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## Rate-Controlled Constrained-Equilibrium Calculations of Methanol-Oxygen Kinetics Using Reduced Chemistry

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According to the underlying concept of the rate-controlled constrained-equilibrium (RCCE) method, the relaxation of a complex reacting system towards the final equilibrium state is governed by a set of active and passive constraints imposed by the internal dynamics of the system that is considerably smaller in dimension than the original system. A set of 10 constraints, able to accurately model the dynamic evolution of the methanol oxidation over a wide range of initial temperatures and pressures is proposed. Based on rational analysis of the important rate-limiting steps a further reduced set is obtained, which when is used in conjunction with RCCE is able to give excellent predictions for dynamic evolution of the system at low temperatures at different pressures. Some salient features of RCCE are explored. The detailed kinetic scheme involves only G chemistry and includes 132 reactions along with 29 species without nitrogen chemistry.

### 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 detailed kinetics. However, detailed kinetics of hydrocarbon systems can easily grow to thousands of chemical species and isomers, and millions of reactions. Consequently, detailed solution is difficult, if not impossible to achieve. The gravity of this problem is even more apparent when considering reacting turbulent flows where the effort required to resolve the complexity of turbulence is similar to that required for the determination of the chemistry.

Several powerful methods for simplifying the chemical kinetics calculations for large chemical systems have been developed over the past couple of decades, which are based on the physico-mathematical considerations of the dynamical evolution of the system. Works on intrinsic low dimensional manifolds (ILDm) [1], computational singular perturbation (CSP) [2], the so-called adaptive chemistry [3] and the Rate-Controlled Constrained-Equilibrium (RCCE) method [4], on which we will focus in this work, are the most prominent.

The RCCE method, originally proposed by Keck and Gillespie [4] and later developed and applied to different cases by Keck and co-workers [5-9], is based on the maximum-entropy principle of thermodynamics and involves the fundamental observation that slow reactions in a complex reacting system impose constraints on its composition, which control the rate at which

it relaxes 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 over the above-mentioned simplifying methods is that it is unnecessary to start with a complete reaction model that must be then simplified by various approximations. Instead, one starts with a small number of constraints to which more can be systematically added to improve the accuracy of the calculations, to any desired level. In the limit where the number of constraints equals the number of species specified for a system, the method becomes similar to an exact calculation with the important caveat that the equilibrium requirement must be satisfied at each time step. 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.

Reduction of the system of reactions for different reduced mechanisms can be trivially obtained subject to different sets of constraints. However, the careful and informed selection of constraints is the key to the successful implementation of RCCE which requires careful examination of the underlying chemistry.

In this study, we consider the stoichiometric oxidation of methanol with pure oxygen over a wide range of initial temperatures (900K-1500K) and pressures (1atm-100atm) in a constant volume reactor. The kinetic scheme involves only C<sub>1</sub> chemistry and comprises 132 reactions along with 29 species without nitrogen chemistry. Based on a careful examination of the chemistry of oxidation a set of 10 constraints have been determined which are capable of exactly reproducing the results from a detailed calculations over the specified range of initial conditions.

The application of the RCCE method will result in a reduction of the system through elimination of reactions that do not change a constraint, and are, therefore, in equilibrium. This results in an initial reduction of the system to 103 reactions. In principle, only one reaction is needed for each constraint to achieve the correct final equilibrium state, and the reaction chosen for each constraint should be the fastest one from the group of reactions which change the constraint. However, a single reaction for each constraint may not, in general, predict the correct evolution of the system. In this work, 12 reactions and 15 species provide an excellent match with the ignition delay times from the detailed kinetic calculation based on 132 reactions. The importance of these drastic reductions will be underscored when dealing with situations involving reacting gas dynamics such as detonation studies, homogeneous combustion in gas turbine engines [10], etc.

## 2. Rate-Controlled Constrained-Equilibrium Method

### 2.1. Different Formulations

The Rate Controlled Constrained Equilibrium (RCCE) method can be implemented in three different formulations that have been explored to various extents by our research group over the past decade. The first method is based on the direct integration of the constraints and the determination of their values at each time step. The results of such calculations have to be

coupled with a generalized equilibrium program (GNASA or GSTANJAN) to determine the constrained-equilibrium state of the system as a function of time [6]. This method has been proved to be inefficient and time consuming [6]. The second method is based on integration of the constraint factors [7]. This method proved to be superior to the first method for the H/O system but is difficult to generalize. The third method involves the direct integration of the constrained potentials conjugate to each constraint. This method was originally proposed by Keck in a review paper [11] and explored and implemented in later works [12-14]. There have been recently published similar formulations and, in some respects, extensions in literature [15,16].

## 2.2 Rate-Controlled Constrained-Equilibrium Method in Constraint-Potentials Form

The detailed formulation of RCCE in constrained-potential form can be found in earlier works [9,12,13], so we avoid repeating the procedure in detail here and address important points. In the present work, as well as all previous applications of RCCE method, 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,

$$C_i = \sum_{j=1}^{ns} a_{ij} N_j, \quad i=1, \dots, N_c \quad (1)$$

where  $a_{i,j}$  is the value of the  $i$ th constraint for the  $j$ th species and  $N_c$  is the number of constraints. Table I represents the  $a_{i,j}$  matrix used in this work and expresses the relationship between the species and the specified constraint.

Table I.  $a_{i,j}$  Matrix for Methanol-Oxygen Mixture

	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	
	H	H <sub>2</sub>	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	O	OH	H <sub>2</sub> O	O <sub>2</sub>	C	CH	CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>4</sub>	CH <sub>3</sub> O	CH <sub>2</sub> OH	CH <sub>3</sub> OH	HCO	CH <sub>2</sub> O	CH <sub>3</sub> OO	CH <sub>2</sub> OO	CH <sub>3</sub> OO	OCHO	HOCO	HOCHO	OOCHO	HOOCO	HOCHO	CO	CO <sub>2</sub>	
EC	0	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	1	1	1	
EO	0	0	2	2	1	1	1	2	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	2	3	3	3	1	2
EH	1	2	1	2	0	1	2	0	0	1	2	3	4	3	3	4	1	2	3	3	4	1	1	2	1	1	2	0	0	
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	
FO	0	0	0	0	1	1	1	0	0	0	0	0	0	1	1	1	1	1	0	0	0	2	2	2	1	1	1	1	2	
FV	1	0	1	0	2	1	0	0	4	3	2	1	0	1	1	0	1	0	1	1	0	1	1	0	1	1	0	0	0	
FU	0	0	0	0	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	
ALC	0	0	0	0	0	0	0	0	0	0	0	1	0	1	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	
OHO	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
HCO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	

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

$$N_j = (V / RT) \exp(-\mathbf{m}_j^0 - \sum_{i=1}^{nc} a_{ij} \mathbf{g}_i), \quad j=1, \dots, N_s \quad (2)$$

where  $m_j^0 = (h_j^0 - Ts_j^0)/RT$  is the standard Gibbs free energy of species  $j$  divided by  $RT$ ,  $g_i$  is the constraint potential (LaGrange multiplier) conjugate to the constraint  $i$ , and  $N_s$  is the number of species in the system. Upon solving the differential equations for the  $g_i$  vector, the constrained-equilibrium composition of the system can be found at each time step from eqn. 2.

### 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 must (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. After a thorough examination of the oxidation chemistry of methanol at low temperatures-high pressures (knock related applications) and high temperatures-low pressures (flame propagation applications) the constraints listed in Table II were identified.

Table II. Definition of the Constraints Used in This Study

	Constraint	Definition of the Constraint
1	EC	Elemental carbon
2	EO	Elemental oxygen
3	EH	Elemental hydrogen
4	M	Total number of moles
5	FV	Moles of free valance (any unpaired valence electron)
6	FO	Moles of free oxygen (any oxygen not directly attached to another oxygen)
7	FU	Moles of fuel molecule (CH <sub>3</sub> OH)
8	ALC	Moles of fuel radicals and formaldehyde (CH <sub>3</sub> O+CH <sub>2</sub> OH+CH <sub>2</sub> O)
9	OHO	Moles of water radicals (O+OH)
10	HCO	HCO+CO

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 [19] 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, in degrees of freedom, to the detailed kinetics approach. It is certainly true that our current ability to model systems using constraints as unknowns is not as well developed as our ability to model systems using species. However, just the fact that so little is known about the chemical kinetics of the rate-controlled constrained-equilibrium states makes this topic such a promising area of research.

## 4. Results and Discussions

### 4.1. Reactor Model

Auto-ignition of combustible charges is one of the most basic combustion processes, and determining the chemical kinetic mechanism involved has been a major goal of combustion research for the past half century [17]. The importance of such analysis relates back to strictly kinetically-controlled processes such as engine knock [17,18] and newly increased interest in distributed combustion in gas turbines to reduce the pollution and engine susceptibility to combustion instabilities [10]. For these reasons we have employed a constant volume, constant energy reactor in this study. The time dependent dynamics of the system are determined by  $N_c$  equations for constraints and one energy equation, totalling  $N_c + 1$  overall. These equations were integrated using DDASSL [20].

Studies include temperatures from 900K to 1500K and pressures from 1 atm to 100 atm. The low temperature-high pressures results are relevant to “knock” applications whereas the high temperature-low-to-high pressures results are of interest to both flame-propagation and distributed (flameless) combustion applications.

### 4.2. Kinetic Mechanism

The kinetic mechanism used in this study is based on the scheme used in [8], and includes 132 reactions with 29 species (Table I). Twenty species and 102 reactions were taken from GRI-Mech 3.0, [21], and 9 species along with 30 additional reactions from [22,23] and estimations by the authors.

### 4.3. Low Temperature – High Pressures

Time-dependent temperature profiles for Detailed and RCCE models are shown in Fig.1 for stoichiometric mixtures of Methanol and oxygen at different pressures.

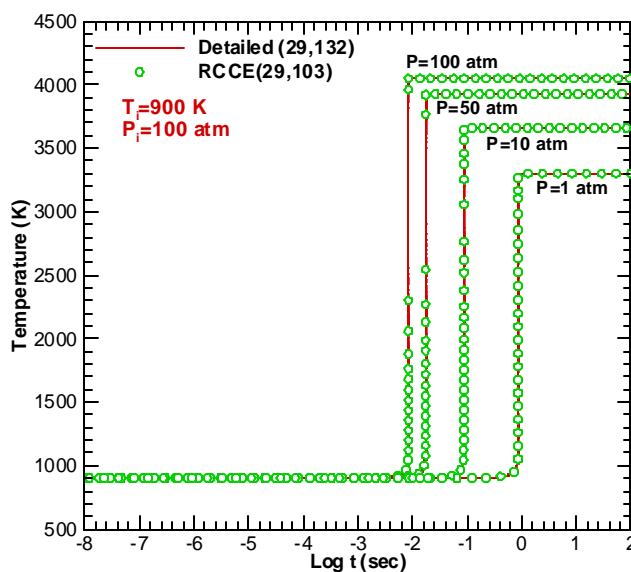


Fig.1: Temperature profiles at different pressures for initial stoichiometric mixtures of fuel and oxidizer.

The initial mixture temperature is 900 K. The set of 10 constraints listed in Table II were used. Clearly, the set of chosen constraints yields excellent results over the entire range of pressures. From the full set including 29 species and 132 reactions, referred to as Detailed (29,132), 29 reactions do not change any constraints and are, therefore, in equilibrium. These reactions are redundant. This results in a reduction to a mechanism containing 29 species and 103 reactions, referred to as RCCE (29,103).

The time-dependent histories of the major species for a stoichiometric mixture at initial temperature of 900K and initial pressure of 100 atm are shown on log-log plots in Fig.2 and Fig.3. Clearly, the agreement is extremely good.

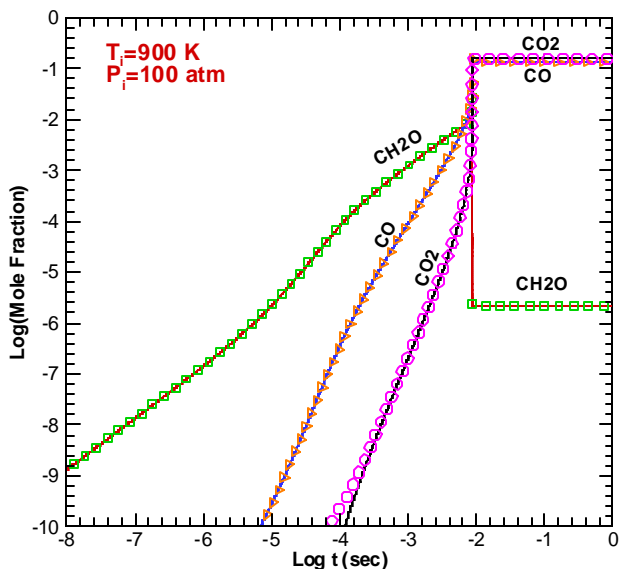


Fig.2: RCCE(29,103) calculations of CH<sub>2</sub>O, CO and CO<sub>2</sub> profiles compared against Detailed (29,132) calculations at initial pressure of 100 atm and initial temperature of 900 K. Symbols represent RCCE and solid lines represent Detailed calculations respectively.

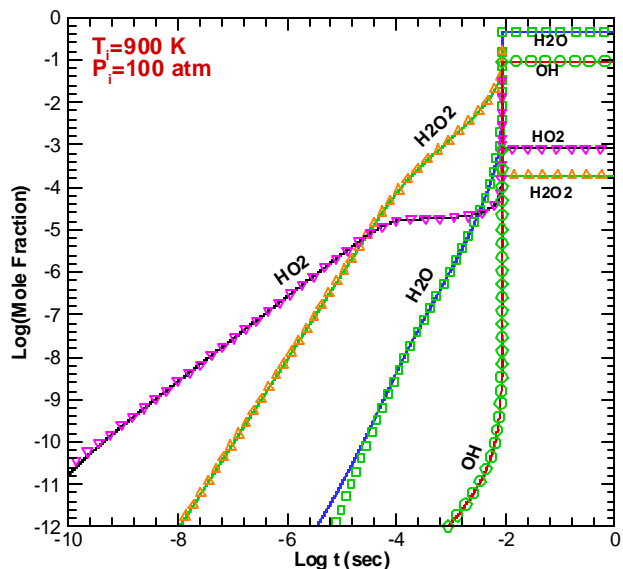
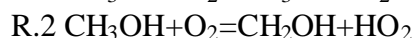
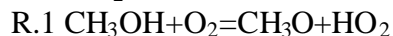
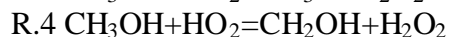


Fig.3: RCCE (29,103) calculations of important H<sub>2</sub>-O<sub>2</sub> species profiles compared against Detailed (29,132) calculations at initial pressure of 100 atm and initial temperature of 900 K. Dashed lines represent RCCE and solid lines represent Detailed.

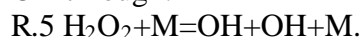
The initiation reactions, being the only active reactions during the early stages of ignition, depending on where the hydrogen is abstracted, convert CH<sub>3</sub>OH into CH<sub>3</sub>O and CH<sub>2</sub>OH, and O<sub>2</sub> into HO<sub>2</sub>:



These reactions are endothermic and are, therefore, slow. The next important attacks on the fuel molecule are by the newly generated HO<sub>2</sub> radicals:



The generated H<sub>2</sub>O<sub>2</sub> breaks on the weak O-O bond and produces free oxygen by converting to OH through:



R.5 is a three body reaction and involves forming free oxygen and free valance, thus changes M, FO and FV. Other important steps involve conversion of the species CH<sub>3</sub>O and CH<sub>2</sub>OH to CH<sub>2</sub>O. Whether the fuel radical initially formed has the CH<sub>3</sub>O or CH<sub>2</sub>OH structure is thought to be unimportant, as the isomerization and formaldehyde (CH<sub>2</sub>O) formation are generally fast steps. The dynamics of the system is then controlled by conversion of CH<sub>2</sub>O down to CO through formation of CHO. These steps are listed in Table III.

Table III: Reduced Reaction Set

M	FU	ALC	FO	OHO	HCO	FV		
-1	0	0	-2	-2	0	-2	OH + OH + M = H2O2 + M	1
0	-1	1	0	0	0	2	CH3OH + O2 + = CH2OH + HO2	2
0	-1	1	0	0	0	2	CH3OH + O2 + = CH3O + HO2	3
0	-1	1	0	0	0	0	CH3OH + HO2 + = CH2OH + H2O2	4
0	-1	1	0	-1	0	0	CH3OH + OH + = CH3O + H2O	5
0	0	-1	0	0	1	2	CH2O + O2 + = HCO + HO2	6
0	0	-1	0	0	1	0	CH2O + HO2 + = HCO + H2O2	7
0	0	0	2	1	-1	0	CO + HO2 + = CO2 + OH	8
0	0	0	2	2	0	2	H + O2 + = OH + O	9
0	0	0	0	-1	0	-2	HCO + OH + = CO + H2O	10
0	0	0	0	-1	-1	0	HCO + OH + = OCHO + H	11
0	0	0	0	0	0	-2	HO2 + HO2 + = H2O2 + O2	12

#### 4.4. Reduced Reaction Set

Based on the above observations of the important steps of the ignition mechanism a reduced set of 12 reactions, Table III, is obtained which when used in conjunction with RCCE is able to give perfect predictions for the ignition delay times at both low and high pressures. Results are shown in Fig. 4.

The real power of RCCE becomes evident when comparing the results of such reduced RCCE calculations with detailed kinetics calculations using the full 132 reaction set.

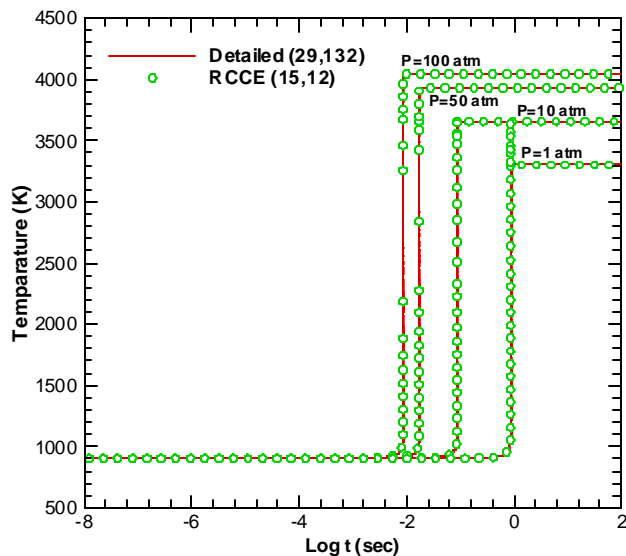


Fig.4: RCCE (15,12) predictions of temperature profiles at different pressures using the reduced reaction list, (Table III) compared with the detailed kinetics predictions using the original 132 reactions, Detailed (29,132).

In Fig 4, the results of the RCCE calculations with the 15-species and 12-reaction set (Table III), referred to as RCCE (15,12), are compared with detailed calculations using the full mechanism, referred to as Detailed (29,132). All RCCE calculations reach the correct final equilibrium state, although at low pressures additional legitimate recombination reactions have to be included in the reduced model. The effect of such reactions is effectively felt during the burning time, when the energy released acts to dissociate some of the newly-formed species and reduce the temperature. This is equivalent to saying these reactions shorten the relaxation time of the system to its final equilibrium state at low pressures. It is also of interest to see how the RCCE (15,12) calculations compare with detailed calculations using the same reduced reaction set, referred to as Detailed (15,12). Fig. 5 represents such a comparison. Clearly, the former does give the correct final equilibrium state.

In the detailed kinetic approach, the set of chemical species is explicitly determined by the mechanism (set of reactions), i.e. no information is available for non-participating species. Conversely, in the RCCE approach, the constrained-equilibrium concentration of any species for which the standard Gibbs free energy is known can be found from eqn. 2, whether or not it appears explicitly in the kinetic model. The  $a_{i,j}$  matrix expresses the relationship between the species and the specified constraint potentials, Table I. It can be seen that any species included in the  $a_{i,j}$  matrix will evolve dynamically and reach the correct equilibrium value even if there is no kinetic path explicitly provided in the mechanism. Fig.6 illustrates this important feature of the RCCE method for the case of  $H_2$ .  $H_2$  is not included in the reduced reaction list, yet its final equilibrium amount is accurately predicted by RCCE. *This feature uniquely distinguishes RCCE from all the other methods available for kinetics modeling.* This distinct feature of RCCE also enables one to obtain a good estimate of the kinetic behavior of a system using a relatively small number of reactions and avoids the necessity of having to estimate the rates of a large number of uncertain fast reactions. Another salient feature of RCCE is that while, in principle, only one reaction for each constraint is required for the system to go to the correct final equilibrium state, in general, a single reaction for each constraint may not be sufficient to give the desired accuracy



for its evolution. In this case, more reactions can be added one at a time to improve the accuracy of the calculations.

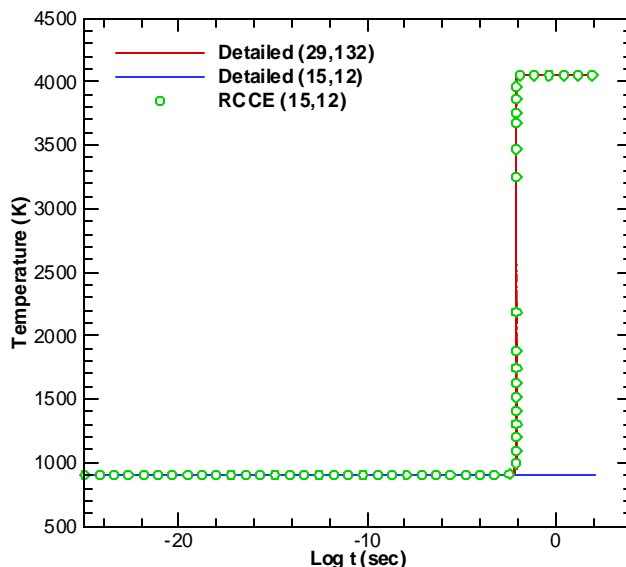


Fig.5: RCCE (15,12) predictions of the temperature profile at  $P_1=100$  atm and  $T_1=900$  K using the reduced reaction set in Table III compared with the detailed kinetics using the original 132 reactions, Detailed (29,132), and the detailed kinetics using the same reduced reaction list, Detailed (15,12)

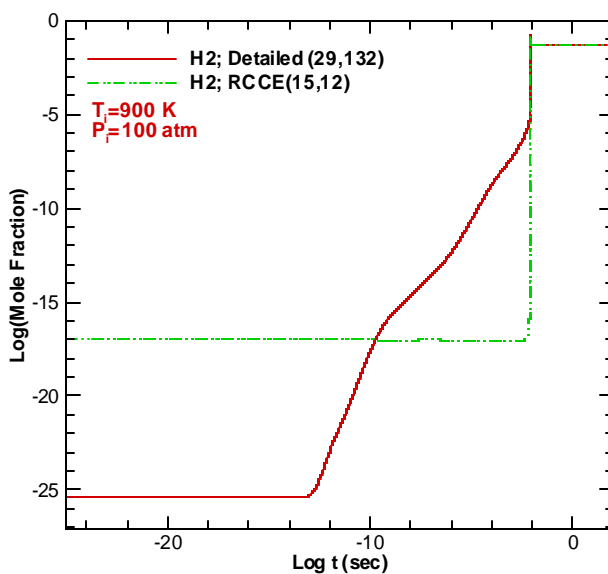


Fig.6: RCCE (15,12) prediction of the H2 mole fraction using the reduced reaction list, Table III, compared against detailed calculations using the original 132 reactions, Detailed (29,132).

#### 4.5. High Temperature Results

High-temperature RCCE calculations of methanol oxidation were performed with using the same set of constraints in Table 1 in conjunction with the full mechanism. Sample results of such

calculations are shown in Fig. 7. Predicted temperature profiles are in excellent agreement with the detailed calculations.

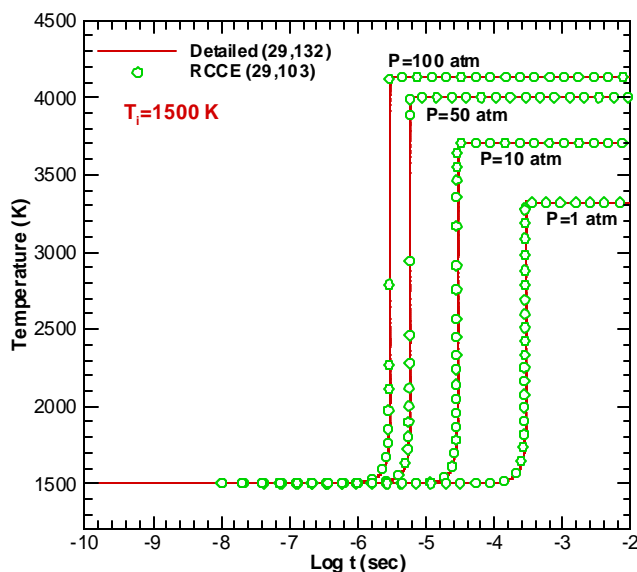


Fig.7 High-temperature results for a stoichiometric mixture at  $T_i=1500$ K and different initial pressures using the 10-constraint list, Table II.

## 5. Concluding Remarks

RCCE calculations of methanol oxidation over a wide range of initial temperatures and pressures have been made using 10 constraints and 132 reactions and good agreement with “detailed” calculations using 29 species and 132 has been obtained. In addition a reduced set of 12 reactions and 15 species has been identified which when employed in the RCCE calculations gives results identical to those obtained using the full 132 reactions.

Among the unique features that distinguish the RCCE method from all other methods available for kinetics studies are: 1) it enables one to obtain a good estimate of the kinetic behavior of a complex chemically reacting system using a relatively small number of known reactions thus avoiding the necessity of having to estimate the rates of a large number of uncertain fast reactions, 2) the entropy always increases as the system evolves and an approach to the correct final equilibrium is guaranteed, 3) an estimate of the concentrations of any species for which the standard Gibbs free energy is known can be obtained even though the species is not explicitly included in the reaction set used, 4) the accuracy of the results can be systematically improved by adding reactions one at a time, and finally 5) it is based on the well established Maximal Entropy Principle of thermodynamics rather than mathematical approximations.

## 6. Acknowledgments

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## 7. References

- [1] Mass, U., and Pope, S.B., *Combust. Flame* 88: 239 (1992)
- [2] Lam, S.H. and Goussis, D.A., *22<sup>nd</sup> Symposium (Int.) on Combustion*, the Combustion Institute, Pittsburgh, 1988, p. 931
- [3] Oluwayemisi O., *et.al, Combust. Flame*, 146, 1-2, 2006, p. 348-365
- [4] Keck, J.C., and Gillespie, D., *Combust. Flame*, 17: 237 (1971)
- [5] Law, R., Metghalchi, M. and Keck, J.C., *22<sup>nd</sup> Symposium (Int.) on Combustion*, The Combustion Institute, Pittsburgh, 1988, p. 1705
- [6] Bishnu, P., Hamiroune, D., Metghalchi, M., and Keck, J.C., *Combust. Theory Modeling*, 1, p. 295-312, (1997)
- [7] Hamiroune, D., Bishnu, P., Metghalchi, M. and Keck, J.C., *Combust. Theory Modeling*, 2:81 (1998)
- [8] Ugarte, S., Gao, Y., Metghalchi, H. *Int. J. Thermodynamics*, 3:21(2005)
- [9] Janbozorgi, M, Gao, Y., Metghalchi, H., Keck, J. C., *Proc. ASME (Int.)*, November 5-10, 2006, Chicago
- [10] Gupta, A. K. *ASME J. Engineering for Gas Turbine and Power*, Vol. 126, No. 1, January/February 2004, pp. 9-19.
- [11] Keck, J.C., *Prog. Energy Combust. Sci.*, 16:125 (1990)
- [12] Gao, Y., PhD Thesis, Northeastern University, Boston, 2003.
- [13] Ugarte, S., PhD Thesis, Northeastern University, Boston, 2005.
- [14] Goldthwaite, D., PhD Thesis, Northeastern University, Boston, to be completed by June 2007.
- [15] Tang, Q., Pope, S. B., *Combustion Theory and Modeling*, 8, 255—279 (2004).
- [16] Jones, W. P., Rigopoulos, S., *Proc. Comb. Inst.*, 30 (2005) p. 1325-1331
- [17] Hu, H., Keck, J. C., SAE 872110, 1998
- [18] Li, S. C., Williams, F. A., Gebert, K., SAE 2001-01-0957
- [19] Reynolds, W. C., STANJAN Program, Stanford University, ME270, HO#7
- [20] Petzold, L., *SIAM J., Sci. Stat. Comput.* 3:367 (1982)
- [21] [Http://www.me.berkeley.edu/gri-mech/version30/text30.html](http://www.me.berkeley.edu/gri-mech/version30/text30.html)
- [22] Tsang, W., Hampson, R. F., 1986, *J. Phys. Chem. Ref. Data*, Vol. 15 (3), p. 1087-1193
- [23] Tsang, W., Hampson, R. F., 1986, *J. Phys. Chem. Ref. Data*, Vol. 16 (3), p. 471-508