

**RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM USING  
CONSTRAINT POTENTIALS APPLIED TO HYDROGEN-OXYGEN SYSTEM**

*Proc ASME - AES* Hamiroune, D., Bishnu, P., Metghalchi, M.  
Mech. Eng. Dept.  
Northeastern University, Boston

*Vol 33 1993*

**Keck, J. C.**  
Mech. Eng. Dept.  
M. I. T., Cambridge

**INTRODUCTION**

The development of models to describe the time evolution of complex reacting systems is a fundamental objective of non-equilibrium thermodynamics. The differential rate equations describing the behavior of such systems can be obtained from the laws of thermodynamics and quantum mechanics, but for complicated systems containing many species and a corresponding number of rate equations, their integration is difficult. The alternative is to model such systems by reducing the number of species included and a number of methods for doing this have been proposed. This method is based on the assumption 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. As a consequence the system relaxes to complete equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. The constrained composition can be determined by maximizing the entropy or minimizing the appropriate free energy subject to the constraints. The time dependence of the composition can then be calculated by integrating the rate equations for the constraints. The theoretical foundations of the method are described by Keck [1]. In an attempt to solve both problems, Keck and Gillespie [2] proposed an approach based on the second law of thermodynamics called RCCE. In this method, it is assumed that slow reactions impose slowly changing constraints on the allowed composition of a complex system. The most important advantage of RCCE over all other methods of simplifying chemical kinetics is that it is unnecessary to start with a "complete" reaction model which must then be simplified by various mathematical approximations. Instead, one starts with a small number of constraints to which one can add more constraints, if necessary, to improve the accuracy of the calculations. However, as with all thermodynamic systems, the number of constraints necessary to describe state of the system within measurable accuracy is expected to be very much smaller than the number of species in the system. In past applications of the method, the equations for the constraints have been integrated and an equilibrium program has been used to determine the composition at each step. Because of the time required for the constrained equilibrium calculations, this technique is relatively inefficient. To eliminate these intermediate constrained-equilibrium calculations, Keck [1] has proposed an alternative approach based on the integration of the rate equations of the constraint potentials (Lagrange multipliers) conjugate to the constraints rather than the rate equations for the constraints themselves. Hamiroune et Al. [3] have tested the method on hydrogen/oxygen system.

The purpose of this paper is to develop this method in greater detail and to compare it with a complete model for the case of hydrogen oxidation. The real advantage of the method lies in its potential application to very large systems such as the C/H/O systems where the number of possible chemical species and reactions is essentially infinite.

**RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM**

The constraints imposed on the composition of the system are assumed to be of the form:

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

Where  $N_j$  is the number of moles of species  $j$ ,  $a_{ij}$  is the value of constraint  $i$  for species  $j$ ,  $ns$  is the number of species included and  $nc$  is the number of constrained imposed on the system.

**Rate equations for constraints**

The rate equation for the constraints can be determined by differentiating equation (1) and eliminating  $\dot{N}_j$  using the rate equations for the species.

$$\dot{C}_i = \sum_j^{ns} a_{ij} \dot{N}_j = V \sum_k^{nr} b_{jk} r_k, \quad (2)$$

where  $b_{ik} = \sum_j^{ns} a_{ij} \nu_{jk}$  is the change in constraint  $i$  due to reaction  $k$ ,  $\nu_{jk}$  is the difference between the reverse and forward stoichiometric constants for species  $j$  in reaction  $k$ ,  $r_k$  is the net rate of reaction  $k$ , and  $nr$  is the number of reactions for which  $b_{ik} \neq 0$ . The constrained composition can be easily determined in terms of the constraint potentials by maximizing the entropy:

$$N_j = Q_j \exp\left(-\sum_i^{nc} a_{ij} \gamma_i\right), \quad j=1, \dots, ns \quad (3a)$$

Where  $\gamma_i$  is the dimensionless constraint potential (Lagrange multiplier) conjugate to the constraint  $C_i$ ,  $Q_j = \frac{p_o V}{RT} \exp(-\mu_j^o)$  is the partition function for the species  $j$  and  $\mu_j^o = \frac{F_j^o}{RT}$  is the dimensionless standard Gibbs free energy for species  $j$ . It can be seen that a problem arises in equation (3a) if any of the species is zero this implies that one of the  $\gamma_i$  is infinite. The problem can be eliminated by substitution  $\Gamma_i = \exp(-\gamma_i)$ , so that equation (3a) becomes:

$$N_j = Q_j \prod_i^{nc} \Gamma_i^{a_{ij}} \quad j=1, \dots, ns \quad (3b)$$

### Rate equations for Constraint Potentials

In the case where the independent thermodynamic variables are  $T$  and  $V$ , the rate equations for the constraints potentials can be easily found by substituting equation (3b) in equation (1) and differentiating:

$$\sum_n^{nc} C_{in} \dot{\Gamma}_n + C_{iT} \frac{\dot{T}}{T} + C_{iV} \frac{\dot{V}}{V} - \sum_j^{nr} b_{ij} r_k = 0, \quad n=1, \dots, nc \quad (4)$$

Where  $C_{iV} = \sum_j^{ns} a_{ij} N_j$ ,  $C_{iT} = \sum_j^{ns} a_{ij} \frac{E_j(T)}{RT} N_j$  and  $C_{in} = \sum_j^{ns} a_{ij} d_{nj} Q_j$  ( $i=1, \dots, nc$ )

in which  $d_{nj} = 0$  for  $a_{nj} = 0$  and  $d_{nj} = a_{nj} \prod_k^{nc} \Gamma_k^{a_{kj} - \delta_{kn}}$  for  $a_{nj} \neq 0$ .

If  $E$  and  $V$  are the independent variables, an additional equation for  $T$  can be obtained by substituting equation (3b) in the expression

$$E = \sum_j^{ns} N_j E_j \quad (5)$$

and differentiating with respect to time. This gives:

$$\sum_n^{nc} C_{En} \dot{\Gamma}_n + C_{ET} \frac{\dot{T}}{T} + C_{EV} \frac{\dot{V}}{V} - \dot{E} = 0 \quad (6)$$

Where  $C_{EV} = \sum_j^{ns} E_j(T) N_j$ ,  $C_{ET} = \sum_j^{ns} \left(c_{vj}(T)T + \frac{E_j^2(T)}{RT}\right) N_j$  and  $C_{En} = \sum_j^{ns} E_j(T) d_{nj} Q_j$

In equations (4) and (6), the unknowns are the modified constraints potentials themselves; the number of unknowns is reduced from the full set calculations by  $(ns-nc)$ .

### PRACTICAL APPLICATIONS

The first step in the practical application of the RCCE method involves determining the time dependent constraints. The most obvious constraints are those imposed by the conservation of elements. These are time independent and must be included in all kinetic calculations. Among the most important time dependent constraints are those imposed by slow dissociation/recombination reactions which determine the total moles of gas and slow branching reactions which determine total moles of radicals. In addition there are at least two rules which must be carefully observed in choosing constraints: 1) The method of Lagrange multipliers requires they be linearly independent and 2) they must be capable of holding the system in the specified initial state within measurable accuracy. The final set of differential equations to be integrated is nonlinear system of first order differential equations in the following form:

$$[C_m(\Gamma)]\dot{\Gamma}_n + [F_i(\Gamma, t)] = 0 \quad (7)$$

where  $[C_m(\Gamma)]$  is a square matrix whose elements are the  $C_m$  in equation (4) and  $[F_i(\Gamma, t)]$  is a column vector representing the remaining terms in equation (4).

### The initial value problem

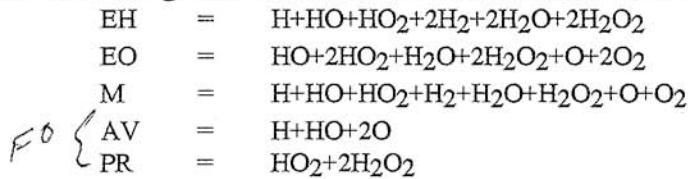
Equation (7) can be integrated using DASSL [4] or LSODI [5]. This requires an inversion of the matrix  $[C_m(\Gamma)]$  which must be non singular. Inspection of the equations for the  $C_m$  shows that if the value of one of  $\Gamma$ 's is zero, then the matrix will be singular unless the constraints matrix  $[a_{ij}]$  is carefully chosen. A sufficient condition for the  $[C_m]$  matrix to be non singular is that the  $[a_{ij}]$  matrix can be partitioned as shown below

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ 0 & I & A_{23} \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} \quad (8)$$

where  $[C_2]$  is a column matrix containing the constraints which can have a zero value,  $[I]$  is a unit matrix of the same order as  $[C_2]$  and  $[A_{23}]$  is a matrix whose elements must be zero or a positive integer. The remaining elements may have any values subject only to the condition that both the  $C_i$  and the  $N_j$  are positive definite. If the original constraints matrix does not have the form (8), it must be possible to transform it to that form by linear combinations of different rows.

### H<sub>2</sub>/O<sub>2</sub> system

Premixed Hydrogen-oxygen mixtures in an adiabatic constant volume chamber have been studied using Rate-Controlled Constrained Equilibrium (RCCE). A full set of rate equations with 18 reactions and 8 species were integrated to obtain exact solutions for comparison with RCCE calculations. The species included are O, H, O<sub>2</sub>, H<sub>2</sub>, HO, H<sub>2</sub>O, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. The calculations were carried out for a range of pressures between 0.01 ATM to 100 ATM and a range of temperatures between 900 K and 1500 K using DASSL. The constraints used in the RCCE calculations were:



They can be represented in matrix as shown in table 1. By adding and subtracting rows this matrix can be transformed into the form (8) as shown in table 2.

Table 1

	O <sub>2</sub>	*H <sub>2</sub>	H <sub>2</sub> O	H	HO <sub>2</sub>	HO	O	H <sub>2</sub> O <sub>2</sub>
EO	2	0	1	0	2	1	1	2
EH	0	2	2	1	1	1	0	2
M	1	1	1	1	1	1	1	1
AV	0	0	0	1	0	1	2	0
PR	0	0	0	0	1	0	0	2

Table 2

	N1		N2		N3			
	O <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	H	HO <sub>2</sub>	HO	O	H <sub>2</sub> O <sub>2</sub>
EO	2	0	1	0	2	1	1	2
EH	0	2	2	1	1	1	0	2
EH+EO+AV-PR-2M	0	0	1	0	0	1	1	0
AV	0	0	0	1	0	1	2	0
PR = EO + EH + AV - 2M	0	0	0	0	1	0	0	2

Using this transformed matrix the set of equation (4) and (6) were integrated using DASSL[4] for the case of constant E and V.

Figure 1 and 2 shows a plot of temperature as a function of time for both case ( 1500K&1ATM and 900K&100ATM). The solid curves represent the detail calculations, the dotted curves are 5 constraints EO+EH+M+AV+PR calculations. Figure 3 and 4 shows the entropy as a function of time for those cases

### CONCLUSION

The rate equation required to carry out RCCE calculations using the constraints potentials have been developed and successfully integrated for a stoichiometric mixture of H<sub>2</sub> and O<sub>2</sub> over a range of temperatures and pressures. The calculation using 5 constraints were in reasonable agreement with detailed calculations. For this simple running times were comparable but as the size of the system increases-it is anticipated that the RCCE will be faster. Work on implementing such calculations for the C/H/O systems is in progress.

## REFERENCES

1. Keck, J. C., "Rate Controlled Constrained-Equilibrium theory of chemical reactions in complex systems", Prog. Energy Combust. Sci., (1990), Vol. 16, pp. 125-154.
2. Keck, J. C. and Gillette, D. combust. Flame, 17, 237 (1971).
3. Hamiroune, D., Meghalchi, H. and Keck, J. C., AES-Vol 30/HTD-Vol 266, ASME 1993, pp 103-114.
4. Petzold, L., SIAM j. Sci. Stat. Compt. 3, 367 (1982)
5. Hindmarsh, A. C. and Byrne, G. D., "EPISODE" Report No. UCID-30112, Rev. 1, Lawrence Livermore Laboratory, California (1977).

Figure 1: Temperature vs Time

Ti=900K & Pi=100atm.

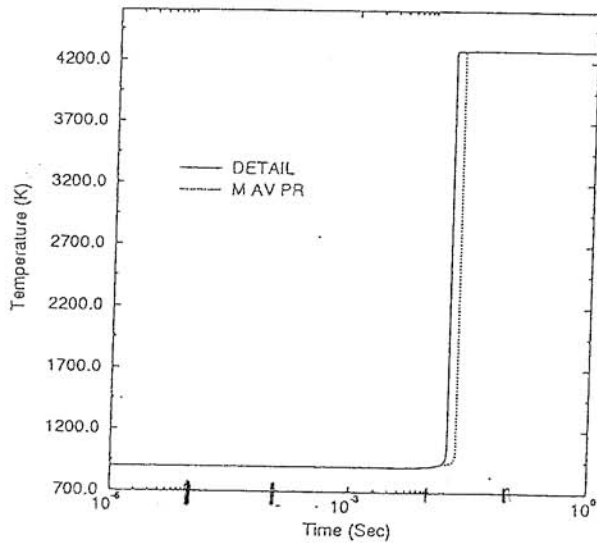


Figure 2: Temperature vs Time

Ti=1500K & Pi=1atm.

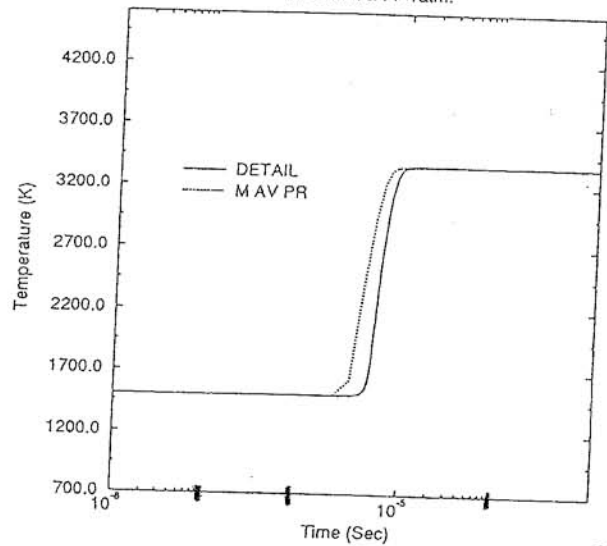


Figure 3: Entropy vs Time

Ti=900 & Pi=100atm.

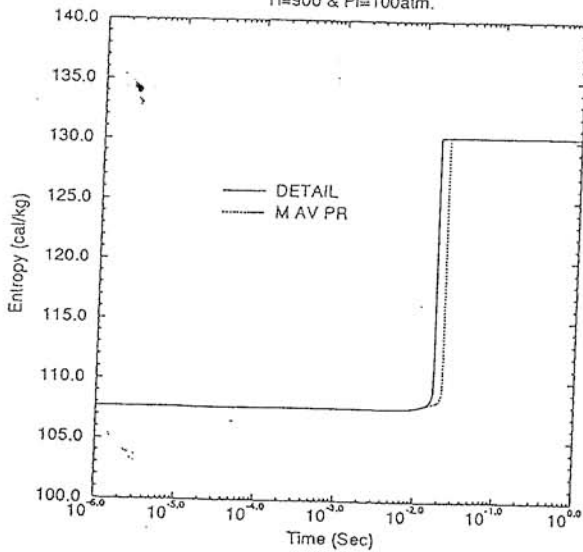


Figure 4: Entropy vs Time

Ti=1500 & Pi=1atm.

