Rate-controlled constrained-equilibrium method using constraint potentials

Djamel Hamiroune†, Partha Bishnu†, Mohamad Metghalchi† and
James C Keck‡

† Mechanical, Industrial and Manufacturing Engineering, Northeastern University, Boston, MA 02115, USA
‡ Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Abstract. A method called rate-controlled constrained equilibrium has been developed. It is based on the assumption that complex chemical systems evolve through a sequence of quasi-equilibrium states determined by the instantaneous values of internal constraints on the system's composition. These constraints are imposed by slow rate-limiting reactions. The technique involves direct integration of the rate equations for the constraint potentials (Lagrange multipliers conjugate to the constraints). The method has been tested for stoichiometric mixtures of hydrogen and air in an adiabatic constant-volume chamber for a range of initial pressures between 0.01 and 1000 atm and initial temperatures between 900 and 1500 K. The state of the system was determined by imposing constraints on the total number of moles, the moles of active valence and the moles of free oxygen. The rate equations for constraint potentials were integrated in conjunction with conservation equations for a constant volume and energy mixture. The results were in good agreement with those obtained by integration of a full set of nine rate equations over a wide range of temperature and pressure.

1. Introduction

The development of models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. Although the rate equations describing the evolution of such systems are well known, for large systems containing hundreds or more species and thousands of possible reactions, their integration can be extremely difficult due to the large number of differential equations involved.

Numerous approaches for simplifying this problem have been made, some involving the reduction of reaction mechanisms [1–9] and truncations of the species list [10] and others involving mathematical approximations that convert differential equations into algebraic equations such as the partial equilibrium approximation and quasi-steady state approximation [11–14]. Another approach discussed in [15, 16] consists of a method identifying the fast time scales of the chemical reaction systems based on an eigenvalue analysis, assuming that fast relaxation processes are in local equilibrium. The state space for the chemical reacting system can be reduced globally and it can be described by only a small number of reaction progress variables. An alternative approach proposed originally by Keck and Gillespie [17] and later developed by Keck and co-workers [18–20] 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. Instead of a full set of rate equations for the species, only the rate equations for the constraints are needed to determine the state of the system and, since the number of constraints required is expected to be very much smaller than the number of species, the task of integrating these equations should be very much simplified. In addition, if a reaction does not change any constraint, it will not affect the evolution of the system, thus only reaction rates of those reactions which change the constraints are required.

The most important advantage of RCCE in terms 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. In the limit where the number of constraints equals the number of species in the 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 expected to be very much smaller than the number of species in the system.

In previous studies using the RCCE method, the rate equations for the constraints were integrated in stepwise fashion and the constrained composition was determined at each step using a generalized version of the NASA equilibrium code CONSEQL [19] that determines the species concentrations by minimizing the Gibbs free energy subject to the specified constraints.

The purpose of this paper is to explore the alternative approach proposed by the authors [20, 21] in which the rate equations for the constraint potentials conjugate to constraints are integrated. Also, we develop this method in greater detail and to compare it with a complete model for the case of hydrogen oxidation. It should be emphasized that, due to the small number of species involved in this system, no significant time saving is expected for the RCCE calculations. The primary purpose of this investigation is to obtain a better understanding of the problems involved in the use of constraint potentials.

2. Detailed treatment of chemical reactions

2.1. Species rate equations

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

$$\sum_{i=1}^{n_s} \nu_{jk}^+ B_j \leftrightarrow \sum_{i=1}^{n_s} \nu_{jk}^- B_j \qquad k = 1, \ldots, n_r \tag{1}$$
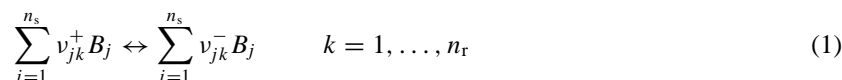
where B_j is the symbol of species j, n_r is the number of reactions, n_s is the number of species, ν_{jk}^+ and ν_{jk}^- are the forward and reverse stoichiometric coefficient of species j for reaction k.

The most accurate method of describing the evolution of the system is the integration of the full set of rate equations for the species. The species composition depends on the reaction mechanism. For a given reaction mechanism (1) the rate equation for an individual

species j is given in terms of all reactions rates involved by

$$\dot{N}_j = V \sum_{k=1}^{n_r} v_{jk} r_k \qquad j = 1, \ldots, n_s \tag{2}$$

where N_j is the number of moles of species j, V is the volume of the system, $v_{jk} = v_{jk}^- - v_{jk}^+$ 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

$$r_k^+ = k_k^+(T) \prod_{j=1}^{n_s} (N_j/V)^{v_{jk}^+} \tag{3a}$$

and

$$r_k^- = k_k^-(T) \prod_{j=1}^{n_s} (N_j/V)^{v_{jk}^-} \qquad k = 1, \ldots, n_r \tag{3b}$$

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

Note that at equilibrium the species composition must be independent of time: the rates of changes (2) of species concentrations are zero thus r_k must vanish. This leads to the equilibrium condition

$$(r_k^+)_e = (r_k^-)_e \qquad k = 1, \ldots, n_r \tag{4}$$

which is the detailed balancing condition where the subscript 'e' denotes equilibrium. This condition must be true at equilibrium for all reactions. Substituting equations (3a) and (3b) into equation (4) gives

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

where K_{Ck} is the equilibrium constant for reaction k based on concentration.

For systems of interest in combustion the number of species is in the hundreds and the number of reactions is in thousands. One could easily notice that the task of integrating these rate equations in conjunction with additional conservation equations is a difficult task.

In the case where the energy and volume are prescribed, the temperature and pressure are unknown. Two additional equations are required. One can be obtained by differentiating the expression for the energy of the system

$$E = \sum_{j=1}^{n_s} N_j e_j(T) \qquad j = 1, \ldots, n_s \tag{6}$$

with respect to time which leads to a rate equation for temperature which constitutes the additional equation

$$\dot{T} = \left(\dot{E} - \sum_{j=1}^{n_s} \dot{N}_j e_j(T) \right) \bigg/ \sum_{j=1}^{n_s} N_j c_{vj}(T) \tag{7}$$

where e_j is the specific internal energy of species j; $c_{vj} = de_j/dT$ is the specific heat at constant volume for species j. The other equation is the equation of state for an ideal gas

$$pV = \sum_{j=1}^{n_s} N_j RT \tag{8}$$

where p is the mixture pressure.

Equation (2) can be integrated in conjunction with equation (7) to obtain the temperature and species composition. The pressure is determined using equation (8).

3. Rate-controlled constrained equilibrium (RCCE)

For systems containing a large number of species, such as C/H/O combustion systems, which are currently being modelled with hundreds of species, the use of a detailed kinetic model and the integration of the full reaction rates is a difficult task. Various methods of reducing the complexity of such systems have been discussed in the introduction. Among these is the rate-controlled constrained-equilibrium method being developed by the authors.

Since only the rate equations for the constraints are needed to determine the state of the system and the number of constraints required is expected to be very much smaller than the number of species, the task of integrating these equations should be very much simplified for large systems.

3.1. Rate equations for constraints

The constraints imposed on the reacting system are assumed to be a linear combination of species compositions present in a given system. They can be written in the form

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j \qquad i = 1, \ldots, n_c \tag{9}$$

where a_{ij} is the value of the constraint i for the species j and n_c is the number of constraints. The rate equations for the constraints can easily be determined by differentiating equation (9):

$$\dot{C}_i = \sum_{j=1}^{n_s} a_{ij} \dot{N}_j \qquad i = 1, \ldots, n_c \tag{10}$$

and using the species rate equations (2):

$$\dot{C}_i = V \sum_{k=1}^{n_b} b_{ik} r_k \qquad i = 1, \ldots, n_c \tag{11}$$

where $b_{ik} = \sum_{j=1}^{n_s} a_{ij} \nu_{jk}$ is the change of constraint i due to the reaction k and n_b is the number of reactions which change the constraints, that is for which $b_{ik} \neq 0$.

Note that since elements are conserved their corresponding constraints are constant, then for elements, $b_{ik} = 0$ and $\dot{C}_i = 0$ for $i = 1, \ldots, n_e$, where n_e is the number of elements in the system. This ensures conservation of elements and reduces the number of rate equations to be integrated by n_e.

Given the initial conditions the $n_c - n_e$ rate equations (10) for the constraints can be integrated in stepwise fashion using standard integration routines such as LSODI [22] or DASSL [23]. At each step the constrained-equilibrium composition

$$N_j(t) = N_j(T(t), V(t), C_1(t), \ldots, C_{n_e}(t), \ldots, C_{n_c}(t)) \tag{12}$$

must be evaluated using the constrained-equilibrium program. This is the technique employed in all previous calculations using the RCCE method.

3.2. Rate equations for constraint potentials

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 Lagrange multipliers method. For each constraint there is a corresponding Lagrange multiplier

(constraint potential). The species composition is then determined as a function of those multipliers:

$$N_j = Q_j \exp\left(-\sum_{i=1}^{n_c} a_{ij}\gamma_i\right) \qquad j = 1, \ldots, n_s \tag{13}$$

where $Q_j = (p_0 V/RT)\exp(-\mu_j^\circ)$ is the partition function for species j, and $\mu_j^\circ = F_j^\circ/RT$ is the dimensionless standard Gibbs free energy and γ_i is the Lagrange multiplier (constraint potential) conjugate to the ith 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 of the number of rate equations to be integrated. Once the constraint potentials γ_i have been determined the constrained composition can easily be calculated using equation (13).

It can be seen from equation (13) that if any of the species moles is zero one of the constraint potentials becomes infinite which results in numerical problems. To overcome this problem the 'constraint factor' is introduced. The constraint factor is defined in terms of constraint potential as $\Gamma_i = \exp(-\gamma_i)$, then the species composition (13) becomes

$$N_j = Q_j \prod_{i=1}^{n_c} \Gamma_i^{a_{ij}} \qquad j = 1, \ldots, n_s. \tag{14}$$

Differentiating equation (14) with respect to time leads to the rate equations for the species composition:

$$\dot{N}_j = N_j \frac{\dot{V}}{V} + N_j \frac{e_j}{RT}\frac{\dot{T}}{T} + Q_j \sum_{n=1}^{n_c} d_{nj}\dot{\Gamma}_n. \tag{15}$$

Substituting the result into equation (10) and using equation (11) leads to a set of implicit rate equations for the constraint factors Γ_i,

$$\sum_{n=1}^{n_c} D_{in}\dot{\Gamma}_n + D_{iT}\dot{T} + D_{iV}\dot{V} - V\sum_{k=1}^{n_b} b_{ik}r_k = 0 \qquad n = 1, \ldots, n_c \tag{16}$$

where

$$D_{in} = \partial C_i/\partial \Gamma_n = \sum_{j=1}^{n_c} a_{ij} d_{nj} Q_j$$

$$D_{iT} = \partial C_i/\partial T = \sum_{i=1}^{n_s} a_{ij} e_j(T) N_j/RT^2$$

and

$$D_{iV} = \partial C_i/\partial V = \sum_{j=1}^{n_s} a_{ij} N_j/V \qquad i = 1, \ldots, n_c$$

in which

$$d_{nj} = 0 \qquad \text{for} \quad a_{nj} = 0$$

and

$$d_{nj} = a_{nj}\prod_{k=1}^{n_c} \Gamma_k^{a_{kj}-\delta_{nk}} \qquad \text{for} \quad a_{nj} \neq 0.$$

In equation (16) the unknowns are the constraint factors Γ_i themselves. In the case where $T(t)$ and $V(t)$ are given, the set of rate equations (16) represent a set of nonlinear first-order differential equations to be integrated, which can be written in the form

$$[D_{in}(\Gamma, T)]\dot{\Gamma} = F(\Gamma, t) \tag{17}$$

where D_{in}, F and Γ are, respectively, an n_c by n_c square matrix and vectors of order n_c.

In the case where E and V are independent variables, an additional equation for the temperature T is obtained by differentiating the expression for the energy previously given which gives the following equation:

$$\sum_{n=1}^{n_c} D_{En}\dot{\Gamma}_n + D_{ET}\dot{T} + D_{EV}\dot{V} - \dot{E} = 0 \tag{18}$$

where

$$D_{En} = \frac{\partial E}{\partial \Gamma_n} = \sum_{j=1}^{n_s} e_j(T)\, d_{nj}\, Q_j$$

$$D_{ET} = \frac{\partial E}{\partial T} = \sum_{j=1}^{n_s} (c_{vj}(T)\, T^2 + e_j^2(T))N_j / RT^2$$

and

$$D_{EV} = \frac{\partial E}{\partial V} = V \sum_{i=1}^{n_s} e_j(T)\, N_j.$$

Combining equation (16) and (18) gives a set of $n_c + 1$ equations of the form

$$\begin{bmatrix} D_{in}(\Gamma, T) & D_{iT} \\ D_{En} & D_{ET} \end{bmatrix}\begin{bmatrix} \dot{\Gamma} \\ \dot{T} \end{bmatrix} = \begin{bmatrix} F(\Gamma, t) \\ 0 \end{bmatrix}. \tag{19}$$

4. Selection of constraints

The first step in the application of the RCCE method involves determining the constraints. To a large extent, the process of identifying useful constraints involves the development of models similar to those used in all kinetic calculations. The difference is that we have had a great deal of experience dealing with species and very little dealing with 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 control the total moles, and slow branching reactions, which control the total moles of radicals. Other promising constraints investigated in the work on the H_2–air system described below are:

- 'Active valence', which includes the most active radicals such as H, O and HO.
- 'Free oxygen', which is defined as any oxygen that is not bonded to another oxygen. Free oxygen is an important constraint in oxidation reaction involving O_2 because for chemistry to take place the O–O bond needs to be broken.

There are also a number of conditions, which must be carefully observed in choosing constraints. The method of Lagrange multipliers requires that these constraints are linearly independent otherwise the matrix D_{in} is singular. The constraints must be capable of holding the system in the specified initial state within reasonable accuracy and the matrix D_{in} in equation (19) must be non-singular to permit inversion. As discussed in the illustrative

calculations below additional insight can also be gained in specific cases from a study of the basic reaction mechanisms involved.

Equations of the form (19) can be integrated using DASSL or LSODI. This requires an inversion of the matrix D_{in} which must be non-singular as mentioned. Inspection of the equations for the D_{in} terms shows that if the value of any of Γ is zero, then the matrix will be singular unless the constraint matrix a_{ij} is carefully chosen. A sufficient condition for the D_{in} matrix to be non-singular is that the a_{ij} matrix can be partitioned as shown below:

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ 0 & I & A_{23} \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} \qquad (20)$$

where C_1 is a vector which contains the constraints that are non-zero initially, C_2 is a vector containing the constraints which can have a zero value, A_{11} is a diagonal matrix of the same order as C_1 which determines the initial non-zero constraint factors, I is a unit matrix of the same order as C_2 and A_{23} a matrix whose elements must be zero or a positive integer. If the original constraint matrix does not have the form (20) it must be possible to transform it to that form by linear combinations of different rows.

5. H$_2$–air system

A major objective of this work is to test the rate-controlled constrained-equilibrium (RCCE) method. The H–O–N system has been chosen because its kinetics are well known and the full set of rate equations can easily be integrated to obtain exact solutions for comparison with RCCE calculations.

Premixed hydrogen–air mixtures in an adiabatic constant-volume chamber have been studied. A full set of rate equations with 19 reactions and nine species were integrated to obtain exact solutions for comparison with RCCE calculations. The species included are O, H, O$_2$, H$_2$, HO, H$_2$O, HO$_2$, H$_2$O$_2$ and N$_2$. The 19 reactions included used in the calculations are listed in table 1 along with their standard reaction enthalpies ΔH°_{300} and the parameters A, n and E_a for calculating the exothermic rate constants using the form $k^+ = AT^n \exp(-E_a/RT)$. Calculations were carried out for a range of pressures between 0.01–1000 atm and a range of temperatures between 900 and 1500 K using DASSL. The calculations using the constraint potentials method included up to six constraints. They are element hydrogen EH, element oxygen EO, element nitrogen EN, total number of moles M, active valence AV and free oxygen FO. These constraints can be written for the hydrogen–air system as follows:

$$EH = \mathrm{H} + \mathrm{HO} + \mathrm{HO_2} + 2\mathrm{H_2} + 2\mathrm{H_2O} + 2\mathrm{H_2O_2}$$
$$EN = 2\mathrm{N_2}$$
$$EO = \mathrm{HO} + 2\mathrm{HO_2} + \mathrm{H_2O} + 2\mathrm{H_2O_2} + \mathrm{O} + 2\mathrm{O_2}$$
$$M = \mathrm{H} + \mathrm{HO} + \mathrm{HO_2} + \mathrm{H_2} + \mathrm{H_2O} + \mathrm{H_2O_2} + \mathrm{O} + \mathrm{O_2} + \mathrm{N_2}$$
$$AV = \mathrm{H} + \mathrm{HO} + 2\mathrm{O}$$
$$FO = \mathrm{H_2O} + \mathrm{HO} + \mathrm{O}.$$

The fixed constraints EH, EO and EN are required by conservation of elements. The constraint on the total number of moles, M, is imposed by the slow rate of dissociation/recombination reactions. The constraint on the active valence, AV, is imposed by the slow rate of branching reactions. Finally, the constraint of the free oxygen FO is imposed by the slow rate of reactions capable of breaking bonds between O atoms.

Table 1. Hydrogen–oxygen reaction mechanism and rate data [24] in cm^3, mole, s and kcal units.

	Reactions	ΔH_{300}^0	$\log_{10} A$	n	E_a	ΔM	ΔAV	ΔFO	ΔPR
1	$H + O_2 + M \rightarrow HO_2 + M$	−47.10	18.32	0	−1	−1	−1	0	1
2	$OH + OH + M \rightarrow H_2O_2 + M$	−51.40	12.50	0	−5.07	−1	−2	−2	2
3	$O + H + M \rightarrow OH + M$	−102.23	15.90	0	0	−1	−2	0	0
4	$H + H + M \rightarrow H_2 + M$	−104.20	16.08	0	0	−1	−2	0	0
5	$O + O + M \rightarrow O_2 + M$	−119.12	17.11	−0.28	0	−1	−4	−2	0
6	$H + OH + M \rightarrow H_2O + M$	−119.33	9.92	−0.50	0	−1	−2	0	0
7	$H_2O_2 + H \rightarrow HO_2 + H_2$	−14.60	12.20	0	3.80	0	−1	0	−1
8	$O + H_2O_2 \rightarrow OH + HO_2$	−14.70	12.10	0	8.00	0	−1	0	−1
9	$O + OH \rightarrow H + O_2$	−16.90	13.17	0	0.68	0	−2	−2	0
10	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	−29.70	13.00	0	1.80	0	−1	0	−1
11	$H + HO_2 \rightarrow H_2 + O_2$	−38.20	14.40	0	0.70	0	−1	0	−1
12	$HO_2 + O \rightarrow O_2 + OH$	−55.10	13.70	0	1.00	0	−1	0	−1
13	$H + HO_2 \rightarrow OH + OH$	−57.10	13.40	0	1.90	0	1	2	−1
14	$OH + HO_2 \rightarrow H_2O + O_2$	−72.20	13.70	0	1.00	0	−1	0	−1
15	$H + H_2O_2 \rightarrow OH + H_2O$	−68.10	13.00	0	3.60	0	0	2	−2
16	$H + OH \rightarrow H_2 + O$	−1.97	23.88	−3	0	0	0	0	0
17	$OH + H_2 \rightarrow H + H_2O$	−15.13	13.34	0	5.15	0	0	0	0
18	$OH + OH \rightarrow H_2O + O$	−17.10	11.67	0	1.10	0	0	0	0
19	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	−42.53	12.30	0	0	0	0	0	0

Table 2. Original $[a_{ij}]$ matrix for the H–O–N_2 system.

	O_2	H_2	N_2	H_2O	H	HO_2	HO	O	H_2O_2
EO	2	0	0	1	0	2	1	1	2
EH	0	2	0	2	1	1	1	0	2
EN	0	0	2	0	0	0	0	0	0
M	1	1	1	1	1	1	1	1	1
AV	0	0	0	0	1	0	1	2	0
FO	0	0	0	1	0	0	1	1	0

The constraints can be represented in matrix forms as shown in table 2. By simple addition and subtraction of rows, this matrix can be transformed into the form (20) as shown in table 3, where $PR = EH + EO + EN + AV - FO - 2M$. Using this transformed matrix, the set of equations (16) and (18) can be integrated. The coefficients b_{ik} appearing in equations (16) and (18) are given in the last four columns of table 1. These coefficients give the change of constraint i in reaction k. Note that there are four reactions which do not change any constraints (i.e. $b_{ik} = 0$) so these reactions are at equilibrium. Since these reactions do not change the constraints, their corresponding rates are not required in the RCCE calculations.

The initial conditions for the constraints are determined by the initial concentrations of the species in the system. Since there are no products in the initial gas mixture, it can be seen from table 3 and equation (14) that the variable constraints FO, AV and PR and the corresponding constraint factors, Γ_i, must be all zero. The constraint factors, Γ_i, for the elements can be determined from the initial concentrations of the reactants by inverting the

Table 3. Transformed a_{ij} matrix for the H–O–N$_2$ system in canonical form, equation (20).

	O$_2$	H$_2$	N$_2$	H$_2$O	H	HO$_2$	HO	O	H$_2$O$_2$
	A_{11}			A_{12}			A_{13}		
EO	2	0	0	1	0	2	1	1	2
EH	0	2	0	2	1	1	1	0	2
EN	0	0	2	0	0	0	0	0	0
				I			A_{23}		
FO	0	0	0	1	0	0	1	1	0
AV	0	0	0	0	1	0	1	2	0
PR[a]	0	0	0	0	0	1	0	0	2

[a] $PR = EH + EO + EN + AV - FO - 2M.$

matrix A_{11} in table 3: they are given by

$$(\Gamma_{EO})_{t=0} = ((N_{O_2})_{t=0}/Q_{O_2})^{1/2}$$
$$(\Gamma_{EH})_{t=0} = ((N_{H_2})_{t=0}/Q_{H_2})^{1/2} \tag{21}$$
$$(\Gamma_{EN})_{t=0} = ((N_{N_2})_{t=0}/Q_{N_2})^{1/2}.$$

Integration of the rate equations (16) and energy equation (18) subject to these initial conditions was carried out at constant E and V for a range of initial pressures between 0.01 and 1000 atm and initial temperatures between 900 and 1500 K using integration routine DASSL. The results are shown in figures 1–5 and discussed below.
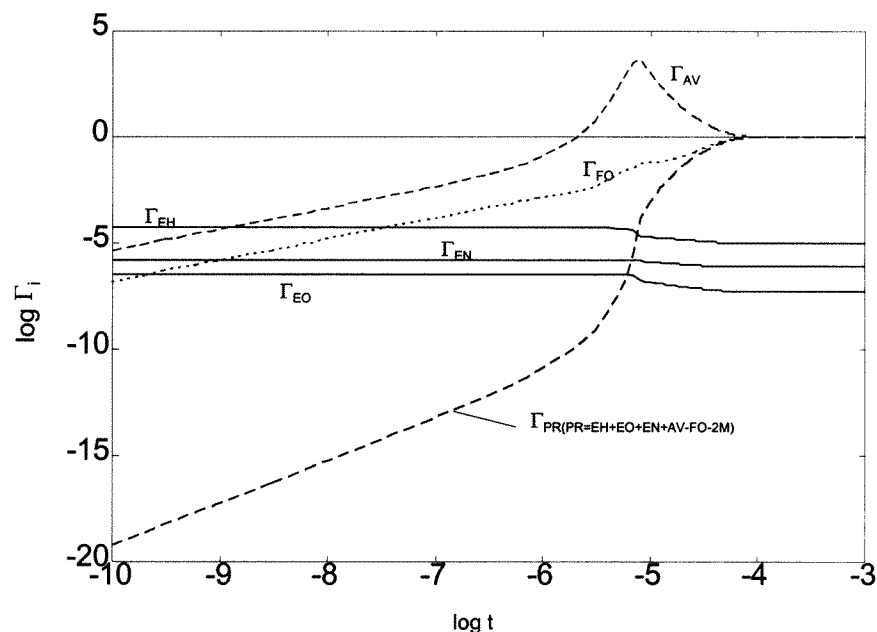

Figure 1. Constraint factors versus time, for constant-E and V case. The initial temperature and pressure are 1500 K and 1 atm. The RCCE calculations were carried out using $(M + AV + FO)$ constraints. The system is hydrogen–air H = 4, O = 2 and N = 7.52. Initially only H$_2$, O$_2$ and N$_2$ are present.
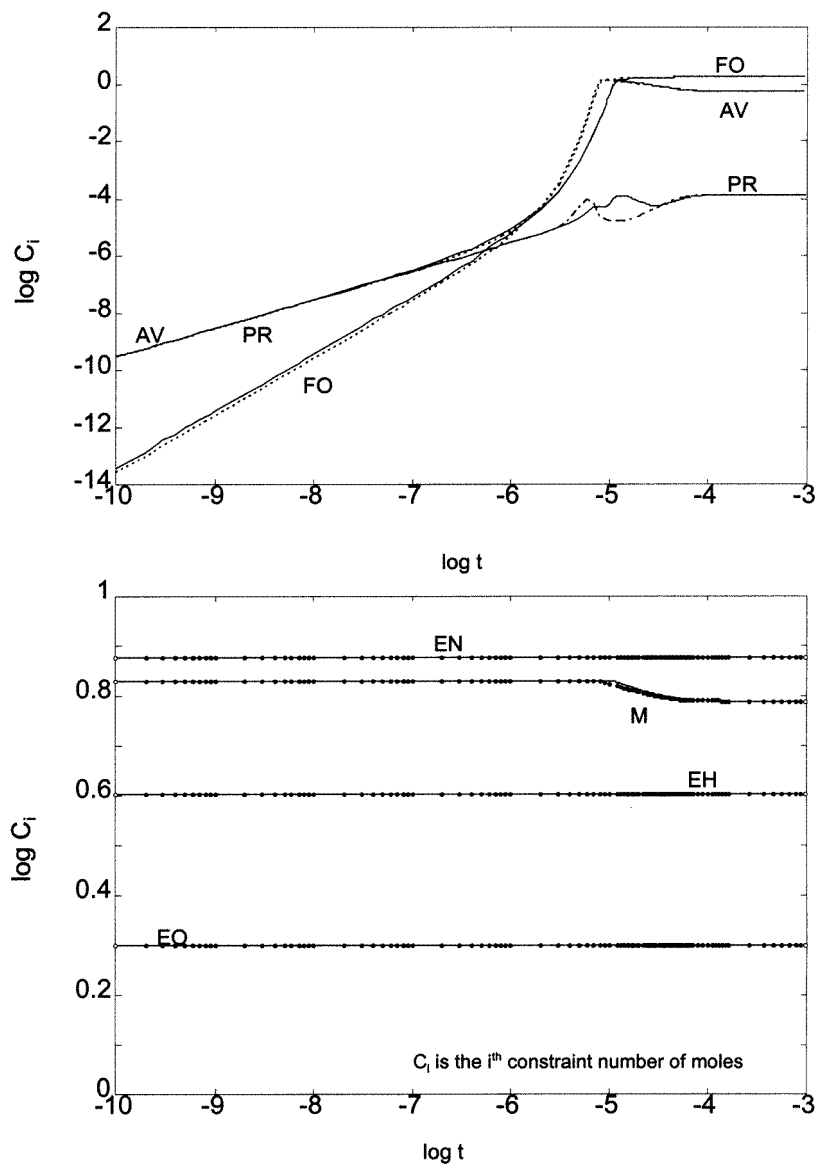
Figure 2. Constraints number of moles versus time, for constant-E and V case. Initial temperature and pressure are 1500 K and 1 atm. The full curves represent the detailed calculations, where the broken and dotted curves represent RCCE calculations with $(M + AV + FO)$ constraints. The system is hydrogen–air H $= 4$, O $= 2$ and N $= 7.52$. Initially only H_2, O_2 and N_2 are present.

6. Discussion

Figure 1 shows the constraint factors as a function of time for a stoichiometric hydrogen–air mixture at 1500 K and 1 atm. Values of the constraint factors for the three elements: EH, EO and EN, the total number of moles, M, the active valence, AV, and the free oxygen, FO, have been plotted. Note that the constraint factors corresponding to the
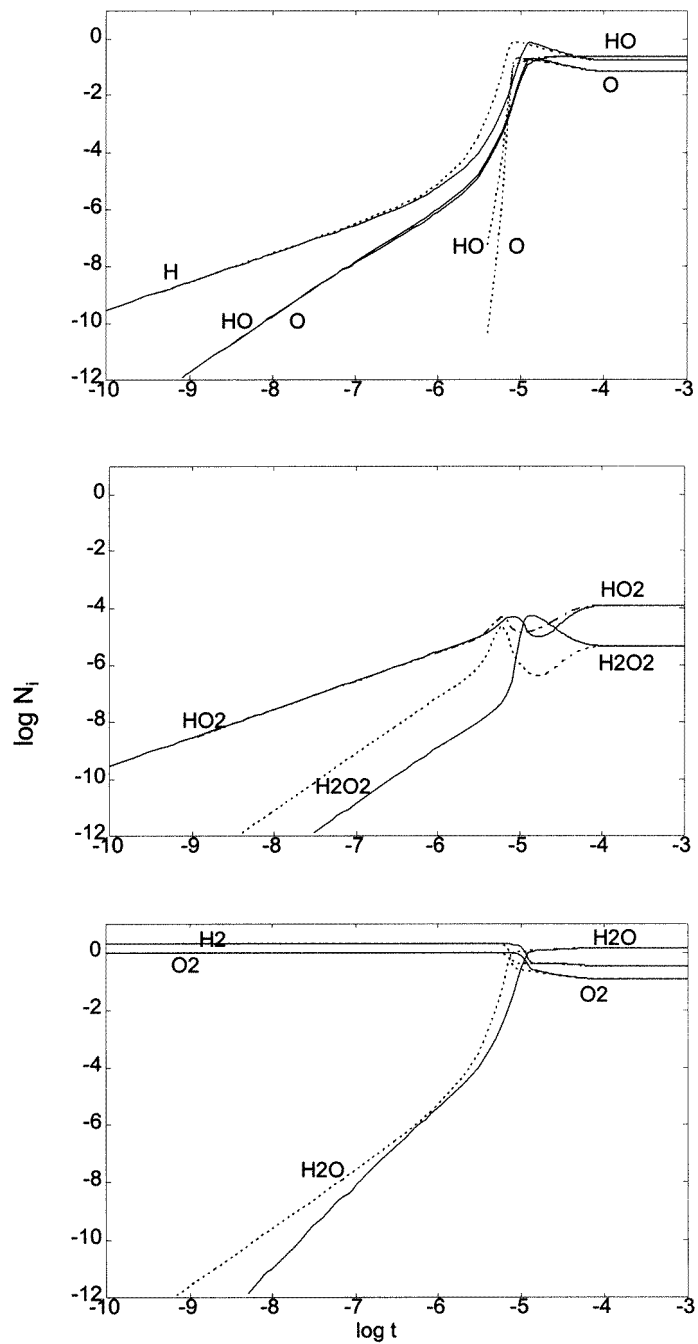
Figure 3. Species number of moles as a function of time, for a constant-E and V case. Initial temperature and pressure are 1500 K and 1 atm. The atomic population is H = 4, O = 2 and N = 7.52. Initially only H_2, O_2 and N_2 are present.

elements are not constant even though, as shown in figure 2, the constraints themselves are. The final equilibrium values of the constraint factors for the elements agree with those
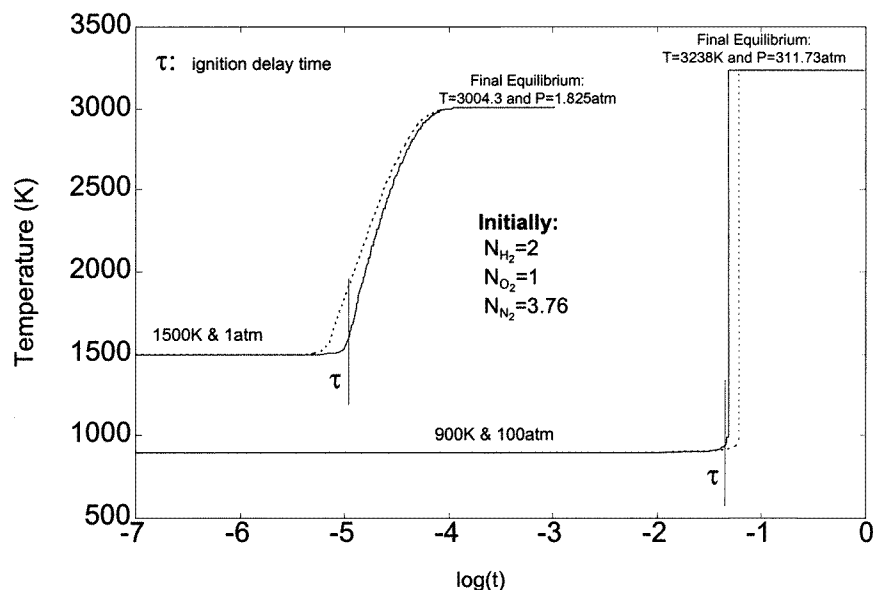
Figure 4. Temperature as a function of time for the hydrogen–air system at constant E and V. Two cases are shown, one with initial temperature and pressure of 1500 K and 1 atm, and the other with initial temperature and pressure of 900 K and 100 atm. The atomic population is $H = 4$, $O = 2$ and $N = 7.52$ for both cases and initially only H_2, O_2 and N_2 are present.

calculated from the equilibrium program STANJAN [25]. The additional constraint factors for FO, AV and PR, which is a modified M, control the evolution of the system from the initial state to the final state. At the final equilibrium state, the values of these constraint factors are equal to unity (constraint potentials $\gamma_i = 0$) which means that at equilibrium the system is well defined by the elemental constraints only.

Figure 2 shows the values of the three elemental constraints and the three variable constraints as a function of time. The full curves are the detailed calculations and the dotted curves are the constrained calculations. It can be seen that the elemental constraints for both calculations are in perfect agreement and constant as required. The variable constraints FO and AV are also in good agreement at all times but those for the constraint PR disagree somewhat during the final approach to equilibrium. The constraints AV and PR, which represent H and HO_2 radicals, respectively, are identical at early times and have a slope of unity due to the initiation reaction $H_2 + O_2 \rightarrow H + HO_2$. The constraint FO represents HO and O initially and has a slope of two due to the reaction $H + O_2 \rightarrow O + HO$ which follows the initiation reaction.

Figure 3 shows the number of moles for the individual species as a function of time. The full curves represent the detailed calculations; the broken and dotted curves represent the RCCE calculations. It can be seen that the major species H_2, O_2, H, H_2O and HO_2 are well represented by the constrained calculations at all times. The minor species H_2O_2, HO and O are not well represented at early times but proceed to the correct equilibrium.

Figure 4 shows a plot of temperature as a function of time for the cases with initial conditions of 1500 K and 1 atm, and 900 K and 1000 atm. The full curves represent the detailed calculations; the broken curves are the RCCE calculations. The curves show the behaviour typical of the low- and high-pressure regimes. The final temperature in the high-pressure case is larger than that in the low-pressure case due to the lower degree of
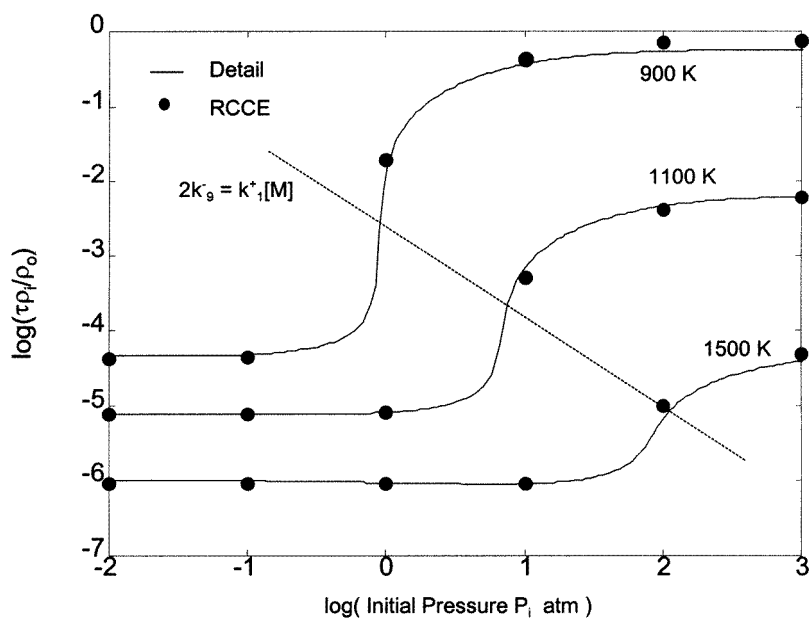
Figure 5. Binary-scaled ignition delay versus time versus initial pressure for the hydrogen–air system with H $=$ 4, O $=$ 2 and N $=$ 7.52. Initially, $H_2 = 2$, $O_2 = 1$ and $N_2 = 3.76$ and all other species are zero. Calculations were carried out for constant-E and V case. The full curves are the detailed calculations, where the circles are the RCCE calculations. The broken line represents the dividing line between the high- and low-pressure regimes.

dissociation. Ignition delay time τ, which represents the time during which the system exhibit a 10% rise in its temperature, is also shown.

Figure 5 shows a summary of the results over a wide range of temperatures and pressures. Here the binary-scaled ignition delay time is plotted as a function of the initial pressure. The binary ignition delay time is the ignition delay time τ multiplied by the density ratio ρ_i / ρ_0, where ρ_i is the initial mixture density and ρ_0 is the density of the mixture at standard state. The full curves are the results of the detailed calculations and the symbols are the results of the RCCE calculations. Also shown is the dividing line between the high- and low-pressure regimes given by the condition $2k_9^- = k_1^+[M]$.

7. Summary

Rate equations for the constraint factors associated with the rate-controlled constrained-equilibrium (RCCE) method have been developed and successfully integrated for a stoichiometric mixture of hydrogen and air over a wide range of initial temperatures and pressures. RCCE calculation using variable constraints on the total moles, active valence and free oxygen in additions to the three elemental constraints were in good agreement with detailed calculations. For this simple case, RCCE running times were comparable with those of the detailed kinetic model. Considerable insight into the use of the method was gained and it is anticipated that for complex C–H–N–O systems, containing a great many more species and reactions, the RCCE method will be faster and more efficient than detailed calculations.

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