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CALCULATIONS OF FORMALDEHYDE-OXYGEN INDUCTION  
TIMES**

**By**

**Yue Gao, Hameed Metghalchi  
Department of Mechanical, Industrial and Manufacturing Engineering  
Northeastern University  
Boston, Massachusetts**

**And**

**James C. Keck  
Massachusetts Institute of Technology  
Cambridge, Massachusetts**

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# RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM CALCULATIONS OF FORMALDEHYDE-OXYGEN INDUCTION TIMES

Yue Gao, Hameed Metghalchi

Northeastern University, Boston, MA 02115

metghal@coe.neu.edu

and

James C. Keck

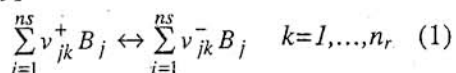
Massachusetts Institute of Technology, Cambridge, MA 02139

## Abstract

The Rate-Controlled Constrained-Equilibrium method (RCCE) is a powerful technique for simplifying the treatment of chemical reactions in complex systems. The method is based on the assumption that slow chemical reactions impose constraints on the allowed composition of such systems. Since the number of constraints can be very much smaller than the number of species, the number of rate equations to be integrated can be considerably reduced. In the present work,  $C_1$  chemistry with 33 species has been used to investigate stoichiometric formaldehyde-oxygen mixtures in a constant energy constant volume chamber. The state of the system was determined by three fixed elemental constraints: elemental carbon, elemental oxygen and elemental hydrogen and six variable constraints: total number of moles, moles of fuel, moles of active valence, moles of fuel radical, moles of O-O bond and moles of CO or moles of  $HO_2$  depending on initial pressure of the mixture. The nine rate equations of constraint potentials (LaGrange multiplier associated with the constraint) were integrated for a wide range of initial temperatures and pressures. The RCCE calculations were in acceptable agreement with detailed calculations and were faster than detailed calculations, which required integration of 33 species rate equations. The saving in CPU time ranged from 20% to 40% depending on initial conditions.

## Detailed treatment of chemical reactions

To describe the detailed evolution of a chemically reacting system, a complete reaction mechanism including all species present in the system is required. The changes in the chemical composition of a given system are the results of reactions of the type



where  $B_j$  is the symbol for species  $j$ ,  $n_r$  is the number of reactions,  $n_s$  is the number of species, and  $\nu_{jk}^+$  and  $\nu_{jk}^-$  are the forward and reverse stoichiometric coefficients of species  $j$  for reaction  $k$ . The corresponding rate equations have the form:

$$\dot{N}_j = V \sum_{k=1}^{n_r} \nu_{jk} r_k \quad j=1, \dots, n_s \quad (2)$$

where  $N_j$  is the number of moles of species  $j$ ,  $V$  is the volume of the system,  $\nu_{jk} = \nu_{jk}^+ - \nu_{jk}^-$  is the net change in moles of species  $j$  due to reaction  $k$ ,  $r_k = r_k^+ - r_k^-$  is the net reaction rate per unit volume, and

$r_k^+$  and  $r_k^-$  are the forward and reverse reaction rates.

In general, the assumption is also made that the system is an ideal gas obeying the equation of state

$$pV = \sum_{j=1}^{n_s} N_j RT \quad (3)$$

where  $p$  is the mixture pressure.

For given initial conditions the above set of equations (2) can be integrated numerically to obtain the species composition as a function of time. The pressure is determined using equation (3).

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 integration of the rate equations is an extremely time consuming and difficult task. In addition, accurate rate constants are known for only a very small fraction of the possible reactions

## Rate equations for Constraint Potentials

An alternative approach proposed originally by Keck [1,2] and later developed by Keck and co-workers [3] is the rate-controlled

constrained-equilibrium (RCCE) method, which is based on the maximum-entropy principle of thermodynamics. In this method it is assumed that slow reactions in a complex reacting system impose constraints on its composition, which retard its relaxation to complete equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to complete equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. The constrained-equilibrium composition is found by maximizing the entropy or minimizing the Gibbs free energy of the mixture subject to a set of constraints using the method of LaGrange multipliers. Previous research has been done for  $H_2/O_2$  system, 8 species and 19 reactions were considered[3-5]. In present work, RCCE was applied to  $C_1$  chemistry with 33 species and 88 reactions. The constraints imposed on the system by the reactions have been assumed to be a linear combination of the mole numbers of the species present in a system. They can be written in the form :

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j \quad i=1, \dots, n_c \quad (4)$$

where  $a_{ij}$  is the value of the constraint  $i$  for the species  $j$  and  $n_c$  is the number of constraints. For each constraint there is a corresponding LaGrange multiplier (constraint potential). The species composition is then determined as a function of the multipliers by

$$N_j = Q_j \exp\left(-\sum_{i=1}^{n_c} a_{ij} \gamma_i\right) \quad j=1, \dots, n_s \quad (5)$$

where  $Q_j = \frac{P_0 V}{RT} \exp(-\mu_j^0)$  is the partition function for species  $j$ ,  $\mu_j^0 = F_j^0 / RT$  is the dimensionless standard Gibbs free energy and  $\gamma_i$  is the LaGrange multiplier (constraint potential) conjugate to  $i$ th constraint. The system is described by  $n_c$  constraint potentials instead of  $n_s$  species. Thus the order of the system is reduced by  $n_s - n_c$  which results in a reduction in the number of

rate equations to be integrated. Once the constraint potentials  $\gamma_i$  have been determined the constrained composition can easily be calculated using Equation (5).

Differentiating Equation (5) with respect to time leads to the rate equations for species composition

$$\frac{\dot{N}_j}{N_j} = \frac{\dot{V}}{V} + N_j \frac{e_j}{RT} \frac{\dot{T}}{T} + N_j \sum_{i=1}^{n_c} a_{ij} \dot{\gamma}_i \quad j=1, \dots, n_s \quad (6)$$

where  $e_j$  is the specific energy of species  $j$ .

In the case where the independent thermodynamic variables are  $T$  and  $V$ , the rate equations for the constraint potentials can be easily found by combining Equations (3) and (6)

$$\sum_{n=1}^{n_c} C_{in} \dot{\gamma}_n - C_{iT} T - C_{iV} \frac{\dot{V}}{V} + \sum_{k=1}^{n_c} b_{ik} r_k = 0 \quad (7)$$

$$i=1, \dots, n_c$$

where

$$C_{in} = \sum_{j=1}^{n_s} a_{ij} a_{nj} [N_j]$$

$$C_{iT} = \sum_{j=1}^{n_s} \left( a_{ij} \frac{e_j}{RT} [N_j] \right)$$

Equation (7) gives the rate equations for constraint potentials of a chemical system subject to  $n_c$  number of constraints. These rate equations can easily be integrated with respect to time to obtain the constraint potentials which can then be used in Equation (5) to get species composition as function of time.

The number of unknowns is reduced from the full set  $n_s$  by  $(n_s - n_c)$ . In addition, the rate constant for those reactions which do not change any of the constraints are not needed. In  $C_1$  chemistry, 20 reactions which don't change any of the constraints can be eliminated.

### The Constraints

The most obvious constraints are those imposed by conservation of the elements. Among the most important time dependent additional constraints which should be considered are those imposed by: (1) dissociation or recombination reactions which control the total moles (2) branching

reactions which control the free valence in the system, (3) O-O bond breaking reactions (4) CO oxidation reactions at low pressure or peroxide reactions at high pressure (5) reactions which destroy fuel molecules or generate fuel radicals.

### Results and Discussion

Illustrative calculations were carried out for premixed stoichiometric formaldehyde-oxygen mixture in a constant volume and constant energy chamber for a range of initial pressures between 1 atm to 100 atm and a range of temperatures between 900K and 1500K. In the model 33 species and 88 reactions were included and the corresponding rate equations were integrated using DASSL [6] to obtain exact solutions for comparison with RCCE calculations.

The following figures are for cases of initial conditions of  $T_i = 1500$  K,  $P_i = 1$  atm and  $T_i = 900$  K,  $P_i = 100$  atm: The solid curves represent RCCE calculations where the dotted curves represent detailed calculation. Figure 1 shows the temperature profile for two cases versus time. Figure 2 shows the constraints themselves while figure 3 show the mole fractions of some major products, radicals and intermediates as functions of time and they are all compared with the detailed calculation for the low pressure case. Figure 4 and 5 show the same information for the high pressure case. It can be seen that the calculated results using two different methods are very close to each other. Both programs were run on Sun workstation Sparc 10 machine. CPU time for RCCE calculation for these two cases are 70% and 61% of the detailed kinetics calculation. It is clear that as number of species increase to a few hundreds while the constraint number may increase to more than 10, the total saving time using RCCE method will be great and may be the only possible method for these calculations.

### Summary

Rate equations for the constraint potentials associated with the Rate-Controlled Constrained-Equilibrium (RCCE) method have been developed and

successfully integrated for induction times for a stoichiometric mixture of  $H_2CO/O_2$  system at different initial temperatures and pressures. RCCE calculation using variable constraints on the total moles, fuel, active valence, OO bond,  $HO_2$  or CO and fuel radical in addition to the three elemental constraints was in good agreement with detailed calculations. For this system including 33 species, there was a gain of 20~30 % in the high temperature cases and a gain of 25~40 % in the low temperature cases in running time.

### References

1. Keck and Gillespie, *Combustion and Flame*, Vol.17,1971,pp.237
2. Keck, Rate controlled constrained – equilibrium theory of chemical reactions in complex systems *Prog. Energy Combust. Sci.* Vol.16, 1990, pp.125-154
3. Law, Metghalchi, Keck in 22<sup>nd</sup> Int. Symp. Combust., The Combustion Institute, 1987, PP.1705-1713
4. Bishnu, Hamiroune, Metghalchi and Keck "Constrained Equilibrium calculations for chemical systems subject to generalized linear constraints using the NASA<sup>1</sup> and STANJAN equilibrium programs", *Combust. Theory Modeling* Vol. 1, 1997, 295-312
5. Hamiroune, Bishnu, Metghalchi and Keck "Rate-Controlled Constrained-Equilibrium method using constraints potentials", *Combust. Theory Modeling* Vol. 2, 1998, 81-94
6. Petzold, *SIAM J., Sci. Stat. Comput.* Vol.3 ,1982, pp.367

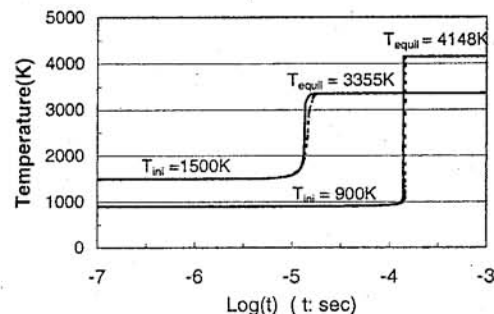


Fig.1 Temperature Comparison

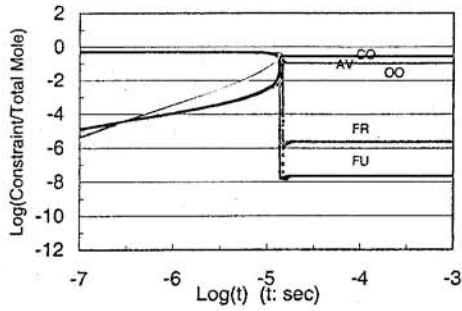


Fig.2 Constraints Comparison for  $T_1=1500K$ ,  $P_1=1$  atm

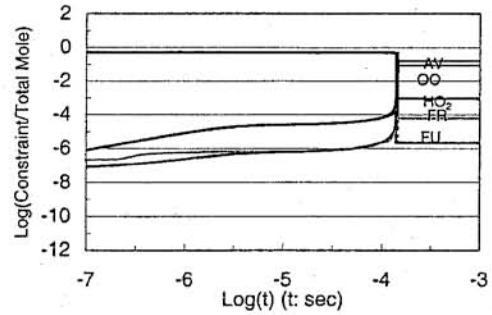


Fig.4 Constraints Comparison for  $T_1=900K$ ,  $P_1=100$  atm

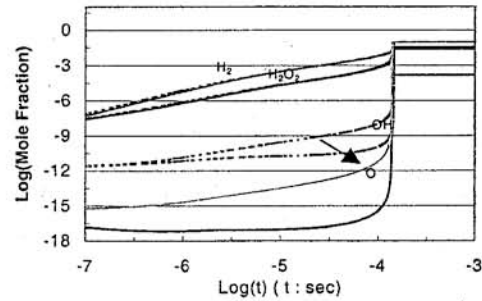
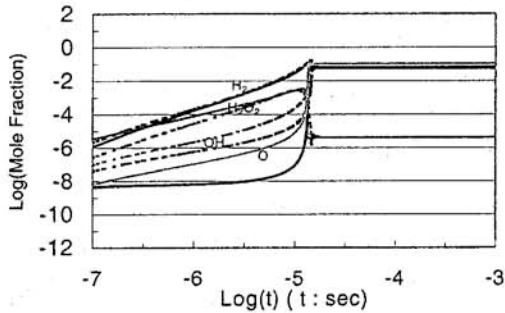
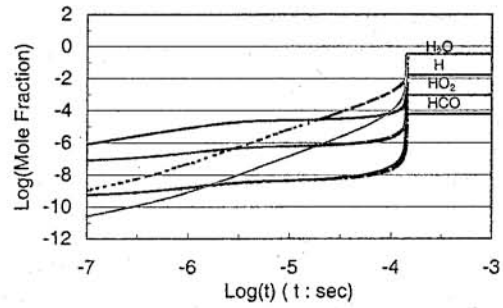
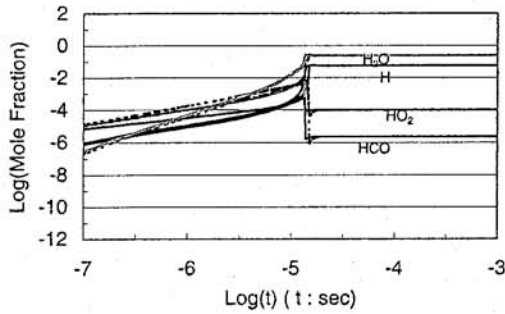
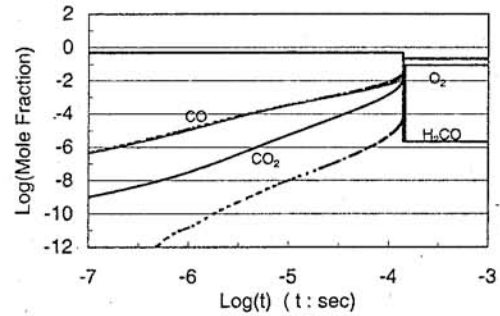
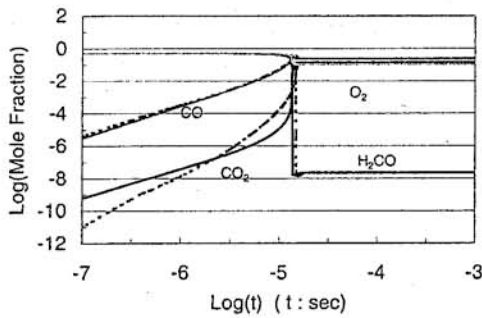


Fig.3 species mole fraction for  $T_1=1500K$ ,  $P_1=1$  atm

Fig.5 Species mole fraction for  $T_1=900K$ ,  $P_1=100$  atm