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METHANOL OXIDATION INDUCTION TIMES USING THE RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM METHOD

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ABSTRACT

Methanol oxidation has been modeled using the Rate-Controlled Constrained-Equilibrium method (RCCE). In this method, composition of the system is determined by constraints rather than by species. Since the number of constraints can be much smaller than the number of species present, the number of rate equations required to describe the time evolution of the system can be considerably reduced. In the present paper, C_1 chemistry with 29 species and 140 reactions has been used to investigate the oxidation of stoichiometric methanol/oxygen mixture at constant energy and volume. Three fixed elemental constraints: elemental carbon, elemental oxygen and elemental hydrogen and from one to nine variable constraints: moles of fuel, total number of moles, moles of free oxygen, moles of free valence, moles of fuel radical, moles of formaldehyde H_2CO, moles of HCO, moles of CO and moles of CH_3O were used. The four to twelve rate equations for the constraint potentials (LaGrange multipliers conjugate to the constraints) were integrated for a wide range of initial temperatures and pressures. As expected, the RCCE calculations gave correct equilibrium values in all cases. Only 8 constraints were required to give reasonable agreement with detailed calculations. Results of using 9 constraints showed compared very

well to those of the detailed calculations at all conditions. For this system, ignition delay times and major species concentrations were within 0.5% to 5% of the values given by detailed calculations. Adding up to 12 constraints improved the accuracy of the minor species mole fractions at early times, but only had a little effect on the ignition delay times. RCCE calculations reduced the time required for input and output of data in 25% and 10% when using 8 and 9 constraints respectively. In addition, RCCE calculations gave valuable insight into the important reaction paths and rate-limiting reactions involved in methanol oxidation.

Keywords: Methanol Oxidation, Ignition Delay, RCCE, Rate-Controlled Constraint-Equilibrium

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 "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,

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except for the hydrogen/oxygen system, they contain only a small fraction of the species and reactions possible. Extensive work and mechanisms have been developed by C.K Westbrook [1] and H. Wang [2]. 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.

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 [3-11]; 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 [12-17]. The methods in the first class increase the speed of the calculations but reduce the level of detail and accuracy of the results. The methods in the second class maintain a reasonable level of detail and accuracy but it is not clear that replacing differential equations by algebraic equations increases the speed or efficiency of the calculations. They also require a complete set of reaction rate constants as input and since only a small fraction of these are known, this introduces a large uncertainty in the results.

Here, we investigate an alternative approach, the Rate-Controlled Constrained-Equilibrium (RCCE) method, originally proposed by Keck and Gillespie [19] and later developed by Keck and co-workers [20-24]. 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.

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 which change the constraints are required and these are the ones most likely to be known.

In previous studies, the RCCE method has been applied to stoichiometric hydrogen/air mixtures [24] and formaldehyde/oxygen system involving C_1 chemistry [34] at constant energy and volume. In this paper, the method is applied to the more complex methanol/oxygen system involving C_1 chemistry with 29 species and 140 reactions. The rate equations for the constraint potentials conjugate to 4-12 constraints were integrated and the results are compared with detailed calculation.

RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM (RCCE)

Before describing the RCCE method of treating chemical reactions in complex systems, a brief summary of the detailed method will be given. This will facilitate both the comparison of the rate-equations used and the results obtained.

Rate-Equations for Species

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

$$PV = \sum_{j=1}^{ns} N_j \widetilde{R} T$$

(1)

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

$$\sum_{j=1}^{ns} v_{jk}^+ B_j \leftrightarrow \sum_{j=1}^{ns} v_{jk}^- B_j \qquad k=1,...nr \qquad (2)$$
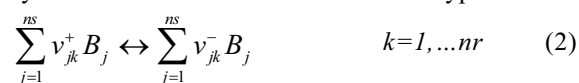
where V is the volume of the system, p is the pressure, T is the temperature, N_j is the number of moles of species j, B_j is the symbol for species j, nr is the number of reactions, ns is the number of species, and v_{jk}^+ and v_{jk}^- are the forward and reverse stoichiometric coefficients of species j for reaction k. The corresponding rate-equations have the form

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

where $v_{jk} = v_{jk}^- - v_{jk}^+$ 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

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

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

where $k_k^+(T)$ and $k_k^-(T)$ are the forward and reverse rate constants for reaction k, and 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

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

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 [26] or DASSL [27] 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.

Rate-equations for Constraints

In the present work, as well as most previous applications of RCCE method [23,28,34], 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 a the system. They can be written in the form

$$C_i = \sum_{i=1}^{ns} a_{ij}N_j \qquad i=1,...nc \tag{6}$$

where a_{ij} is the value of the constraint i for the species j and nc is the number of constraints. Differentiating equation (6) and substituting equation (3) in the result gives the rate-equation for the constraints

$$\dot{C}_i = \sum_{j=1}^{ns} a_{ij}\dot{N}_j = V\sum_{i=1}^{nb} b_{ik}r_k \tag{7}$$

where

$$b_{ik} = \sum_{j=1}^{ns} a_{ij}v_{jk} \tag{8}$$

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 (7) for the constraints can be integrated in stepwise fashion. At each step, the constrained-equilibrium composition

$$N_j(t) = N_j(V(t),T(t),C_1,...C_{ne},C_{ne+1}(t),...C_{nc}(t)) \tag{9}$$

must be evaluated using a generalized equilibrium code such as GNASA[28,29] or GSTANJAN[28,30]. The problem with this method is that it is very slow because of the time required by the generalized equilibrium code.

Rate-equations for Constraint-Potentials

The constrained-equilibrium composition of a system found by maximizing the entropy or by minimizing the free energy subject to a set of constraints using the LaGrange multipliers method is

$$N_j = (V/\widetilde{R}T)\exp(-\mu_j^0 - \sum_{i=1}^{nc} a_{ij}\gamma_i) \qquad j=1,...ns \tag{10}$$

where $\mu_j^0 = (h_j^0 - Ts_j^0)/RT$ is the standard Gibbs free energy for species j divided by RT and γ_i is the constraint potential (LaGrange multiplier) conjugate to the constraint i. Differentiating equation (10) with respect to time, and substituting the result into equation (7) leads to the implicit rate-equation for the constraint-potentials

$$\dot{C}_i = C_{iV}\dot{V}/V + C_{iT}\dot{T}/T - \sum_{n=1}^{nc} C_{in}\dot{\gamma}_n$$
$$i=1,...nc \tag{11}$$

where

$$C_{in} = \sum_{j=1}^{ns} a_{ij}a_{nj}N_j \tag{12a}$$

$$C_{iV} = \sum_{j=1}^{ns} a_{ij}N_j \tag{12b}$$

$$C_{iT} = \sum_{j=1}^{ns} a_{ij}\frac{e_j}{RT}N_j \tag{12c}$$

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

$$E = \sum_{j=1}^{ns} e_j N_j \tag{13}$$

is used to replace T, differentiating equation (13) provides the equation

$$\dot{E} = C_v\dot{T} - V\sum_{k}^{nr} E_k r_k \tag{14}$$

where

$$C_v = \sum_{j=1}^{ns} c_{vj} N_j \tag{15a}$$

$$E_k = \sum_{j=1}^{ns} (h_j - RT) v_{jk} \tag{15b}$$

and $c_{vj} = \partial e_j / \partial T$ 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 which change constraints contribute to the sum in equation (14) since all others which are in equilibrium and r_k is zero for these. Combining equations (11) and (14) then gives,

$$\sum_{n}^{nc} C_{in} \dot{\gamma}_n = C_{iV} \dot{V}/V + C_{iT}(E - V\sum E_k r_k)/C_v T - \dot{C}_i$$

$$i = 1, .. nc \tag{16}$$

Given $E(t)$ and $V(t)$ and initial values for γ_i, the energy equations (14) and the implicit equations (16) for the 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 (10) to obtain the composition as 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 which do not change any of the constraints are not needed.

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-limiting 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 reaction of interest for chemical kinetics are:

(1) initiation reactions which hold the system in the specified initial state
(2) dissociation/recombination reactions which determine the total number of particles
(3) ionization reactions which determine the charge density in a system
(4) branching reactions which control the total free valence of the radicals
(5) O-O bond breaking reactions which control the "fixed oxygen"
(6) reactions that change fuel radical
(7) carbon dioxide forming reactions
(8) reactions which form cyclic molecules.

In this work, three fixed elemental constraints: elemental carbon (EC), elemental oxygen (EO) and elemental hydrogen (EH) and from one to nine variable constraints: moles of fuel (FU), total number of moles (M), moles of free oxygen (FO), moles of free valence (FV), moles of fuel radical (FR), moles of the formaldehyde H_2CO (H2CO), moles of HCO (HCO), moles of CO (CO) and moles of CH_3O (CH3O) as defined in Table 1 were used.

It should be noted that if only the elements are used as constraints, the RCCE method is identical to the element potential method used by STANJAN [30] to calculate the chemical equilibrium composition of a system, while if the number of independent constraints equals the number of species in a system the RCCE method is equivalent to a detailed calculation. This advantage of reducing significantly the number of equations by using the RCCE method is what makes it such a promising area for research.

Table 1: A_{ij} Matrix for Methanol Oxidation

N°	Constraint	Subdeterminant	Symbol	1 CH3OH	2 O2	3 CH2OH	4 CO2	5 HO2	6 H2O	7 CO	8 H	9 H2CO	10 HCO	11 H2	12 CH3O	13 H2O2	14 O	15 HO	16 OCHO	17 HOOCHO	18 HOCHO	19 OOCHO	20 CH3OOH	21 CH4	22 CH3	23 HOCO	24 CH2	25 CH2OOH	26 CH3OO	27 HOOCO	28 CH	29 C
1	Elemental H	4	EH	4	0	3	0	1	2	0	1	2	1	2	3	2	0	1	1	2	2	1	4	4	3	1	2	3	3	1	1	0
2	Elemental O	8	EO	1	2	1	2	2	1	1	0	1	1	0	1	2	1	1	2	3	2	3	2	0	0	2	0	2	0	3	0	0
3	Elemental C	2	EC	1	0	1	1	0	0	1	0	1	1	0	1	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1
4	Fuel	6	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
5	Total Moles	-1	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
6	Free Oxygen	-2	FO	1	0	1	2	0	1	1	0	1	1	0	1	0	1	1	2	1	2	1	0	0	0	2	0	0	1	0	0	0
7	Free Valence	-4	FV	0	0	1	0	1	0	0	1	0	1	0	1	0	2	1	1	0	0	1	0	0	1	1	2	1	1	1	3	4
8	Fuel Radical	-4	FR	0	0	1	0	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
9	Species H2CO	-4	H2CO	0	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
10	Species HCO	-4	HCO	0	0	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
11	Species CO	4	CO	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
12	Species CH3O	4	CH3O	0	0	0	0	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

Initial Conditions

For systems initially in an equilibrium or constrained-equilibrium state, the initial values of the constraint potentials are finite and can easily be determined using constrained-equilibrium programs of the type mentioned above. However, for a system initially in a non-equilibrium state where the concentrations of one or more species is zero it can be seen from equation (10) that one or more constraint potentials must be infinite. This condition is encountered in induction time calculations where the initial values of all species concentrations except the reactants are assumed to be zero. One method of dealing with this problem is to assign small partial pressures to as many product species as required to give finite values for the constraint potentials. Ideally the choice should be made in such a way that the partial pressures of all other product species will be smaller than the assigned partial pressures.

The method for doing this can be most easily described using matrix notation. The constraint equation (6) becomes

$$\mathbf{C} = \mathbf{AN} = \mathbf{A}_{11}\mathbf{N}_1 + \mathbf{A}_{12}\mathbf{N}_2 \tag{17}$$

where $\mathbf{C}$ is the constraint vector, $\mathbf{N}$ is the species vector, $\mathbf{A}$ is the constraint matrix and $\mathbf{A}_{11}$ is a square matrix relating $\mathbf{C}$ to the major species vector $\mathbf{N}_1$.

$$\dot{\mathbf{C}} = \mathbf{BR} \tag{18}$$

and

$$\mathbf{B} = \mathbf{A}\mathbf{\nu} \tag{19}$$

where $\mathbf{\nu}$ is the matrix of stoichiometric coefficients. The implicit equation for the constraint-potential (11) becomes

$$\mathbf{\mu} = \ln \mathbf{P} + \mathbf{\mu}^0 = -\mathbf{A}^T \mathbf{\gamma} \tag{20}$$

where $\mathbf{A}^T$ is the transpose of $\mathbf{A}$.

Assuming $\mathbf{A}_{11}$ is non-singular, i.e. its determinant is non-zero, and that $\mathbf{A}_{12}\mathbf{N}_2$ in Eq. (17) can be neglected, equation (20) can be inverted to give

$$\mathbf{\gamma}_1 = -(\mathbf{A}_{11}^T)^{-1}\mathbf{\mu}_1 = -(\mathbf{A}_{11}^T)^{-1}(\ln \mathbf{P}_1 + \mathbf{\mu}_1^0) \tag{21}$$

where the subscript 1 denotes initial values.

The solution of equation (21) is simplified and the calculations proceed more smoothly if the $\mathbf{A}_{11}$ matrix is diagonalized. This can be accomplished by a transformation of the constraint vector. Multiplying equation (17) by $\mathbf{A}_{11}^{-1}$ gives

$$\widetilde{\mathbf{C}} = \mathbf{A}_{11}^{-1}\mathbf{C} = \mathbf{A}_{11}^{-1}\mathbf{AN} = \mathbf{I}_{11}\mathbf{N}_1 + \mathbf{A}_{11}^{-1}\mathbf{A}_{12}\mathbf{N}_2 = \widetilde{\mathbf{A}}\mathbf{N} \tag{22}$$

and equation (20) becomes

$$\mathbf{\mu} = \ln \mathbf{P} + \mathbf{\mu}^0 = -\widetilde{\mathbf{A}}^T \mathbf{\Gamma} = -(\mathbf{A}_{11}^{-1}\mathbf{A})^T \mathbf{\Gamma} \tag{23}$$

$\widetilde{\mathbf{C}} = \mathbf{A}_{11}^{-1}\mathbf{C}$ and $\mathbf{\Gamma}$ are the transformed constraint and constraint-potential vectors, $\mathbf{I}_{11}$ is the unit matrix, and $\widetilde{\mathbf{A}} = \mathbf{I}_{11} + (\mathbf{A}_{11}^{-1}\mathbf{A}_{12})\widetilde{\mathbf{A}}$ is the transformed constraint matrix. The relation between $\mathbf{\gamma}$ and $\mathbf{\Gamma}$ found by equating equations (20) and (23) is

$$\mathbf{\Gamma} = (\mathbf{A}_{11})^T \mathbf{\gamma} \tag{24}$$

and the initial value of $\mathbf{\Gamma}$ obtained from equation (21) is

$$\mathbf{\Gamma}_1 = -\mathbf{\mu}_1 = -(\ln \mathbf{P}_1 + \mathbf{\mu}_1^0) \tag{25}$$

The transformed reaction rate matrix is

$$\widetilde{\mathbf{B}} = \widetilde{\mathbf{A}} \mathbf{\nu} = \mathbf{A}_{11}^{-1}\mathbf{B} \tag{26}$$

ILLUSTRATIVE CALCULATIONS FOR THE METHANOL – OXYGEN SYSTEM

Illustrative calculations were carried out for premixed stoichiometric methanol-oxygen mixture at constant energy in a constant volume chamber for initial pressures of 1 atm and 100 atm and initial temperatures of 1500 K and 900 K using 4 to 12 constraints. For comparison, corresponding rate-equations in a detailed model which includes 29 species and 140 reactions (20 species and 102 reactions in the GRI-Mech 3.0 model [31] along with other 9 species and 38 additional reactions [32-34]) were integrated using DASSL [27] to obtain exact solutions.

The 12 constraints in the order that they were introduced in the RCCE calculations are defined in Table 1 which forms the constraint matrix $\mathbf{A}$. The sub-determinant column shows the determinant of each sub square matrix $\mathbf{A}_{11}$. It can be seen that each of them is nonsingular which is a prerequisite described in the section of initial conditions for the calculation of initial constraint potentials. Table 2 tabulates all the 140 reactions with their corresponding enthalpy of reaction, rate parameters and the reaction B_{jk} matrix (change of constraints for each reaction) for the most important 9 constraints. Reaction sources are listed in the reference column. It can be noted that only the first 109 reactions change the constraints, all others don't change the value of the constraints; therefore their rate information is not needed and equilibrium composition is reached without them. Figure 1 compares the ignition delay for the case of 1500 K and 1 atm. of pressure; Figure 2 does it for the case of 900 K and 100 atm. It can be seen that the ignition delay times agree within 5 % for 9 -12 constraints calculations. Results for fewer than 8 constraints gave significantly larger errors. Eight is the minimum number of constraints required to give reasonable agreement between ignition delay times at both high and low temperatures. Adding more constraints can continuously improve the results as expected and using 9 constraints can match very well with detailed calculations at both high and low temperature regimes. Using 12 constraints improve the accuracy of the minor species.

Table 2: Reaction Set Mechanism for Methanol Oxidation (includes enthalpies of formati on, reaction parameters and matrix B of constraints change)

N°	Reactions							ΔH_{298}^0 (kcal/mol)	Forward rate (in cm³, mole, sec, and cal) A	n	Ea	FU	M	FO	FV	FR	H2CO	Ref.
1	CH3OH	O		=	OH	CH2OH		-5	3.90E+05	2.5	3100	-1	0	0	0	1	0	31
2	CH3OH	O		=	OH	CH3O		2.38	1.30E+05	2.5	5000	-1	0	0	0	1	0	31
3	CH3OH	H		=	CH2OH	H2		-6.9	1.70E+07	2.1	4870	-1	0	0	0	1	0	31
4	CH3OH	H		=	CH3O	H2		0.48	4.20E+06	2.1	4870	-1	0	0	0	1	0	31
5	CH3OH	OH		=	CH2OH	H2O		-22	1.40E+06	2	-840	-1	0	0	0	1	0	31
6	CH3OH	OH		=	CH3O	H2O		-14.62	6.30E+06	2	1500	-1	0	0	0	1	0	31
7	CH3OH	CH3		=	CH2OH	CH4		-7.81	3.00E+07	1.5	9940	-1	0	0	0	1	0	31
8	CH3OH	CH3		=	CH3O	CH4		-0.43	1.00E+07	1.5	9940	-1	0	0	0	1	0	31
9	CH3OH	H		=	CH3	H2O		-26.09	5.20E+12	0	5340	-1	0	0	0	0	0	35
10	CH3OH	HO2		=	CH2OH	H2O2		9.6	6.30E+12	0	19360	-1	0	0	0	1	0	33
11	CH3OH	O2		=	HO2	CH2OH		48.2	2.00E+13	0	38000	-1	0	0	2	1	0	33
12	CH3OH	O2		=	HO2	CH3O		55.58	2.00E+13	0	45200	-1	0	0	2	-1	0	35
13	CH3O	H2O2		=	CH3OH	HO2		-16.98	2.60E+16	-0.7	17041	-1	0	0	-1	0	0	35
14	CH2OH	H	M	=	CH3OH		M	-97.3	1.10E+12	0.5	86	1	-1	0	-2	-1	0	31
15	CH3O	H	M	=	CH3OH		M	-104.68	2.40E+12	0.5	50	1	-1	0	-2	-1	0	31
16	CH3	OH	M	=	CH3OH		M	-93.21	2.80E+18	-1.4	1330	1	-1	0	-2	0	0	31
17	CH3OH	H2CO		=	CH3O	CH3O		82.46	1.50E+12	0	79570	-1	0	0	2	2	-1	32
18	CH3	O		=	H	H2	CO	-42.61	3.40E+13	0	0	0	1	0	-2	0	0	31
19	CH2	O		=	CO	H	H	-127.67	5.00E+13	0	0	0	1	0	-2	0	0	32
20	HCO	H2O		=	CO	H	H2O	73.46	1.50E+18	-1	17000	0	1	0	0	0	0	31
21	HCO	M		=	CO	H	M	15.66	1.90E+17	-1	17000	0	1	0	0	0	0	31
22	CH2	O2		=	OH	H	CO	-32.27	5.00E+12	0	1500	0	1	2	0	0	0	31
23	CH2	O2		=	H	H	CO2	10.43	5.80E+12	0	1500	0	1	2	0	0	0	31
24	CH3OOH			=	CH3O	OH		44.88	6.00E+14	0	42300	0	1	2	2	1	0	33
25	CH3OOH	O2		=	H2CO	OH	HO2	15	1.00E+13	0	15000	0	1	2	2	0	1	35
26	CH3OOH	HO2		=	H2CO	OH	H2O2	12	1.00E+13	0	0	0	1	2	0	0	1	35
27	CH3OOH	CH3		=	H2CO	OH	CH4	-20.11	1.00E+13	0	0	0	1	2	0	0	1	35
28	CH3OOH	CH3OO		=	H2CO	OH	CH3OOH	11	1.00E+13	0	0	0	1	2	0	0	1	35
29	CH3	O2	M	=	CH3OO		M	-31.11	2.60E+33	-7.13	5351	0	-1	0	0	0	0	32
30	O	O	M	=	O2		M	-119.2	1.20E+17	-1	0	0	-1	-2	-4	0	0	31
31	OH	OH	M	=	H2O2		M	-51.4	7.40E+13	-0.4	0	0	-1	-2	-2	0	0	31
32	OCHO	OH	M	=	HOOCHO		M	-39.18	9.10E+14	0	-5070	0	-1	-2	-2	0	0	35
33	H	O	M	=	OH		M	-102.3	5.00E+17	-1	0	0	-1	0	-2	0	0	31
34	CO	O	M	=	CO2		M	-127.25	1.80E+10	0	2385	0	-1	0	-2	0	0	31
35	H	H	M	=	H2		M	-104.2	1.00E+18	-1	0	0	-1	0	-2	0	0	31
36	H	H	H2	=	H2	H2		-104.2	9.00E+16	-0.6	0	0	-1	0	-2	0	0	31
37	H	H	H2O	=	H2	H2O		-104.2	6.00E+19	-1.3	0	0	-1	0	-2	0	0	31
38	H	H	CO2	=	H2	CO2		-104.2	5.50E+20	-2	0	0	-1	0	-2	0	0	31
39	OH	H	M	=	H2O		M	-119.3	2.20E+22	-2	0	0	-1	0	-2	0	0	31
40	CH2	H	M	=	CH3		M	-110.76	6.00E+14	0	0	0	-1	0	-2	0	0	31
41	CH3	H	M	=	CH4		M	-105.11	1.40E+16	-0.5	536	0	-1	0	-2	0	0	31
42	HCO	H	M	=	H2CO		M	-88.14	1.10E+12	0.5	-260	0	-1	0	-2	0	1	31
43	H2	CH	M	=	CH3		M	-107.59	2.00E+12	0.4	-370	0	-1	0	-2	0	0	31
44	H	O2	M	=	HO2		M	-49.1	2.80E+18	-0.9	0	0	-1	0	0	0	0	31
45	H	O2	O2	=	HO2	O2		-49.1	2.08E+19	-1.24	0	0	-1	0	0	0	0	31
46	H	O2	H2O	=	HO2	H2O		-106.9	1.10E+19	-0.8	0	0	-1	0	0	0	0	31
47	H2CO	H	M	=	CH2OH		M	-29.6	5.40E+11	0.5	3600	0	-1	0	0	1	-1	31
48	H2CO	H	M	=	CH3O		M	-22.22	5.40E+11	0.5	2600	0	-1	0	0	1	-1	31
49	CO	H2	M	=	H2CO		M	0.4	4.30E+07	1.5	79600	0	-1	0	0	0	1	31
50	O2	HCO	M	=	OOCHO		M	-41.84	2.00E+13	0	8000	0	-1	0	0	0	0	35
51	CH2	HO2		=	OH	H2CO		-113.37	2.00E+13	0	0	0	0	2	-2	0	1	31
52	O2	C		=	O	CO		-137.6	5.80E+13	0	576	0	0	2	-2	0	0	31
53	O2	CH2		=	CO2	H2		-187.82	6.90E+11	0	500	0	0	2	-2	0	0	32
54	HO2	H		=	O	H2O		-53.3	4.00E+12	0	671	0	0	2	0	0	0	31
55	HO2	H		=	OH	OH		-36.3	8.40E+13	0	635	0	0	2	0	0	0	31
56	H2O2	H		=	OH	H2O		-67.9	1.00E+13	0	3600	0	0	2	0	0	0	31
57	CO	HO2		=	OH	CO2		-61.25	1.50E+14	0	23600	0	0	2	0	0	0	31
58	O2	CH		=	O	HCO		-73.06	6.70E+13	0	0	0	0	2	0	0	0	31
59	O2	CH3		=	OH	H2CO		-51.71	2.30E+12	0	20315	0	0	2	0	0	1	31
60	O2	CH2		=	O	H2CO		-60.17	2.40E+12	0	1500	0	0	2	0	0	1	31
61	CH3	HO2		=	OH	CH3O		-24.83	3.80E+13	0	0	0	0	2	0	1	0	31
62	CO	O2		=	O	CO2		-8.05	2.50E+12	0	47800	0	0	2	2	0	0	31
63	CH3OO	CH3		=	CH3O	CH3O		-31.35	2.41E+13	0	0	0	0	2	0	2	0	32
64	O2	H		=	OH	O		16.9	2.60E+16	-0.7	17041	0	0	2	2	0	0	31
65	O2	CH3		=	CH3O	O		28.37	3.60E+13	0	30480	0	0	2	2	1	0	31
66	CH	O		=	H	CO		-176.6	5.70E+13	0	0	0	0	0	-4	0	0	31
67	C	OH		=	H	CO		-154.5	5.00E+13	0	0	0	0	0	-4	0	0	31
68	CH2	O		=	CO	H2		-179.77	3.00E+13	0	0	0	0	0	-4	0	0	32
69	CH2OH	O		=	OH	H2CO		-72.7	1.00E+13	0	0	0	0	0	-2	-1	1	31

Table 2 (continuation)

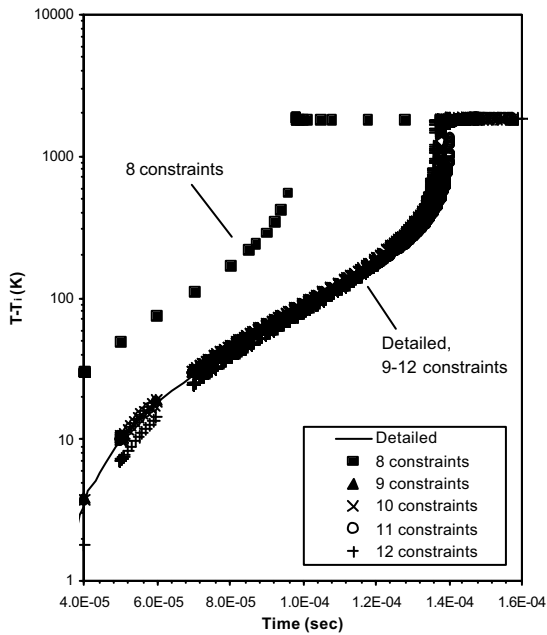| N°		Reactions				ΔH$_{298}^0$ (kcal/mol)	Forward rate (in cm³, mole, sec, and cal)			Constraints						Ref.
							A	n	Ea	FU	M	FO	FV	FR	H2CO	
71	CH2OH	H	=	H2	H2CO	-74.6	2.00E+13	0	0	0	0	0	-2	-1	1	31
72	CH3O	H	=	H2	H2CO	-81.98	2.00E+13	0	0	0	0	0	-2	-1	1	31
73	CH2OH	OH	=	H2O	H2CO	-89.7	5.00E+12	0	0	0	0	0	-2	-1	1	31
74	CH3O	OH	=	H2O	H2CO	-97.08	5.00E+12	0	0	0	0	0	-2	-1	1	31
75	HO2	O	=	OH	O2	-53.2	2.00E+13	0	0	0	0	0	-2	0	0	31
76	CH2	O	=	H	HCO	-91.23	8.00E+13	0	0	0	0	0	-2	0	0	31
77	CH3	O	=	H	H2CO	-68.61	5.10E+13	0	0	0	0	0	-2	0	1	31
78	HCO	O	=	OH	CO	-86.64	3.00E+13	0	0	0	0	0	-2	0	0	31
79	HCO	O	=	H	CO2	-111.59	3.00E+13	0	0	0	0	0	-2	0	0	31
80	HO2	H	=	O2	H2	-55.1	4.50E+13	0	1068	0	0	0	-2	0	0	31
81	HCO	H	=	H2	CO	-88.54	7.30E+13	0	0	0	0	0	-2	0	0	31
82	HO2	OH	=	O2	H2O	-70.2	1.40E+13	0	-500	0	0	0	-2	0	0	31
83	CH	OH	=	H	HCO	-89.96	3.00E+13	0	0	0	0	0	-2	0	0	31
84	CH2	OH	=	H	H2CO	-77.07	2.00E+13	0	0	0	0	0	-2	0	1	31
85	HCO	OH	=	H2O	CO	-103.64	5.00E+13	0	0	0	0	0	-2	0	0	31
86	HO2	HO2	=	O2	H2O2	-38.6	1.30E+11	0	-1630	0	0	0	-2	0	0	31
87	CH3	HO2	=	O2	CH4	-56.01	1.00E+12	0	0	0	0	0	-2	0	0	31
88	H2O	CH	=	H	H2CO	-58.8	5.70E+12	0	-755	0	0	0	-2	0	1	31
89	CO2	CH	=	HCO	CO	-65.01	1.90E+14	0	15792	0	0	0	-2	0	0	31
90	HCO	CH3	=	CH4	CO	-89.45	2.60E+13	0	0	0	0	0	-2	0	0	31
91	CH3	OH	=	H2	H2CO	-70.51	8.00E+09	0.5	-1755	0	0	0	-2	0	1	31
92	OCHO	OH	=	H2O	CO2	-123.63	5.00E+12	0	0	0	0	0	-2	0	0	34
93	CO2	CH2	=	H2CO	CO	-52.12	1.10E+11	0	1000	0	0	0	-2	0	1	32
94	HCO	HO2	=	H2O2	CO	-72.04	2.00E+13	0	12000	0	0	0	-2	0	0	35
95	H2CO	O2	=	HO2	HCO	39.04	1.00E+14	0	40000	0	0	0	2	0	-1	31
96	HOCHO	O2	=	HOCO	HO2	39	1.00E+14	0	40000	0	0	0	1	0	0	35
97	HOCHO	O2	=	OCHO	HO2	55.58	2.00E+13	0	45200	0	0	0	2	0	0	35
98	CH3OO	HO2	=	CH3OOH	O2	-38.6	4.64E+10	0	2581.8	0	0	0	-2	0	0	32
99	CH2OH	H	=	OH	CH3	-4.09	1.60E+11	0.7	-284	0	0	0	0	-1	0	31
100	CH3O	H	=	OH	CH3	-11.47	1.50E+12	0.5	-110	0	0	0	0	-1	0	31
101	CH3O	HO2	=	CH3OO	OH	6.52	2.00E+13	0	0	0	0	0	0	-1	0	35
102	O2	CH2OH	=	HO2	H2CO	-19.5	1.80E+13	0	900	0	0	0	0	-1	1	31
103	O2	CH3O	=	HO2	H2CO	-26.88	4.30E-13	7.6	-3530	0	0	0	0	-1	1	31
104	H2CO	O	=	OH	HCO	-14.16	3.90E+13	0	3540	0	0	0	0	0	-1	31
105	H2CO	H	=	HCO	H2	-16.06	5.70E+07	1.9	2742	0	0	0	0	0	-1	31
106	H2CO	OH	=	HCO	H2O	-31.16	3.40E+09	1.2	-447	0	0	0	0	0	-1	31
107	H2CO	HO2	=	HCO	H2O2	0.44	5.60E+06	2	12000	0	0	0	0	0	-1	31
108	H2CO	CH3	=	HCO	CH4	-16.97	3.30E+03	2.8	5860	0	0	0	0	0	-1	31
109	H2CO	OOCHO	=	HOOCHO	HCO	0.44	2.00E+13	0	5000	0	0	0	0	0	-1	35
110	O2	HCO	=	HO2	CO	-33.44	1.40E+13	0	400	0	0	0	0	0	0	31
111	HCO	OH	=	H	OCHO	-4.96	3.00E+13	0	0	0	0	0	0	0	0	35
112	H2	O	=	OH	H	1.9	3.90E+04	2.7	6260	0	0	0	0	0	0	31
113	H2O2	O	=	OH	HO2	-14.6	9.60E+06	2	4000	0	0	0	0	0	0	31
114	CH4	O	=	OH	CH3	2.81	1.00E+09	1.5	8600	0	0	0	0	0	0	31
115	H2O2	H	=	HO2	H2	-16.5	1.20E+07	2	5200	0	0	0	0	0	0	31
116	CH	H	=	C	H2	-24	1.60E+14	0	0	0	0	0	0	0	0	31
117	CH4	H	=	CH3	H2	0.91	6.60E+08	1.6	10840	0	0	0	0	0	0	31
118	CH3O	H	=	H	CH2OH	-7.38	4.20E+07	1.6	1924	0	0	0	0	0	0	31
119	H2	OH	=	H	H2O	-15.1	2.20E+08	1.5	3430	0	0	0	0	0	0	31
120	OH	OH	=	O	H2O	-17	3.60E+04	2.4	-2110	0	0	0	0	0	0	31
121	H2O2	OH	=	HO2	H2O	-31.6	2.00E+12	0	427	0	0	0	0	0	0	31
122	CH2	OH	=	CH	H2O	-18.27	1.10E+07	2	3000	0	0	0	0	0	0	31
123	CH3	OH	=	CH2	H2O	-8.54	5.60E+07	1.6	5420	0	0	0	0	0	0	31
124	CH4	OH	=	CH3	H2O	-14.19	1.00E+08	1.6	3120	0	0	0	0	0	0	31
125	CO	OH	=	H	CO2	-24.95	4.80E+07	1.2	70	0	0	0	0	0	0	31
126	H2	CH	=	H	CH2	3.17	1.10E+14	0	3110	0	0	0	0	0	0	31
127	H2	CH2	=	H	CH3	-6.56	5.00E+05	2	7230	0	0	0	0	0	0	31
128	CH4	CH2	=	CH3	CH3	-5.65	2.50E+06	2	8270	0	0	0	0	0	0	31
129	H2O2	CH3	=	HO2	CH4	-17.41	2.40E+04	2.5	5180	0	0	0	0	0	0	31
130	H	HOCHO	=	H2	OCHO	0.48	1.00E+13	0	0	0	0	0	0	0	0	35
131	OOCHO	OH	=	HO2	OCHO	-12.22	1.80E+11	0	0	0	0	0	0	0	0	35
132	HOOCHO	HO2	=	H2O2	OOCHO	0	1.50E+12	0	0	0	0	0	0	0	0	35
133	HOOCHO	H	=	H2	HOOCO	-16.1	1.00E+14	0	0	0	0	0	0	0	0	35
134	CH3OOH	HO2	=	H2O2	CH3OO	0	2.00E+13	0	0	0	0	0	0	0	0	35
135	CH3OOH	H	=	H2	CH2OOH	-6.9	2.00E+13	0	0	0	0	0	0	0	0	35
136	HOCHO	H	=	H2	HOCO	-16.1	1.00E+13	0	0	0	0	0	0	0	0	35
137	CH3OH	CH3O	=	CH2OH	CH3OH	-7.38	1.50E+12	0	7000	0	0	0	0	0	0	33
138	CH3OO	CH4	=	CH3OOH	CH3	17.41	1.81E+11	0	18470	0	0	0	0	0	0	35
139	CH3OO	H2O2	=	CH3OOH	HO2	0	2.41E+12	0	9930	0	0	0	0	0	0	35

Figure 1 Ignition Delay for Methanol-Oxygen Mixture at 1500K and 1 atm. of Pressure Using Detailed Kinetics and 8-12 Constraints
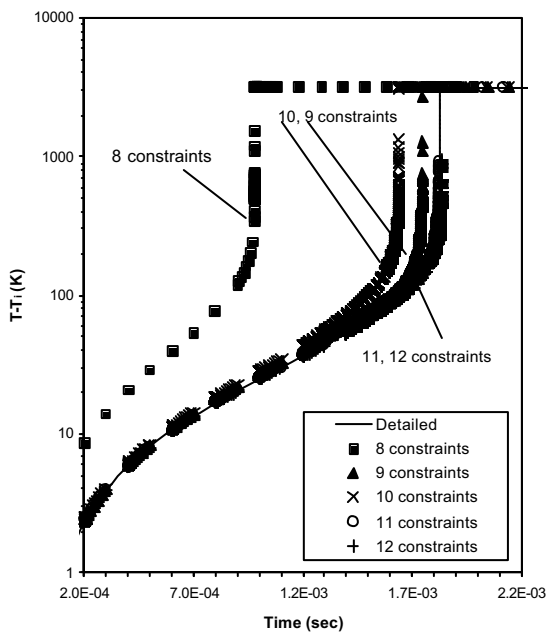

Figure 2 Ignition Delay for Methanol-Oxygen Mixture at 900K and 100 atm. of Pressure Using Detailed Kinetics and 8-12 Constraints

Figures 3 - 5 show the mole fraction evolution for different species using 9 constraints. Agreement is very good for all of them when compared to detailed

calculations. Figure 3 shows the mole fraction evolution for methanol, oxygen, formaldehyde (H_2CO) and CO. Figure 4 does for H, HO and HO_2 and Figure 5 for H_2, H_2O_2, H_2O and CO_2
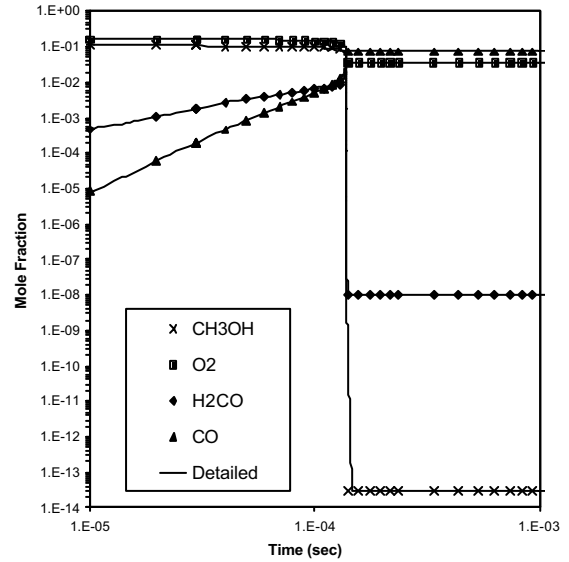
Figure 3 Mole Fraction Evolution of CH_3OH, O_2, H_2CO and CO for Methanol-Oxygen Mixture at 1500 K and 1 atm. of Pressure Using Detailed Kinetics and 9 Constraints
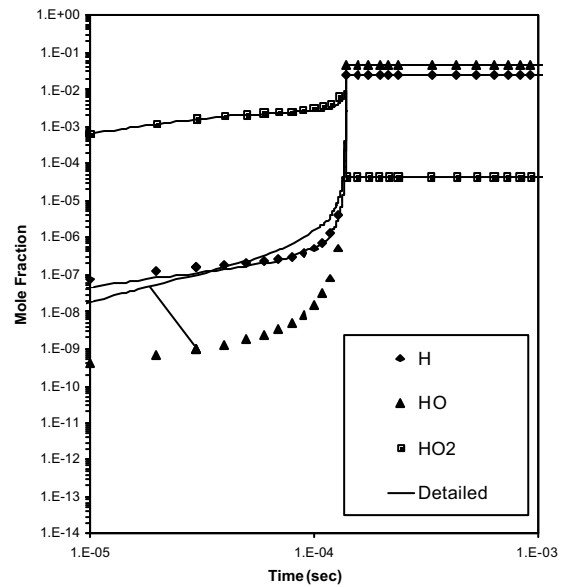
Figure 4 Mole Fraction Evolution of H, HO and HO_2. for Methanol-Oxygen Mixture at 1500 K and 1 atm. of Pressure Using Detailed Kinetics and 9 Constraints
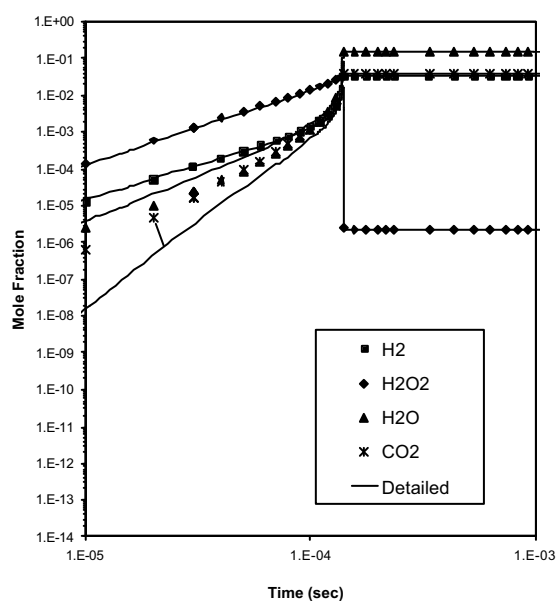
Figure 5 Mole Fraction Evolution of H_2, H_2O_2, H_2O and CO_2 for Methanol-Oxygen Mixture at 1500 K and 1 atm. of Pressure Using Detailed Kinetics and 9 Constraints

Both RCCE and detailed 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. Time saving was of 25% and 10% for 8 and 9 constraints respectively. Although the CPU time saved by the RCCE method is modest in this case, it is expected to. improve by many folds 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.

CONCLUSIONS

Rate equations for the constraint potentials associated with the Rate-Controlled Constrained-Equilibrium (RCCE) method have been developed and successfully integrated for induction times of methanol-oxygen system at stoichiometric conditions over a wide range of initial temperatures and pressures. RCCE calculation using variable constraints on the moles of fuel, total number of moles, moles of free oxygen, moles of free valence, moles of fuel radical and moles of formaldehyde (H_2CO) gives excellent agreement with detailed calculation. Adding variable constraints as moles of HCO, moles of CO and moles of CH_3O improved the calculation of the minor species concentration. Only 8 constraints were required to give reasonable agreement with detailed calculation for ignition time delay. For this system including 29

species, there was a gain of 10~25 % in computer running time.

Finally, the RCCE method gives valuable insight into the important reaction paths and rate-limiting reactions involved in the evolution of complex chemical systems.

ACKNOWLEDGEMENTS

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