	-2	-2	0	0	37	1.99E+18	-1.57	29232
76	OH	O		=	O2	H		-16.5	0	-2	-2	0	0	37	1.69E+17	-0.9	17388
77	CO2	O		=	CO	O2		7.2	0	-2	-2	0	0	36	2.50E+12	0	47800
78	HOCHO	O2		=	OCHO	HO2		55.2	0	-2	0	0	0	39	2.00E+13	0	0
79	CH	O2		=	HCO	O		-73.1	0	0	2	0	1	36	6.70E+13	0	0
80	H2O2	H		=	OH	H2O		-69.3	0	0	2	0	0	36	1.00E+13	0	3600
81	CO	HO2		=	CO2	OH		-60.5	0	0	2	0	0	36	1.50E+14	0	23600
82	CH2	O2		=	H2CO	O		-60.4	0	0	2	1	0	36	2.40E+12	0	1500
83	HO2	H		=	O	H2O		-54.1	0	0	2	0	0	36	4.00E+12	0	671
84	CH3	O2		=	H2CO	OH		-52.0	0	0	2	1	0	36	2.30E+12	0	20315
85	HO2	H		=	OH	OH		-36.8	0	0	2	0	0	36	8.40E+13	0	635
86	CH3	CH3OO		=	CH3O	CH3O		-36.0	0	0	2	0	0	37	2.41E+13	0	0
87	CH3	HO2		=	CH3O	OH		-25.0	0	0	2	0	0	36	3.80E+13	0	0
88	H2CO	OH		=	HCO	H2O		-31.3	0	0	0	-1	1	36	3.40E+09	1.2	-447
89	H2CO	H		=	HCO	H2		-16.0	0	0	0	-1	1	36	1.00E+07	1.9	2742
90	H2CO	O		=	HCO	OH		-14.0	0	0	0	-1	1	36	3.90E+13	0	3540
91	H2CO	HO2		=	HCO	H2O2		1.2	0	0	0	-1	1	36	5.60E+06	2	12000
92	H2CO	OOCHO		=	HCO	HOOCHO		1.5	0	0	0	-1	1	39	2.00E+13	0	5000
93	CH4	HCO		=	CH3	H2CO		17.3	0	0	0	1	-1	36	3.30E+03	2.8	5860
94	H2CO	HO2		=	CH2OH	O2		20.4	0	0	0	-1	0	36	1.80E+13	0	900
95	H2CO	HO2		=	CH3O	O2		27.0	0	0	0	-1	0	36	4.30E-13	7.6	-3530
96	HCO	O2		=	CO	HO2		-33.6	0	0	0	0	-1	36	1.40E+13	0	400
97	HCO	OH		=	OCHO	H		-4.1	0	0	0	0	-1	39	3.00E+13	0	0
98	H2O2	OH		=	HO2	H2O		-32.5	0	0	0	0	0	36	2.00E+12	0	427
99	HOOCHO	H		=	HOOCO	H2		-30.2	0	0	0	0	0	39	1.00E+13	0	0
100	CH	H		=	C	H2		-23.7	0	0	0	0	0	36	3.00E+13	0	0
101	CO	OH		=	CO2	H		-23.6	0	0	0	0	0	36	4.80E+07	1.2	70
102	CH3OH	OH		=	CH2OH	H2O		-22.2	0	0	0	0	0	36	1.40E+06	2	-840
103	CH2	OH		=	CH	H2O		-18.6	0	0	0	0	0	36	1.10E+07	2	3000
104	OH	OH		=	O	H2O		-17.3	0	0	0	0	0	36	3.60E+04	2.4	-2110
105	H2O2	H		=	HO2	H2		-17.2	0	0	0	0	0	36	1.20E+07	2	5200
106	CH3O	H2O2		=	CH3OH	HO2		-16.9	0	0	0	0	0	39	8.00E+15	-0.7	17041
107	H2	OH		=	H	H2O		-15.3	0	0	0	0	0	36	2.20E+08	1.5	3430
108	H2O2	O		=	OH	HO2		-15.2	0	0	0	0	0	36	9.60E+06	2	4000
109	CH4	OH		=	CH3	H2O		-14.0	0	0	0	0	0	36	1.00E+08	1.6	3120
110	OOCHO	OH		=	OCHO	HO2		-13.5	0	0	0	0	0	39	1.80E+11	0	0

TABLE II. (CONTINUATION)

N°	Reactions							ΔHTref kcal/mol	Constraints					Ref.	Reaction Rates		
									M	FV	FO	FU	FR		A	n	Ea (cal)
111	CH3	OH		=	CH2	H2O		**-8.9**	0	0	0	0	0	36	5.60E+07	1.6	5420
112	HOCHO	H		=	HOCO	H2		**-8.1**	0	0	0	0	0	39	1.00E+13	0	0
113	CH3OH	H		=	CH2OH	H2		**-6.8**	0	0	0	0	0	36	2.00E+06	2.1	4870
114	CH3O	H		=	CH2OH	H		**-6.6**	0	0	0	0	0	36	4.20E+07	1.6	1924
115	CH3O		CH3OH	=	CH2OH		CH3OH	**-6.6**	0	0	0	0	0	38	1.50E+12	0	7000
116	CH4	CH2		=	CH3	CH3		**-5.1**	0	0	0	0	0	36	2.50E+06	2	8270
117	CH3OO	H2O2		=	CH3OOH	HO2		**-5.1**	0	0	0	0	0	37	2.41E+12	0	9930
118	CH3OH	O		=	CH2OH	OH		**-4.9**	0	0	0	0	0	36	9.00E+04	2.5	3100
119	CH3OOH	H		=	CH2OOH	H2		**-3.1**	0	0	0	0	0	39	2.00E+13	0	0
120	CH3O	OH		=	CH3OH	O		**-1.7**	0	0	0	0	0	36	1.30E+05	2.5	5000
121	HOOCHO	HO2		=	OOCHO	H2O2		**-0.3**	0	0	0	0	0	39	1.50E+12	0	0
122	HOCHO	H		=	OCHO	H2		**-0.1**	0	0	0	0	0	39	1.00E+13	0	0
123	CH3O	H2		=	CH3OH	H		**0.2**	0	0	0	0	0	36	4.20E+06	2.1	4870
124	CH4	H		=	CH3	H2		**1.3**	0	0	0	0	0	36	6.60E+08	1.6	10840
125	CH4	CH3O		=	CH3	CH3OH		**1.5**	0	0	0	0	0	36	1.00E+07	1.5	9940
126	H2	O		=	OH	H		**1.9**	0	0	0	0	0	36	3.90E+04	2.7	6260
127	CH4	O		=	CH3	OH		**3.3**	0	0	0	0	0	36	1.00E+09	1.5	8600
128	CH	H2		=	CH2	H		**3.3**	0	0	0	0	0	36	3.00E+13	0	3110
129	CH3OOH	HO2		=	CH3OO	H2O2		**5.1**	0	0	0	0	0	39	2.00E+13	0	0
130	CH3	OH		=	CH2OH	H		**5.2**	0	0	0	0	0	36	1.60E+11	0.7	-284
131	CH3	H		=	CH2	H2		**6.5**	0	0	0	0	0	36	5.00E+05	2	7230
132	CH4	CH2OH		=	CH3	CH3OH		**8.2**	0	0	0	0	0	36	3.00E+07	1.5	9940
133	CH3OH	HO2		=	CH2OH	H2O2		**10.3**	0	0	0	0	0	38	6.30E+12	0	19360
134	CH3O	HO2		=	CH3OO	OH		**11.0**	0	0	0	0	0	39	3.00E+13	0	16000
135	CH3	OH		=	CH3O	H		**11.8**	0	0	0	0	0	36	1.50E+12	0.5	-110
136	CH4	CH3OO		=	CH3	CH3OOH		**13.4**	0	0	0	0	0	37	1.81E+11	0	18470
137	CH3O	H2O		=	CH3OH	OH		**15.5**	0	0	0	0	0	36	6.30E+06	2	1500
138	CH4	HO2		=	CH3	H2O2		**18.5**	0	0	0	0	0	36	2.40E+04	2.5	5180
139	CH3	H2O		=	CH3OH	H		**27.4**	0	0	0	0	0	39	5.20E+12	0	5340

Figure 1 shows the temperature and pressure history for the case with initial conditions of 1500 K and 1 atm. As was reported earlier, eight is the minimum number of constraints required to give very good agreement between detailed and RCCE calculations.

Figure 2 shows the mole fraction of major species: H_2CO, O_2, CO and CO_2 for the same case. The concentrations of major species are almost the same using the two different methods. *Figure 3* shows the mole fraction of minor species HO_2, HCO, H_2O_2, and H_2. It can be seen that agreement between the detailed and RCCE calculations is very good, and they all have the same concentration at the equilibrium state.

Figure 4 shows the temperature and pressure evolution for an extreme case with initial conditions of 900 K and 100 atm. Again the results of RCCE are in excellent agreement with the detailed kinetics calculation. *Figure 5* shows the mole fraction evolution of H_2CO, O_2, CO and CO_2 for the same case, and *Figure 6* shows the mole fraction evolution of HO_2, HCO, H_2O_2 and H_2O. As in the previous cases the agreement between detailed and RCCE calculations are remarkable. The comparison for minor species will be improved if more than 8 constraints are used in the RCCE calculations but for all practical purposes 8 constraints will be enough. The additional constraints can be used to improve the concentration of minor species calculation if pollutants at very low concentrations need to be modeled.

Calculations for a broad range of pressures and temperatures have been performed. *Figure 7* shows ignitions delay times (τ) at different pressures and temperatures. Ignition delay time is defined as a 90% rise in temperature of the mixture. In all cases, RCCE calculations compare very well to the detailed calculations, which is quite remarkable.

Finally, both the RCCE and detailed kinetics calculations were done on a Sun workstation Sparc 10 machine. CPU time increases with the number of differential equations to be solved and the number of reactions involved. The computation time of the RCCE calculations was about 50% of the CPU time required for the detailed kinetics. Although the CPU time saved by the RCCE method is modest in this case, it is expected to improve by several fold for larger systems where detailed calculations can involve thousands of species and millions of possible reactions. Of equal importance is the potential reduction in the time required for the input of reaction mechanisms and the analysis of the resulting output.

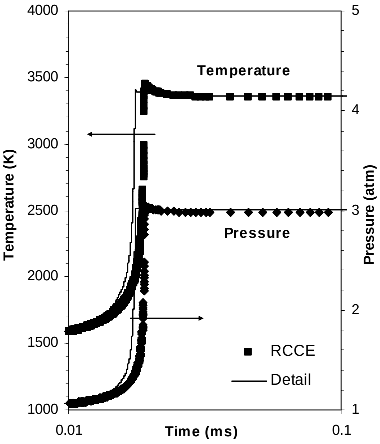

Figure 1. Temperature and pressure evolution for the formaldehyde-oxygen mixture at 1500 K and 1 atm using detailed kinetics and RCCE with 8 constraints

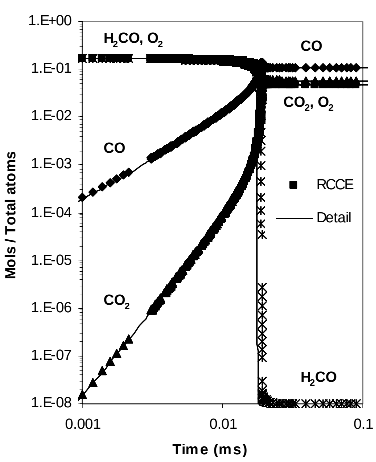

Figure 2. Mole fraction evolution of H_2CO, O_2, CO and CO_2 for the formaldehyde-oxygen mixture at 1500 K and 1 atm using detailed kinetics and RCCE with 8 constraints

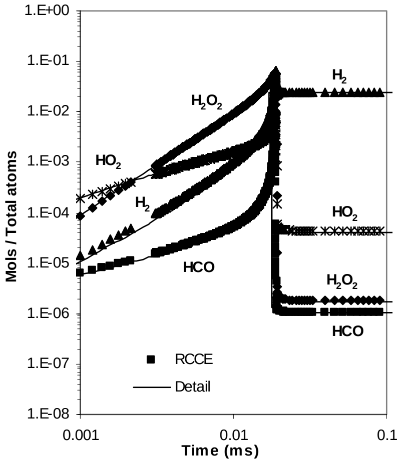

Figure 3. Mole fraction evolution of HO_2, HCO, H_2O_2, and H_2 for the formaldehyde-oxygen mixture at 1500 K and 1 atm using detailed kinetics and RCCE with 8 constraints

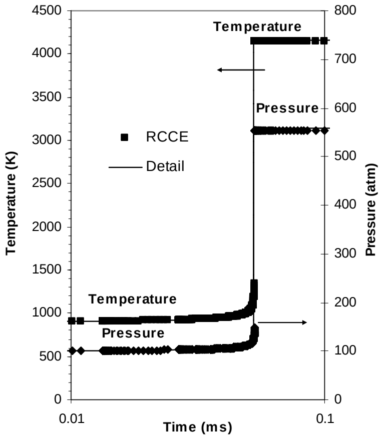

Figure 4. Temperature and pressure evolution for the formaldehyde-oxygen mixture at 900 K and 100 atm using detailed kinetics and RCCE calculation using 8 constraints

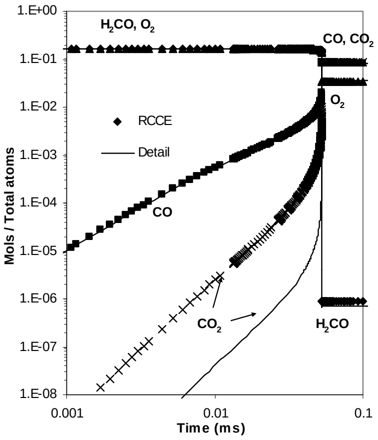

Figure 5. Mole fraction evolution of H_2CO, O_2, CO and CO_2 for the formaldehyde-oxygen mixture at 900 K and 100 atm using detailed kinetics and RCCE calculations using 8 constraints

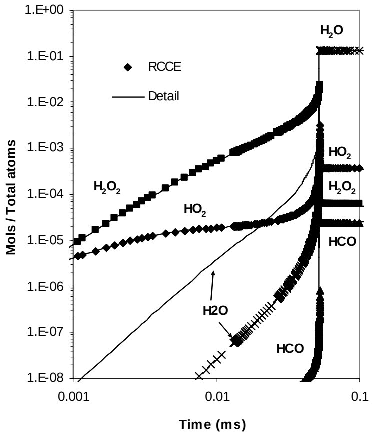

Figure 6. Mole fraction evolution of HO_2, HCO, H_2O_2, and H_2O for the formaldehyde-oxygen mixture at 900 K and 100 atm using detailed Kinetics and RCCE calculations using eight constraints

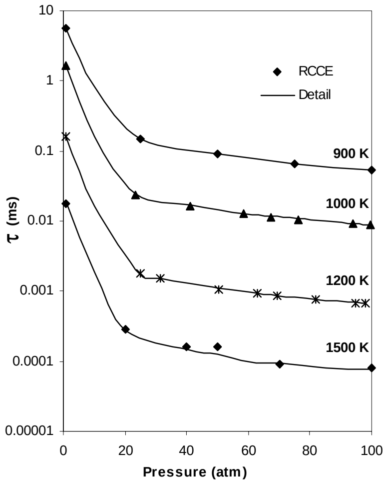

Figure 7. Ignition delay times (τ) at different temperatures and pressures for the formaldehyde-oxygen mixture using detailed kinetics and 8 constraints

5. Conclusions

The Maximum Entropy Principle has been successfully applied to non-equilibrium thermodynamics. Rate equations for the constraint potentials associated with the Rate-Controlled Constrained-Equilibrium (RCCE) method have been developed and successfully integrated for modeling formaldehyde-oxygen system at stoichiometric conditions over a wide range of initial temperatures and pressures. Rate-Controlled Constrained-Equilibrium calculation using 8 basic constraints are in excellent agreement with detailed kinetics results. Adding more variable constraints improves the calculation of the minor species concentration. Saving in computer times of up to 50% has been achieved for these cases. It is anticipated that for larger systems, time savings will be achieved by several fold. Finally, the RCCE method gives valuable insight into the important reaction paths and rate-limiting reactions involved in the evolution of complex chemical systems on their journey through non-equilibrium states.

Acknowledgements

This work was partially supported by the US Army Research Lab, Grant number DAAD19-01-1-0587, under the technical monitoring of Dr. David Mann

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