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Calculations of Formaldehyde Oxidation**

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Rate-Controlled Constrained-Equilibrium (RCCE) Calculations of Formaldehyde Oxidation

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Abstract

The Rate-Controlled Constrained-Equilibrium method (RCCE) has been used to calculate the rate of formaldehyde oxidation. In this method, constraints rather than species are used to determine the composition of the system. 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, C₁ chemistry with 29 species and 126 reactions has been used to investigate the oxidation of stoichiometric formaldehyde and oxygen mixtures 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 CO₂, moles of OH, moles of O and moles of H₂O were used. The four to twelve rate equations for the constraint potentials (LaGrange multiplier conjugate to the constraint) 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 excellent agreement with detailed calculations. For this case, ignition delay times and major species concentrations were within 1 to 2% 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 didn't alter the ignition delay times. It was also found that the number of reactions could be reduced from 126 to 11 without affecting the accuracy of the RCCE calculations. The resulting CPU time savings for various numbers of constraints were 45~48%, 35~39%, 25~27%, 16~18%, 9~10% for 8, 9, 10, 11, 12 constraints respectively. In addition, the RCCE calculations significantly reduced the time required for input and output of data and gave valuable insight into the important reaction paths and rate-limiting reactions involved in formaldehyde oxidation.

Introduction:

The development of models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. It is also of great importance for a variety of practical problems related to combustion, hypersonic aerodynamics, chemical processing and biology. 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, except for the hydrogen/oxygen system, they contain only a small fraction of the species and reactions possible. 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.

In this work, we investigate the Rate-Controlled Constrained-Equilibrium (RCCE) method, originally proposed by Keck and Gillespie [1] and later developed by Keck and co-workers [2-4]. 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.

In previous studies, the RCCE method has been applied to stoichiometric H₂/Air mixtures containing 9 species and 19 reactions at constant energy and volume.

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Satisfactory agreement with detailed calculations was obtained over a wide range of initial pressures and temperatures using 5 constraints [3]. In this paper, the method is applied to the more complex formaldehyde/oxygen system involving C_1 chemistry with 29 species and 126 reactions. The rate equations for the constraint potentials conjugate to 4-12 constraints were integrated and the results are compared with detailed calculation.

Rate-Equations for Constraints

In the present work, as well as most previous applications of RCCE method [4], 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

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

where a_{ij} is the value of the constraint i for the species j and nc is the number of constraints. Differentiating Eq. (1) gives the rate-equation for the constraints

$$\dot{C}_i = \sum_{j=1}^{ns} a_{ij} \dot{N}_j = \sum_{k=1}^{nb} b_{ik} r_k \quad (2)$$

where

$$b_{ik} = \sum_{j=1}^{ns} a_{ij} \nu_{jk} \quad (3)$$

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

$$N_j(t) = N_j(V(t), T(t), C_1, \dots, C_{ne}, C_{ne+1}(t), \dots, C_{nc}(t)) \quad (4)$$

must be evaluated using a generalized equilibrium code such as GNASA[4,5] or GSTANJAN[4,6]. 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 minimizing the free energy subject to a set of constraints using the method of LaGrange multipliers is

$$N_j = (V/RT) \exp(-\mu_j^0 - \sum_{i=1}^{nc} a_{ij} \gamma_i) \quad j=1, \dots, ns \quad (5)$$

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 Eq. (5) with respect to time, and substituting the result into Eq.(2) leads to the implicit rate-equation for the constraint-potentials

$$\sum_{n=1}^{nc} C_{in} \dot{\gamma}_n + C_{iV} (\dot{V}/V) + C_{iT} (\dot{T}/T) = \dot{C}_i / V = \sum_{k=1}^{nb} b_{ik} r_k / V \quad i=1, \dots, nc \quad (6)$$

where

$$C_{in} = -\sum_{j=1}^{ns} a_{ij} a_{nj} (N_j / V) \quad (7a)$$

$$C_{iV} = \sum_{j=1}^{ns} a_{ij} (N_j / V) \quad (7b)$$

$$C_{iT} = \sum_{j=1}^{ns} a_{ij} \frac{e_j}{RT} (N_j / V) \quad (7c)$$

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

$$E = \sum_{j=1}^{ns} e_j N_j \quad (8)$$

is used to replace T , differentiating Eq. (8) provides the equation

$$\sum_{n=1}^{nc} C_{En} \dot{\gamma}_n + C_{EV} (\dot{V}/V) + C_{ET} (\dot{T}/T) = \dot{E} / V \quad (9)$$

where

$$C_{En} = -\sum_{j=1}^{ns} e_j a_{nj} (N_j / V) \quad (10a)$$

$$C_{EV} = \sum_{j=1}^{ns} e_j (N_j / V) \quad (10b)$$

$$C_{ET} = \sum_{j=1}^{ns} (c_{vj} T + e_j^2 / RT) (N_j / V) \quad (10c)$$

and $C_{vj} = \partial e_j / \partial T$ is the constant volume specific heat for species j .

Given initial values for γ_i , the rate-equations (6) and (9) can be integrated with respect to time to obtain the constraint-potentials which can then be used in Eq. (5) to get the composition as function of time. The number of unknowns is reduced from the "detailed" set ns to nc . In addition, the rate-constants for those reactions which do not change any 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 and recombination reactions which determine the total number of particles,
- (3) branching reactions which control the total free valence of the radicals,
- (4) O-O bond breaking reactions which control the "fixed oxygen", and
- (5) reactions that change fuel radical.

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 [6] to calculate the chemical equilibrium composition of a system.

Results and Discussion

RCCE calculations of the oxidation of stoichiometric $\text{H}_2\text{CO} + \text{O}_2$ mixtures in a constant volume and constant energy combustion chamber in both high and low temperature regimes have been carried out using 4 to 12 constraints. For comparison, corresponding calculations were also made using a "detailed" model with 29 species and 126 reactions which includes all C_1 reactions in GRI-Mech 3.0 along with some additional reactions.

The matrix for the 12 constraints used in the RCCE calculations in the order that they were introduced is shown in Table 1. Temperature vs. time plots for RCCE calculations with for 7 to 12 constraints are compared with "detailed" calculations in Figures 1. Typical results for the high temperature-low pressure regime, $T_i=1500\text{K}$, $P_i=1\text{atm}$, and low temperature-high pressure regime, $T_i=900\text{K}$, $P_i=100\text{atm}$, are shown in the upper and lower plots. The solid curves represent RCCE calculations and the dotted curves represent detailed calculations. It can be seen that the equilibrium values for the RCCE and "detailed" calculations agree perfectly and the ignition delay times agree within 5 percent for 8 -12 constraints calculations. The induction time is defined as the time for a 10% rise in temperature. Eight was the minimum number of constraints required to give reasonable agreement between induction times at both high and low temperatures. Using up to 12 constraints improved the accuracy of the minor species mole fractions at early times, but didn't affect the ignition delay times.

The fractional difference between the induction times for the RCCE and "detailed" calculations is shown in Figures 2 for 7 to 12 constraints. It can be seen that the results for 8 constraints are in excellent agreement with detail calculations and that no significant improvement was obtained by adding more constraints. Results for fewer than 7 constraints gave significantly larger errors and are not shown. Detailed results for 8 constraints are presented below.

Figures 3. compare the constraint potentials as functions of time for RCCE calculations using the full set of 126 reactions in the GRI-Mech 3.0 model and a reduced set of 11 reactions listed in Table 2. It can be seen that RCCE calculations using the reduced set of 11 reactions gave results indistinguishable from those using 126 reactions.

Values for the variable constraints as a function of time obtained from RCCE calculations using both 126 and 11 reaction sets are compared with "detailed" calculations in Figures 4. As can be seen the agreement is excellent for all constraints.

Species mole fractions as a function time for the various cases studied are shown in Figures 5 for H_2CO , O_2 , CO , and CO_2 and the agreement between RCCE and "detailed" is seen to be excellent except for CO_2 at early times where it is a minor species. Figures 6 shows similar results for HO_2 , HCO , H_2O and H . Here the agreement is excellent except for H_2O and H at early times where they are minor species. The results are similar for all other minor species at early times but all species go to the correct equilibrium values.

Both RCCE and "detailed" calculations were done on a Sun workstation Sparc 10 machine. The CPU times required for the calculations are shown in Figures 7 as a function of the number of constraints. Also shown are the results for the 29 species "detailed" calculations. As anticipated the CPU time increases with the number of differential equations to be solved. Although the CPU time saved by the RCCE method is modest in this case, it is expected to improve considerably 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. Finally, the RCCE method gives valuable insight into the important reaction paths and rate-limiting reactions involved in the evolution of complex chemical systems. The fact that "detailed" calculations of formaldehyde oxidation involving 29 species and 126 reactions can be reproduced by RCCE calculations using only 8 constraints and 11 rate-limiting reactions certainly provides considerable "food for thought".

References

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5. Gordon, S. and McBride, B.J., *Computer Program for Calculating of Complex Chemical Equilibrium Compositions and Applications: Analysis*, NASA reference publication, 1311, 1994

Table 1. A_{ij} matrix

No.	Constraint Name	Symbol	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
			H2CO	O2	CO2	O	HCO	H2O	HO2	H2	CO	H	HO	HOCO	OOCHO	H2O2	OCHO	HOCHO	CH3OH	CH3OOH	CH4	CH3	CH3O	CH2OH	CH2	CH2OOH	CH3OO	HOOCO	CH	C	
1	Elemental Hydrogen	EH	2	0	0	0	1	2	1	2	0	1	1	1	1	2	1	2	4	4	4	3	3	3	2	3	3	1	1	0	
2	Elemental Oxygen	EO	1	2	2	1	1	1	2	0	1	0	1	2	3	2	2	3	2	1	2	0	0	1	1	0	2	2	3	0	0
3	Elemental Carbon	EC	1	0	1	0	1	0	0	0	1	0	0	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
4	Fuel	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	
5	Total Moles	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	
6	Free Oxygen	FO	1	0	2	1	1	1	0	0	1	0	1	2	1	0	2	1	2	1	0	0	0	1	1	0	0	0	1	0	0
7	Free Valence	FV	0	0	0	2	1	0	1	0	0	1	1	1	1	0	1	0	0	0	0	0	1	1	1	2	1	1	3	4	
8	Fuel Radical	FR	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
9	Species CO2	CO2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
10	Species OH	OH	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	
11	Species O	O	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
12	Species H2O	H2O	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	

Table 2. B_{jk} matrix for reduced 11 reactions

						ΔEH	ΔEO	ΔEC	ΔFU	ΔM	ΔFO	ΔFV	ΔFR	$\Delta CO2$	ΔOH	ΔO	$\Delta H2O$
H2CO	H	=	HCO	H2	0	0	0	-1	0	0	0	1	0	0	0	0	0
H2CO	HO2	=	HCO	H2O2	0	0	0	-1	0	0	0	1	0	0	0	0	0
H2CO	O2	=	HO2	HCO	0	0	0	-1	0	0	2	1	0	0	0	0	0
O2	CH2OH	=	HO2	H2CO	0	0	0	1	0	0	0	0	0	0	0	0	0
H	O2	M	=	HO2	M	0	0	0	0	-1	0	0	0	0	0	0	0
OH	H	M	=	H2O	M	0	0	0	0	-1	0	-2	0	0	-1	0	1
CO	H	M	=	HCO	M	0	0	0	0	-1	0	0	1	0	0	0	0
OH	O	=	O2	H	0	0	0	0	0	0	-2	-2	0	0	-1	-1	0
CO	HO2	=	OH	CO2	0	0	0	0	0	0	2	0	0	1	1	0	0
HO2	HO2	=	O2	H2O2	0	0	0	0	0	0	0	-2	0	0	0	0	0
O2	HCO	=	HO2	CO	0	0	0	0	0	0	0	0	-1	0	0	0	0

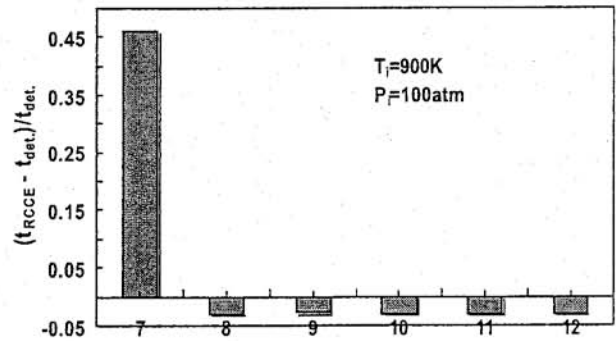
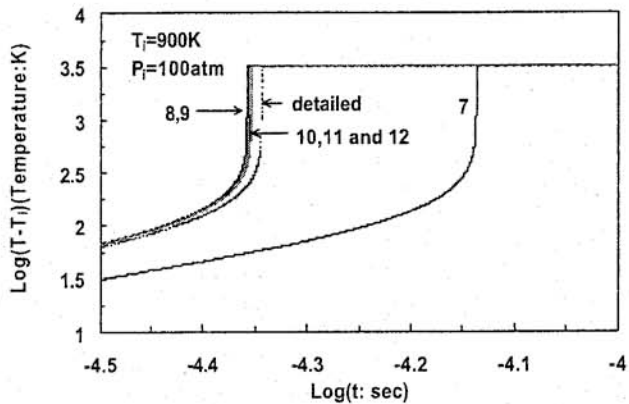
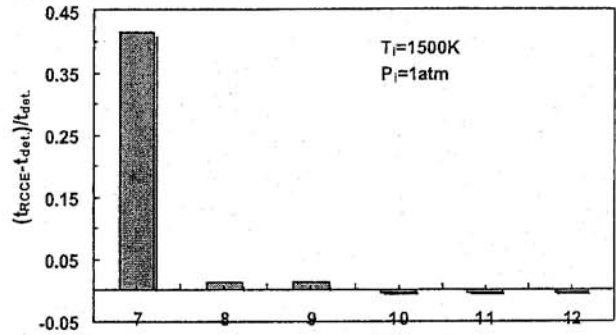
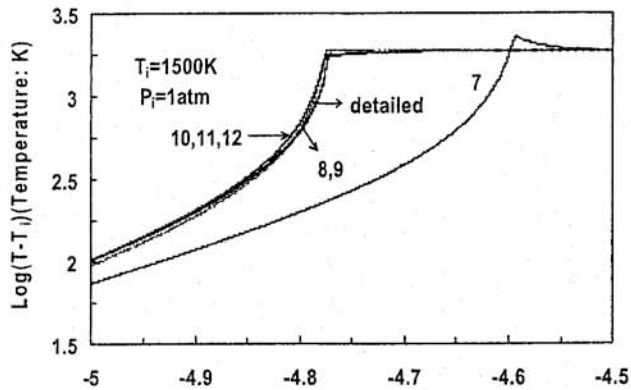


Fig.1 Temperature Comparison

Fig.2 Ignition Delay Time Comparison

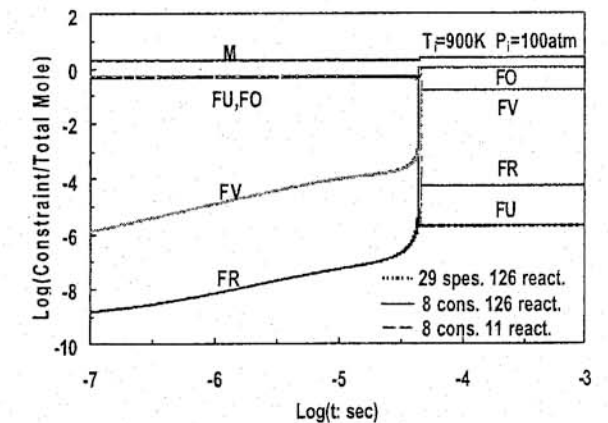
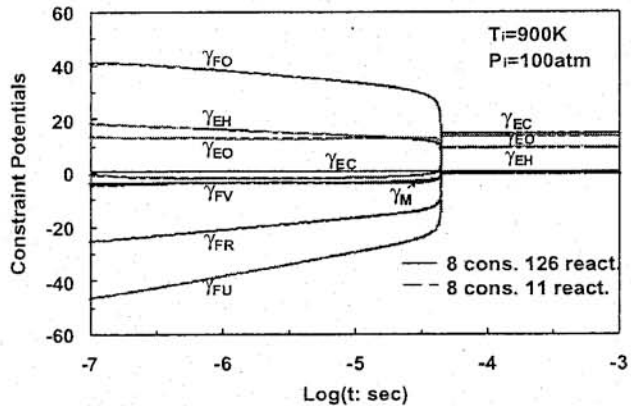
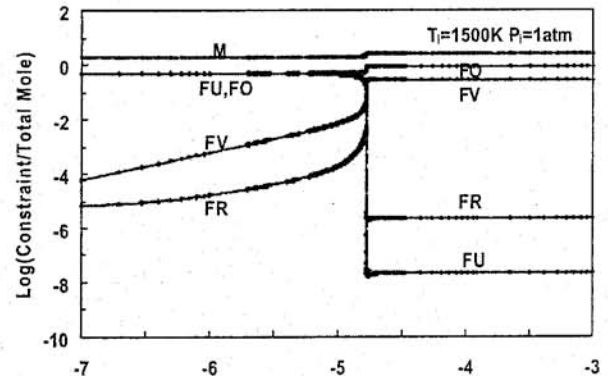
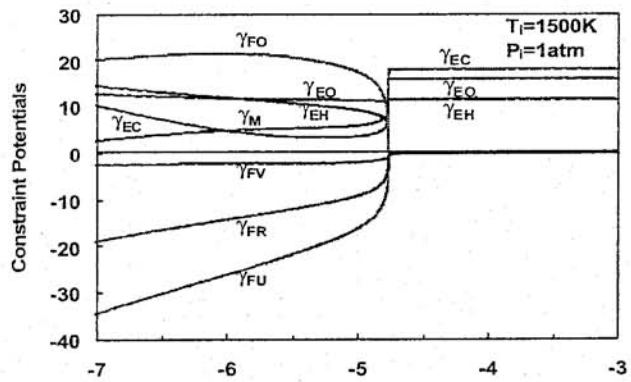


Fig.3 Constraint Potentials Comparison

Fig.4 Variable Constraints Comparison

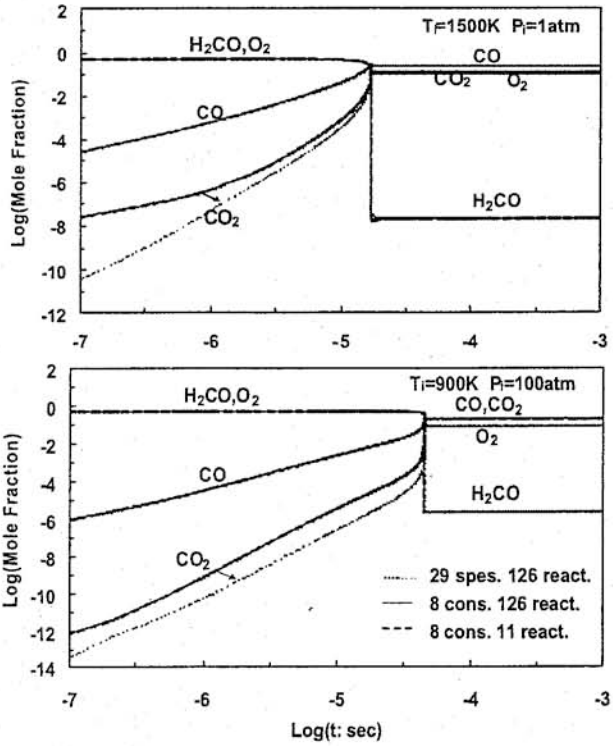


Fig.5 Species Mole Fractions Comparison

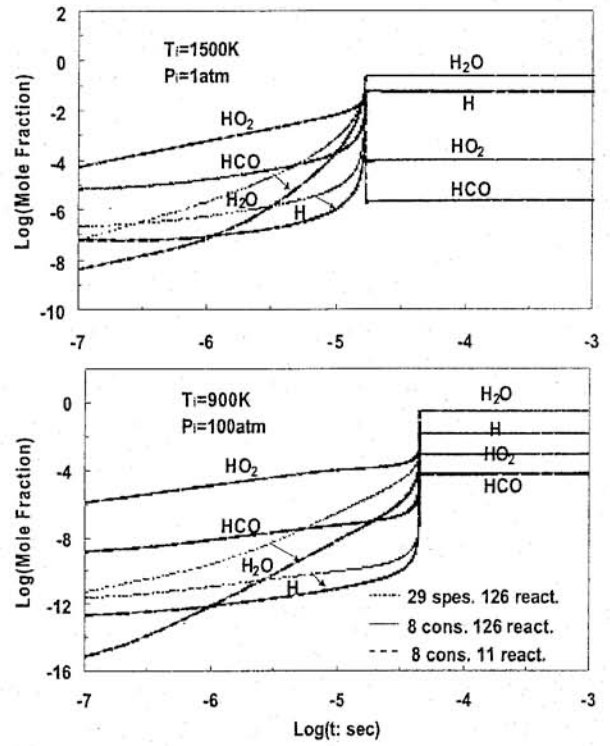


Fig.6 Species Mole Fractions Comparison

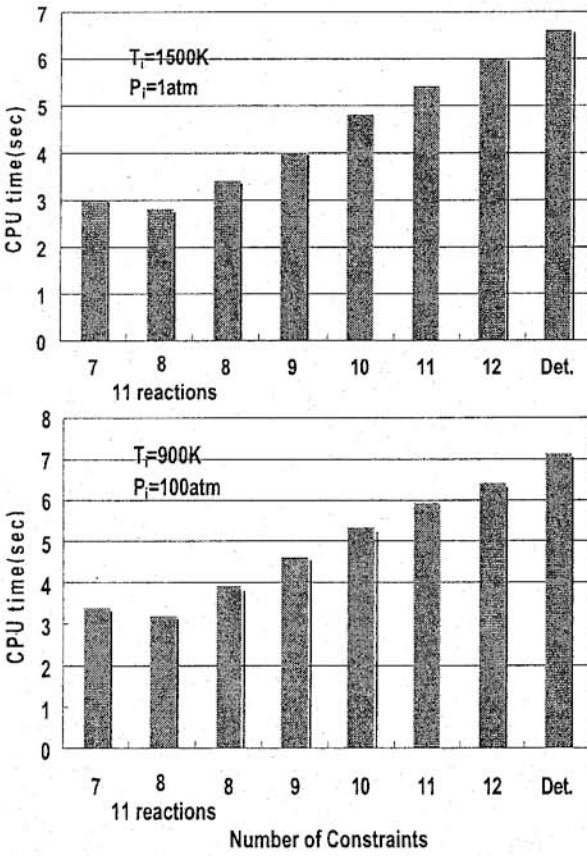


Fig.7 CPU Time Comparison