Rate-Controlled Constrained-Equilibrium (RCCE) Modelling of C$_1$-Hydrocarbon Fuels

A Dissertation Presented

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Dedicated to the memory of

Prof. James C. Keck

who introduced me to the wonderful world of

Constrained Equilibrium
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Abstract

This dissertation is focused on an important problem faced in chemical kinetic modelling, that is, model order reduction. The method of Rate-Controlled Constrained-Equilibrium (RCCE) firmly based on the Second Law of Thermodynamics, has been further developed and used for this purpose. The main challenge in RCCE lies in selection of the kinetic constraints. Two classes of problems were looked at: 1) far-from-equilibrium problem of ignition and 2) relaxations away from equilibrium due to interactions with the environment.

Regarding the first class, a unified RCCE model for combustion of C1-hydrocarbon fuels (CH$_4$, CH$_3$OH and CH$_2$O) and their corresponding reduced models were developed. The model is composed of a set of structural constraints controlling the chemical conversion from fuel into combustion products.

For the second class it was shown that a subset of the constraints identified in the first class is able to equally well predict the main features of expansion of combustion products within the power stroke of an internal combustion engine as well as supersonic expansion through a rocket nozzle and also expansion through a heat exchanger as a model for sudden cooling in gas turbine.

A method based on the degree of disequilibrium of chemical reactions was also suggested for selection of kinetic constraints. This approach has potentials to reduce the level of chemical knowledge required for selection of kinetic constraints and it was shown how the application of this method reproduces the generalized constraints used in the second class of problems without any chemical intuition.
**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 first specifying the state and species variables to be included in the model, compiling a “full set” of rate-equations for these variables, and integrating this set of equations to obtain the time-dependent behaviour of the system. Such models are frequently referred to as “detailed kinetic models” (DKM). The problem is that the detailed kinetics of C/H/O/N molecules can easily involve hundreds of chemical species and isomers, and thousands of possible reactions even for system containing only C$_1$ molecules. Clearly, the computational effort required to treat such systems is extremely large. The difficulties are compounded when considering reacting turbulent flows, where the complexity of turbulence is added to that of the chemistry.

As a result a great deal of effort has been devoted to developing methods for simplifying the chemical kinetics of complex systems. Among the most prominent are: Quasi Steady State Approximation (QSSA) [1], Partial Equilibrium Approximation [2], Intrinsic Low Dimensional Manifolds (ILDM) [3], Computational Singular Perturbation (CSP) [4], Adaptive Chemistry [5], Directed Relation Graph (DRG) [6] and The ICE-PIC method [7].

A common problem shared by all the above methods is that they start with DKMs containing a large number of reactions for which only the orders of magnitude of the reaction-rates are known. Thus, unless the simplified model effectively eliminates these uncertain reactions, the resulting model will be equally uncertain. The question is: If the uncertain reactions are to be eliminated, does it make any sense to include them in the first place?

An alternative approach, originally proposed by Keck and Gillespie [8] and later developed and applied by Keck and co-workers [9-11], and others [12-15] is the Rate-Controlled Constrained-Equilibrium (RCCE) method. This 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 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
reaction. 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 others mentioned above is that it does not require a DKM as a starting point. Instead, one starts with a small number of rate-controlled constraints on the state of a system, to which more can be systematically added to improve the accuracy of the results. If the only constraints are those imposed by slowly changing state variables, the RCCE method is equivalent to a local chemical equilibrium calculation. If the constraints are the species, the RCCE model is similar to a DKM having the same species with the important difference that RCCE calculations always approach the correct final chemical equilibrium state whereas DKM calculations do not. The reason for this is that the equilibrium state approached by a DKM contains only the species included in the model whereas the equilibrium state approached by an RCCE model includes all possible species that can be formed from the elements of which it is composed.

As with all thermodynamic systems, the number of constraints necessary to describe the state of the system within measurable accuracy can be very much smaller than the number of species in the system. Therefore fewer equations are required to determine the state of a system. A further advantage is that only the reaction-rates of slow reactions which change the constraints are needed and these are the ones most likely to be known. Reactions which do not change any constraint are not required. It should be emphasized that the successful implementation of the RCCE method depends critically on the constraints employed.

The structure of this thesis is as follows: in chapter 1 an RCCE model is developed for C1 fuels of CH₄, CH₂O and CH₃OH with detailed presentation of the working equations under thermodynamic state variables (E,V) along with a method to initialize the RCCE calculations. Three sets of reduced RCCE kinetic models for these fuels are also presented, the union of which involves 20 elementary reactions and the same number of species in the DKM. The model has the interesting feature of structurally constraining the kinetic patterns of oxidations of these fuels down to CO₂ and H₂O. However, only the C₁ chemistry has been considered. This is so that in fuel rich mixtures or at higher pressures where the recombination processes become important, the path to higher
hydrocarbons, more importantly C$_2$ becomes more active. As a result, in chapter 2 the interaction between C$_1$ and C$_2$ kinetics is considered and an extra set of three constraints is identified. This set, when added to the previously discovered set, has an acceptable predictive capability over the entire working range of the kinetic model. The importance of C$_1$ and C$_2$ kinetics cannot be over-emphasized due to the fact that once the beta-scission is activated, combustion of almost any hydrocarbon fuels, except for an immediate fuel-molecule-dependent chemistry within the low temperature cycle, soon becomes a matter of burning a mixture of C$_1$/C$_2$/C$_3$ Components. This fact underlies the observation that most straight chain hydrocarbon fuels have almost the same laminar burning speeds.

In chapters 3 and 4 another class of problems, in which a highly dissociated equilibrium mixture is thrown out of equilibrium due to interactions with the surrounding environment, is looked at. The main question at this stage is whether or not a subset of the kinetic constraints already identified for ignition of C$_1$ and C$_2$ is capable of predicting the dynamic behaviour of the re-activated kinetic effects in these systems. It is shown, by physical reasoning and rational analysis that the answer is yes. A rational for such a question is that the equilibrium composition of almost all hydrocarbon fuels is almost fuel independent and is mainly composed of the H/O and a number of C/H/O species and is therefore, controlled by their corresponding kinetics. Chapter 3 specifically considers expansion of combustion products within the power stroke of an internal combustion engine and chapter 4 studies the kinetics of H/O relaxation within a supersonic nozzle. The IC engine modelling assumes an adiabatic expansion, starting from equilibrium products over a prescribed time-dependent volume. Also, in chapter 4 a new approach based on the degree of disequilibrium (DOD) of chemical reactions is proposed for selecting the kinetic constraints. It is shown there how the application of DOD reconstructs, without any requirement of chemical kinetic knowledge, the generalized constraints identified by physical reasoning in chapter 3. This method has been so far applied only to starting-from-equilibrium problems, but has promising potentials to be further extended to starting-from-a-non-equilibrium-state problems as well.

Chapter 5 draws conclusions and the future works.
Each chapter has been published in the literature as a separate paper and is therefore, self contained. There are as a result, overlapping materials, equations and references among different chapters.
Chapter 1
Combustion Modelling of Mono-Carbon Fuels Using the Rate-Controlled Constrained-Equilibrium Method

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Abstract

The Rate-Controlled Constrained-Equilibrium (RCCE) method for simplifying the kinetics of complex reacting systems is reviewed. This method is based on the maximum-entropy-principle of thermodynamics and involves the assumption that the evolution of a system can be described using a relatively small set of slowly changing constraints imposed by the external and internal dynamics of the system. As a result, the number of equations required to determine the constrained state of a system can be very much smaller than the number of species in the system. In addition, only reactions which change constraints are required; all other reactions are in equilibrium. The accuracy of the method depends on both the character and number of constraints employed and issues involved in the selection and transformation of the constraints are discussed. A method for determining the initial conditions for highly non-equilibrium systems is presented.

The method is illustrated by applying it to the oxidation of methane (CH\textsubscript{4}), methanol (CH\textsubscript{3}OH) and formaldehyde (CH\textsubscript{2}O) in a constant volume adiabatic chamber over a wide range of initial temperatures and pressures. The RCCE calculations were carried out using 8 to 12 constraints and 133 reactions. Good agreements with “detailed” calculations using 29 species and 133 reactions were obtained. The number of reactions in the RCCE calculations could be reduced to 20 for CH\textsubscript{4}, 16 for CH\textsubscript{3}OH and 12 for CH\textsubscript{2}O without changing the results. “Detailed” calculations with less than 29 reactions are indeterminate.

Keywords: Rate-controlled Constrained-equilibrium, Maximum entropy principle, Detailed modelling, Reduced kinetics, Methane, Methanol, Formaldehyde.

2.1 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 first specifying the state and species variables to be included in the model, compiling a “full set” of rate-equations for these variables, and integrating this set...
of equations to obtain the time-dependent behaviour of the system. Such models are frequently referred to as “detailed kinetic model”s (DKM). The problem is that the detailed kinetics of C/H/O/N molecules can easily involve hundreds of chemical species and isomers, and thousands of possible reactions even for system containing only C₁ molecules. Clearly, the computational effort required to treat such systems is extremely large. The difficulties are compounded when considering reacting turbulent flows, where the complexity of turbulence is added to that of the chemistry.

As a result a great deal of effort has been devoted to developing methods for simplifying the chemical kinetics of complex systems. Among the most prominent are: Quasi Steady State Approximation (QSSA) [1], Partial Equilibrium Approximation [2], Intrinsic Low Dimensional Manifolds (ILDM) [3], Computational Singular Perturbation (CSP) [4], Adaptive Chemistry [5], Directed Relation Graph (DRG) [6] and The ICE-PIC method [7].

A common problem shared by all the above methods is that they start with DKMs containing a large number of reactions for which only the orders of magnitude of the reaction-rates are known. Thus, unless the simplified model effectively eliminates these uncertain reactions, the resulting model will be equally uncertain. The question is: If the uncertain reactions are to be eliminated, does it make any sense to include them in the first place?

An alternative approach, originally proposed by Keck and Gillespie [8] and later developed and applied by Keck and co-workers [9-11], and others [12-15] is the Rate-Controlled Constrained-Equilibrium (RCCE) method. This 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 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 others mentioned above is that it does not require a DKM as a starting point. Instead, one starts with a small number of rate-controlled constraints on the state of a system, to which more can be systematically
added to improve the accuracy of the results. If the only constraints are those imposed by slowly changing state variables, the RCCE method is equivalent to a local chemical equilibrium calculation. If the constraints are the species, the RCCE model is similar to a DKM having the same species with the important difference that RCCE calculations always approach the correct final chemical equilibrium state whereas DKM calculations do not. The reason for this is that the equilibrium state approached by a DKM contains only the species included in the model whereas the equilibrium state approached by an RCCE model includes all possible species that can be formed from the elements of which it is composed.

As with all thermodynamic systems, the number of constraints necessary to describe the state of the system within measurable accuracy can be very much smaller than the number of species in the system. Therefore fewer equations are required to determine the state of a system. A further advantage is that only the reaction-rates of slow reactions which change the constraints are needed and these are the ones most likely to be known. Reactions which do not change any constraint are not required. It should be emphasized that the successful implementation of the RCCE method depends critically on the constraints employed.

The primary objectives of this paper are to (1) review the working equations required to implement the RCCE method for chemically reacting systems, (2) discuss the issues involved in the selection and transformation of the constraints, and (3) present a method for determining the initial conditions for highly non-equilibrium systems for which concentrations of some species are zero. To illustrate the method, RCCE calculations of the oxidation of C₁ hydrocarbon in a constant volume adiabatic chamber have been made and compared with the results of a DKM.

2.2 Rate-Controlled Constrained-Equilibrium (RCCE) Method

A detailed description of the Rate-Controlled Constrained-Equilibrium (RCCE) method is given in reference [16]. A concise summary of the working equations for chemically reacting gas mixtures is given below.
It is assumed that energy exchange reactions are sufficiently fast to equilibrate the translational, rotational, vibrational, and electronic degrees of the system subject to constraints on the volume, $V$, and the total energy $E$, of the system. Under these conditions, the energy can be written

$$E = E^T(T)N$$

(1.1)

where $E^T(T)$ is the transpose of the species molar energy vector and $T$ is the temperature. It is further assumed that, consistent with the perfect gas model, the species constraints, $C$, can be expressed as a linear combination of the species mole numbers, $N$, in the form

$$C = AN$$

(1.2)

where, $A$ is the $n_c \times n_sp$ constraint matrix, $n_c$ is the number of constraints, $n_sp$ is the number of species and $C$ and $N$ are column vectors of length $n_c$ and $n_sp$. Maximizing the Entropy, $S(E, V, C)$, subject to the constraints (1) and (2) using the method of undetermined Lagrange multipliers, [16] we obtain the constrained composition of the system

$$N^c = (M / p) \exp(-\mu^0 - \mu^c)$$

(1.3)

where $M$ is the mole number, $p=MRT/V$ is the pressure, $\mu^0 = (h^0 - T \xi^0) / RT$ is the vector of dimensionless standard Gibbs free energy of species vector $N$, and

$$\mu^c = -A^T \gamma$$

(1.4)

is the dimensionless constrained-equilibrium Gibbs free energy of the species, where $A^T$ is the transpose of the constraint matrix, and $\gamma$ is the dimensionless constraint potential (Lagrange multiplier) conjugate to the constraint, $C$. 
Knowing the values of the constraints and energy of the system, substituting Equation (3) into Eqs. (1) and (2) gives a set of \( n_c + 1 \) transcendental equations which can be solved for the temperature, \( T(E,V,C,\mu^n) \), and the constraint potentials, \( \gamma(E,V,C,\mu^n) \). Using generalized equilibrium codes such as GNASA [17] or GSTANJAN [17]. Finally substituting Equation (4) into Equation (3) gives the constrained-equilibrium composition of the system, \( N^c(E,V,C,\gamma) \).

### 1.2.1 Rate-equations for the constraints

It is assumed that changes in the chemical composition of the system are the results of chemical reactions of the type

\[
\nu^- X \leftrightarrow \nu^+ X \tag{1.5}
\]

where \( X \) is the species vector, \( \nu^- \) and \( \nu^+ \) are \( n_r \times n_{sp} \) matrices of stoichiometric coefficients of reactants and products respectively, and \( n_r \) is the number of reactions. The corresponding rate-equations for the species can be written

\[
\dot{\nu} = V_{\nu} \nu \tag{1.6}
\]

where \( \nu = \nu^+ - \nu^- \), \( r = r^+ - r^- \), and \( r^+ \) and \( r^- \) are the forward and reverse reaction rate column vectors of length \( n_r \).

Differentiating equations (1.1) and (1.2) with respect to time and using equation (1.6), we obtain equations for the energy and constraints

\[
\dot{E} = \dot{E}^c + E^c \dot{\nu} \tag{1.7}
\]

and

\[
\dot{\gamma} = A \dot{\nu} = Br \tag{1.8}
\]

where

\[
B = A \nu \tag{1.9}
\]
is an \( n_v \times n_r \) matrix giving the rate of change of constraints due to elementary chemical reactions among species and \( C_v = \partial E / \partial T \) is the molar specific heat vector at constant volume. It follows from equation (1.9) that a reaction \( k \) for which all \( B_{ik} \) are zero will be in constrained equilibrium and that a constraint \( i \) for which all \( B_{ik} \) are zero will be conserved. The latter is the case for the elements.

Given equations for the state-variables, \( V(t) \) and \( E(t) \), and initial values for the species, \( N(0) \), equations (1.7) and (1.8) can be integrated in stepwise fashion to obtain the temperature, \( T(t) \) and species constraints, \( C(t) \). At each time step, a generalized equilibrium code, such as those previously mentioned, must be used to determine the temperature, \( T(E,V,C,\mu^\circ) \), and constrained-equilibrium composition, \( N^e(E,V,C,\mu^\circ) \). These, in turn, can be used to evaluate the reaction rates \( r(T,V,\mu^\circ,N^e) \) required for the next step. Note that only the rates of reactions which change constraints, i.e. those for which \( B_{ik} \neq 0 \), are required for RCCE calculations. All other reactions are in constrained-equilibrium.

### 1.2.2 Rate equations for the constraint potentials

Although direct integration of the rate-equations for the constraints is relative straightforward and simple to implement, it has proved to be relatively inefficient and time consuming due to the slowness of the constrained-equilibrium codes currently available [17]. An alternative method, first proposed by Keck [16] and implemented in later works [18-19], and also applied by Tang and Pope [13] and Jones and Rigopoulos [14], is the direct integration of the rate-equations for the constraint potentials.

Differentiating equation (1.3) with respect to time and substituting the result into equation (1.7) and (1.8) yields the \( n_c+1 \) implicit equation for the constraint-potentials and temperature:

\[
D_r^T \& C = D_V \frac{\partial C}{\partial V} - D_T \frac{\partial C}{\partial T} + \& = 0
\]  

(1.10)
where

\[
D_{ri} = \sum_j a_{ij} E_j N_j^r
\]  \hspace{1cm} (1.10a)

\[
D_V = \sum_j E_j N_j^c
\]  \hspace{1cm} (1.10b)

\[
D_T = \sum_j (C_{ij} T + \frac{E_j^2}{RT}) N_j^r
\]  \hspace{1cm} (1.10c)

and

\[
C_T = C_T - \frac{C_T}{V} - \frac{C_T}{T} + B_T = 0
\]  \hspace{1cm} (1.11)

where

\[
C_{r,ik} = \sum_j a_{ij} a_{kj} N_j^r
\]  \hspace{1cm} (1.11a)

\[
C_{v,i} = \sum_j a_{ij} N_j^c
\]  \hspace{1cm} (1.11b)

\[
C_{t,i} = \sum_j a_{ij} E_j N_j^r / RT
\]  \hspace{1cm} (1.11c)

In this case, given equations for the state variables, \(V(t)\) and \(E(t)\), and initial values for the constraint-potentials \(\gamma(0)\), equations (1.10) and (1.11) can be integrated using implicit ODE integration routines such as DASSL [20] to obtain the constraint potentials, \(\gamma(t)\), and temperature, \(T(t)\). The constrained-equilibrium composition, \(N^c(E, V, t)\), of the system can then be determined using equation (13). The number of unknowns is reduced from the number of species, \(n_{sp} + 1\) included in a DKM calculation to the number of constraints, \(n_c + 1\) used in the RCCE calculations. As previously noted, only the rate constants for those reactions which change constraints, i.e. \(B_{ik} \neq 0\), are needed. Note that, once the constraint-potentials have been determined, the constrained concentration of any species for which the standard Gibbs free energy is known can be calculated whether or not it is explicitly included in the reaction mechanism. Finally, the entropy of the system always increases and the system goes to the correct chemical equilibrium state for the specified state variables and elemental composition. This is not true for DKM.
calculations where only the concentrations of the species included in the species list, which explicitly participate in the reaction mechanism, can be determined. This difference becomes increasingly significant for DKM-derived reduced models, in which only the major energy containing species are included and many minor species of potential interest for air pollution and chemical processing are omitted.

2.3 Selection of constraints

The careful selection of constraints is the key to the success of the RCCE method. Among the general requirements for the constraints are that they must a) be linearly independent combinations of the species mole numbers, b) hold the system in the specified initial state, c) prevent global reactions in which reactants or intermediates go directly to products and, d) determine the energy and entropy of the system within experimental accuracy. In addition, they should reflect whatever information is available about rate-limiting reactions which control the evolution of the system on the time scale of interest. Slower reactions lead to fixed constraints; faster reactions will be in equilibrium.

In the present work, the focus is on applications of the RCCE method to chemically reacting gas phase mixtures. In the temperature and pressure range of interest, the rates of nuclear and ionization reactions are negligible compared to those for chemical reactions and the fixed constraints are the neutral elements of hydrogen, carbon, oxygen, nitrogen, etc., designated by EH, EC, EO, EN, in this case.

Under these conditions, the slowest reactions controlling the chemical composition are three-body dissociation/recombination reactions and reactions which make and break valence bonds. Such reactions are slow in endothermic direction because of the high activation energies required, and in the exothermic direction because of the small radical concentrations involved. They impose slowly varying time-dependent constraints on the number of moles, \( M \), of gas and the free valence, \( FV \), of the system respectively. A finite value of \( FV \) is a necessary condition for chemical reaction.

A third important time-dependent constraint, imposed by slow OO bond-breaking reactions, is the free-oxygen, FO, defined as any O atom not directly bound to another O atom. An increase in FO is a necessary condition for the formation of the major reaction products of hydrocarbon oxidation, \( H_2O, CO_2 \) and CO.
Two additional time-dependent constraints which have been found useful for RCCE calculations are: \( \text{OHO} = \text{OH} + \text{O} \) and \( \text{DCO} = \text{HCO} + \text{CO} \). The former is a consequence of the relatively slow OHO changing reaction \( \text{RH} + \text{OH} \Leftrightarrow \text{H}_2\text{O} + \text{R} \) coupled with the fast reaction \( \text{RH} + \text{O} = \text{OH} + \text{R} \) which equilibrates OH and O. The later is a consequence of the slow spin-forbidden reaction \( \text{CO} + \text{HO}_2 \Leftrightarrow \text{CO}_2 + \text{OH} \) coupled with the fast reaction \( \text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2 \) which equilibrates HCO and CO.

The 8 constraints EH, EO, EC, M, FV, FO, OHO, and DCO are problem independent and may therefore be considered “universal” constraints. Along with the equilibrium reactions

\[
\begin{align*}
\text{H}_2\text{O} &= \text{OH} + \text{H} \\
\text{H}_2\text{HOO} &= \text{H}_2\text{O}_2 + \text{H} \\
\text{HCO} + \text{O}_2 &= \text{CO} + \text{HO}_2
\end{align*}
\] (CE1) (CE2) (CE3)

they are sufficient to determine the constrained-equilibrium mole fractions of the fuel and the 10 major hydrocarbon combustion products H, O, OH, HO\(_2\), H\(_2\), O\(_2\), H\(_2\)O, H\(_2\)O\(_2\), CO and CO\(_2\).

In the present investigation of C\(_1\)-hydrocarbon oxidation, 4 additional fuel-dependent constraints have been used. The first is a constraint on the fuel, \( \text{FU} \), imposed by slow H – abstraction reactions of the type \( \text{FU} + \text{O}_2 \leftrightarrow \text{FR} + \text{HO}_2 \) and even slower dissociation/recombination of the type \( \text{AB} + \text{M} \leftrightarrow \text{A} + \text{B} + \text{M} \). This constraint is necessary to hold the system in its initial state. The second is a constraint on fuel radicals, \( \text{FR} \), which is necessary to prevent the equilibration of forbidden exothermic global reactions of the type \( \text{FR} + 2\text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O}_2 + \text{H}_2 + \text{CO} \) which would otherwise convert fuel radicals directly to CO. The third is a constraint on alkylperoxides, \( \text{APO} = \text{CH}_3\text{OOH} + \text{CH}_3\text{OO} + \text{CH}_2\text{OOH} \), imposed by slow reactions which convert APO to hydroperoxides coupled with fast reactions which equilibrate the species comprising APO, and the fourth is a constraint on alcohol plus formaldehyde, \( \text{ALCD} = \text{CH}_3\text{OH} + \text{CH}_3\text{O} + \text{CH}_2\text{OH} + \text{CH}_2\text{O} \) imposed by relatively slow reactions which generate/remove ALCD coupled with fast reactions which equilibrate the species comprising ALCD.

3.1 Transformation of constraints
The integration of equations (1.10) and (1.11) for the constraint-potentials requires inversion of the $C_i$ matrix. The performance of the implicit integrators, such as DASSL, are quite sensitive to the structure of this matrix. In general, the codes work best when the large elements of the matrix lie on or close to the main diagonal. This is not usually the case for the initial set of constraints chosen and a variety of error messages such as “singular matrix” or “failure to converge” may be encountered. The problem can almost always be solved by a transformation of the square sub-matrix relating the major species and the constraints to a diagonalized form. The physical meaning of the transformed matrix may not be clear in all cases but if it improves the speed and reliability of the integrator, the desired objective will have been achieved. In this connection, it is important to note that any linear combination of the original linearly independent constraints for which the integrator works should give the same final result. This can be a useful check on the numerical results.

A general transformation of the constraint matrix can be made as follows. Assume $G$ is a square transformation matrix of order $n_c$. Multiplying equation (1.2) through by this matrix yields

$$\tilde{C} = GC = \tilde{A} N$$

(1.12)

where

$$\tilde{A} = GA$$

(1.13)

is the transformed $n_c \times n_{sp}$ constraint matrix that relates the transformed constraint vector, $\tilde{C}$, to the species vector, $N$. The corresponding transformation for the reaction matrix is

$$\tilde{B} = GB$$

(1.14)

The transformation equations for the constraint potentials can be obtained by noting that the Gibbs free energy, $\mu^c$, is invariant under the transformation. Equation (4) then gives
\[- \mu^c = A^T \gamma = \tilde{A}^T \gamma = (GA)^T \gamma = A^T G^T \gamma \]  \tag{1.15}

Multiplying Equation (15) by \( A \) we obtain

\[- A \mu^c = S \gamma = SG^T \gamma \]  \tag{1.16}

where

\[ S = AA^T \]  \tag{1.17}

is a symmetric matrix of order \( n_c \). Assuming that \( S \) is non-singular, it follows from Equation (16) that

\[ \gamma = G^T \tilde{\gamma} \]  \tag{1.18a}

and, since \( G \) is non-singular,

\[ \tilde{\gamma} = (G^T)^{-1} \gamma \]  \tag{1.18b}

2.4 Determination of initial conditions

For systems initially in a constrained-equilibrium state, the initial values of the constraint potentials are finite. However, for a system initially in a non-equilibrium state, where the concentrations of one or more species is zero, it can be seen from equation (1.3) and (1.4) that one or more constraint-potentials must be infinite. This condition is encountered in ignition-delay-time calculations, where the system is initially far from equilibrium and the initial concentrations of all species except the reactants are assumed to be zero.

One method of dealing with this problem is to assign small partial pressures to as many major product species as required to give finite values for the constraint potentials. Ideally the choice should be made in such a way that the partial pressures of all other product species will be smaller than the assigned partial pressures. A reasonable initial
choice for a major species corresponding to a constraint is the one with the minimum standard Gibbs free energy in the group of species included in the constraint.

To implement this method, equation (1.2) is decomposed in the form

$$
\mathbf{C} = \mathbf{AN} = \begin{bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \end{bmatrix} \begin{bmatrix} \mathbf{N}_1 \\ \mathbf{N}_2 \end{bmatrix}
$$

(1.19)

where $\mathbf{A}_{11}$ is an $n \times n$ non-singular, square matrix giving the contribution of the major species vector, $\mathbf{N}_1$, to the constraint vector, $\mathbf{C}$, and $\mathbf{A}_{12}$ is an $n \times (n - n)$ matrix, giving the contribution of $\mathbf{N}_2$ to $\mathbf{C}$. The corresponding decomposition of equation (1.4) is

$$
\mathbf{\mu} = \begin{bmatrix} \mu_1 \\ \mu_2 \end{bmatrix} = -\mathbf{A}_1^T \mathbf{\gamma} = -\begin{bmatrix} \mathbf{A}_{11}^T \\ \mathbf{A}_{12}^T \end{bmatrix} \mathbf{\gamma}
$$

(1.20)

Initial values for the constraint potentials can now be obtained by assuming $\mu_1(0) >> \mu_2(0)$. This gives

$$
\gamma(0) = -(\mathbf{A}_{11}^T)^{-1} \mu_1(0) = -(\mathbf{A}_{11}^T)^{-1} (\ln p_1(0) + \mu^0)
$$

(1.21)

Having determined the initial values of the constraint-potential vector, one can now check the assumption that the initial partial pressures of the minor species are small using the relation

$$
\ln p_2(0) = -\mathbf{A}_{12}^T \gamma(0) - \mu_2^0
$$

(1.22)

If they are not, an alternative choice for the major species will usually solve the problem.

In initial RCCE calculations using constraints based on kinetic considerations, problems involving the convergence of the implicit integrators used were frequently encountered. These were caused primarily by the fact the $\mathbf{C}_{11}$ matrix in equation (1.11) contained large off diagonal elements. These problems were solved by a transformation which diagonalized the $\mathbf{A}_{11}$ matrix. Using the transformation matrix $\mathbf{G} = \mathbf{A}_{11}^{-1}$ we obtain from equation (1.12)
\[ \tilde{C} = A_{11}^{-1} C = A_{11}^{-1} A_{12} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} = \begin{bmatrix} I_{11} & A_{11}^{-1} A_{12} \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} = \tilde{A} N \]  

(1.23)

and it follows from equation (1.15) that

\[ \mu_1(0) = \ln p_1(0) + \mu^0 = -I_{11} \tilde{\gamma}(0) = -\tilde{\gamma}(0) \]  

(1.24)

It can be seen from this equation, that in the diagonalized representation, the initial constraint potentials are simply the initial Gibbs free energies of the major species chosen as surrogates. The transformed reaction rate matrix is

\[ \tilde{B} = A_{11}^{-1} B \]  

(1.25)

### 2.5 RCCE calculations for C\textsubscript{1} hydrocarbon oxidation

To illustrate the RCCE method, we consider the homogeneous stoichiometric oxidation of three mono-carbon fuels, namely methane (CH\textsubscript{4}), methanol (CH\textsubscript{3}OH) and formaldehyde (CH\textsubscript{2}O) with pure oxygen in a constant volume reactor over a wide range of initial temperatures (900K-1500K) and pressures (1atm-100atm). The 12 constraints used in the RCCE calculations are summarized in Table 1.

The DKM calculations with which the RCCE results are compared involve only C\textsubscript{1} chemistry and include 29 species and 133 reactions, without nitrogen chemistry. Twenty species and 102 reactions were taken from the widely known and used GRI-Mech3.0 [21] mechanism. This model does not include alkyl peroxides and therefore is not expected to be valid under high-pressure low-temperature conditions. To obtain a model valid under these conditions an additional 9 alkyl peroxides and organic acids were included along with 31 reactions with rates taken from [22] or estimated by the authors.

Of the 133 reactions employed in the DKM calculations only 102 reactions change one or more constraints of the constraints in Table 1 and are therefore of interest. The remaining 31 are in constrained-equilibrium and are therefore redundant in RCCE calculations, in principle, only the fastest reaction in a group which changes a given constraint is required for a system to go from the specified initial state to the correct final
chemical-equilibrium state. However in practice, it is usually necessary to include additional reactions to achieve the desired accuracy for the time-evolution of the system. In this work, excellent agreement between DKM calculations and RCCE calculations was obtained for all $C_1$ species using 12 constraints and 102 reactions and acceptable agreement was obtained using 12 constraints and 20 reactions for methane, 10 constraints and 16 reactions for methanol, and 9 constraints and 12 reactions for formaldehyde.

1.5.1 Methane (CH4) Oxidation

The constraint matrix for CH$_4$ used in this work is shown in Table 2a and the corresponding diagonalized matrix used to set the initial conditions and carry out the numerical calculations is shown in Table 2b. Diagonalized 12 constraints and 29 species are included. The corresponding RCCE reaction flow diagram is shown in figure 1.1. The constrained species are enclosed by dashed lines. Except for the initiation steps, this diagram also includes the sub-mechanisms involved in the oxidation of CH$_3$OH and CH$_2$O.

As can be seen, the oxidation process is initiated by the highly endothermic CH$_4$ constraint changing H-abstraction reaction

$$\text{CH}_4 + \text{O}_2 \leftrightarrow \text{CH}_3 + \text{HO}_2$$  \hspace{1cm} (RC1)

This is followed by the two competing CH$_3$ constraint-changing reactions

$$\text{CH}_3 + \text{O}_2 + \text{M} \leftrightarrow \text{CH}_3\text{OO} + \text{M}$$  \hspace{1cm} (RC2)
$$\text{CH}_3 + \text{O}_2 \leftrightarrow \text{CH}_3\text{O} + \text{O}$$  \hspace{1cm} (RC3)

The first is most important at low temperatures and is followed by the constrained-equilibrium reactions

$$\text{CH}_3\text{OO} + \text{H}_2\text{O}_2 = \text{CH}_3\text{OOH} + \text{HO}_2$$  \hspace{1cm} (CE1)
$$\text{CH}_3\text{OOH} + \text{HO}_2 = \text{CH}_2\text{OOH} + \text{H}_2\text{O}_2$$  \hspace{1cm} (CE2)

which equilibrate the alkylperoxides in APO. The second is most important at high temperatures and is followed by the constrained-equilibrium reactions

$$\text{H}_2 + \text{O} = \text{OH} + \text{H}$$  \hspace{1cm} (CE3)

which equilibrates the water radicals in OHO, and constrained-equilibrium reactions
CH$_3$O+ H$_2$O$_2$=CH$_3$OH+ HO$_2$ (CE4)
CH$_3$OH+HO$_2$=CH$_3$OH+H$_2$O$_2$ (CE5)
CH$_3$O+O$_2$=CH$_2$O+HO$_2$ (CE6)

which equilibrate the free oxygen species in ALCD. The CH$_4$ constraint-changing reaction

$$\text{OH}+\text{CH}_4 \leftrightarrow \text{CH}_3+\text{H}_2\text{O}$$ (RC4)

converts OH in OHO to the product H$_2$O and regenerates CH$_3$.

The stable intermediate CH$_2$O in ALCD is oxidized by the constraint-changing H-abstraction reaction

$$\text{CH}_2\text{O}+\text{O}_2 \leftrightarrow \text{CHO}+\text{HO}_2$$ (RC5)

and the constrained-equilibrium reaction and the fast equilibrium reaction

$$\text{CHO}+\text{O}_2 = \text{CO}+\text{HO}_2$$ (CE7)

to form DCO. The CO in DCO is converted to the product CO$_2$ by the FO constraint-changing reaction

$$\text{CO}+\text{HO}_2 \leftrightarrow \text{CO}_2+\text{OH}$$ (RC6)

Finally the 8 major H/O species are determined by the 4 constraint-changing reactions

$$\text{HO}_2 \leftrightarrow \text{H}+\text{O}_2$$ (RC7)
$$\text{HO}_2+\text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2+\text{O}_2$$ (RC8)
$$\text{HO}_2+\text{H} \leftrightarrow \text{OH}+\text{OH}$$ (RC9)
$$\text{H}+\text{O}_2 \leftrightarrow \text{OH}+\text{O}$$ (RC10)

which change M, FV, FO, and OHO respectively, plus the 2 constrained-equilibrium reactions

$$\text{H}_2+\text{O} = \text{OH}+\text{H}$$ (CE3)
$$\text{H}_2+\text{HO}_2 = \text{H}_2\text{O}_2+\text{H}$$ (CE8)

and the elemental constraints EH and EO.

As the above reactions proceed, the radical population increases rapidly and all constraint-changing reactions included in the kinetic model become involved in determining the evolution of the system and its approach to final chemical-equilibrium. Of particular importance are reactions of the type

$$\text{CH}_4+\text{Q} \leftrightarrow \text{CH}_3+\text{HQ}$$ (RC1.1)
and

\[ \text{CH}_2\text{O} + \text{Q} \leftrightarrow \text{CHO} + \text{HQ} \quad \text{(RC5.1)} \]

where \( \text{Q} \) can be any radical, e.g. \( \text{HO}_2 \), \( \text{OH} \), \( \text{H} \), \( \text{O} \).

1.5.2 \( \text{CH}_4 \) Results for Full 133 Reaction Set

Time-dependent temperature profiles of stoichiometric mixtures of methane and oxygen at initial temperatures of 900K and 1500K and different initial pressures are shown in figure 1.2. All 12 constraints listed in Table 2 have been included. As previously noted, only 102 of the reactions in the full set of 133 reactions change constraints and are therefore required. The remaining 31 are in constrained-equilibrium and are redundant in RCCE calculations.

It can be seen that the agreement with DKM calculations is excellent over the entire range of pressure and temperature covered. Note that the temperature overshoot at low pressures due to slow three-body recombination and dissociation reactions is well reproduced by the constraint \( \text{M} \) on the total moles. Also, the same comparisons have been made for rich \((\phi = 1.2)\) and lean \((\phi = 0.8)\) mixtures in figure 1.3. RCCE predictions of ignition delay times at low temperature, high pressure are within 1% of those by DKM. At high temperature, low pressure the results agree within 1%-5% of accuracy.

More complete results are shown on log-log plots in figure 1.4 for the initial conditions 900 K, 100 atm, where the dominant radicals are \( \text{HO}_2 \approx \text{CH}_3 \) at early times and \( \text{CH}_3\text{OO} \) at late times, and in figure 1.5 for the initial conditions 1500 K, 1atm, where the dominant radicals are \( \text{HO}_2 \approx \text{CH}_3\text{OO} \) at all times. As can be seen in figures 1.3a and 1.4a, the temperature first decreases due to the fact that the initiation reactions are all endothermic then later increases as exothermic reactions become important. The agreement between RCCE and DKM calculations, especially with regard to the time at which the temperature difference becomes positive, is excellent.

Figures 1.3b and 1.4b show the time dependence of the constraint-potentials for the diagonalized constraint-matrix and figures 1.3c and 1.4c show the corresponding constraint-potentials for the original constraint matrix. Note that for the original constraint matrix, all the time-dependent constraint-potentials go to zero at equilibrium as
required, while those for the elements go to values identical with those obtained from the STANJAN equilibrium code [23]. Once the constraint-potentials have been determined, the constrained–equilibrium mole fractions of any species for which the standard Gibbs free energy is known can be calculated from Equation (3).

The fixed elemental constraints and the most important time-dependent constraints M, FV, FO, FU and FR are shown in figures 1.3d and 1.4d and the mole fractions of the major species are shown in figures 1.3e-h and 1.4e-h. It can be seen that overall agreement is very good.

To investigate the sensitivity of the ignition delay time to the number of constraints used, a series of RCCE calculations was carried out starting with the 8 constraints EH, EC, EO, M, FV, FO, OHO FU and adding additional constraints one at a time. The results for both high and low temperature conditions are compared with those of the DKM in figure 1.6. It can be seen that for high temperature conditions, 9 constraints are sufficient to give the agreement within 5%, while for low temperature conditions, 11 constraints are required to give the same agreement.

5.1.2 Reduced CH\textsubscript{4} reaction mechanism

In the initial studies, a full set of 133 reactions was used for both the RCCE and DKM calculations. Clearly not all of these are of equal importance especially in RCCE calculations where, in principle, only one independent reaction for each time-dependent constraint is required to allow the system to relax from the specified initial state to the correct final chemical-equilibrium state. In general, however, this does not give the correct time evolution of the system and additional reactions are required to achieve the desired degree of accuracy.

By systematically eliminating unimportant reactions, a reduced mechanism for C\textsubscript{1} hydrocarbons involving the 24 constraint-changing reactions in Table 3 has been found. The minimum set of reactions required for the individual fuels: CH\textsubscript{4}, CH\textsubscript{3}OH and CH\textsubscript{2}O, are indicated by cross marks in the left columns of the Table. The constraints required for each one of the fuels are indicated by cross marks in the top rows of the Table. Arrhenius
rate-parameters and uncertainty factors taken from Tsang and Hampson [22] are also shown in the right hand columns of the Table. It can be seen that many of the rates have estimate uncertainties greater than a factor of 3 even though these are among the simplest and best known reactions. For each constraint where more than one reaction is listed, the redundant reactions are important at different stages in the evolution of the system.

The reduced RCCE calculations for CH$_4$ were carried out using 9 time-dependent constraints and 20 reactions. The results are shown in figure 1.7 and it can be seen that the RCCE calculations give ignition delay times at both low and high temperatures within a few percent of those obtained using the DKM.

It is also of interest to compare the reduced RCCE calculations for CH$_4$ with DKM calculations using 15 species and the same reduced reaction set. The resulting temperatures vs. time histories are shown in figure 1.8. The initial pressures are 100 atm and 1 atm for low and high temperatures respectively. It can be seen that the DKM calculations using the reduced mechanism do not give either the correct ignition delay time or final chemical-equilibrium state. The reason is that the number of independent reactions required for a DKM calculation must at least equal the number of species included and, in this case, there are 29 species and only 20 reactions in the model. Conversely, in the RCCE approach, the moles of any species can be found from the constraint-potentials using Equation (3). It follows that any species represented in the constraint matrix will evolve dynamically even if there is no kinetic path provided in the mechanism. This point is illustrated in figure 1.9 which compares reduced RCCE(12,20) and DKM(29,133) results for the mole fractions of H$_2$ as a function of time. Although no reactions involving H$_2$ are explicitly included in the RCCE(12,20) calculations, both the ignition delay time and the equilibrium mole fractions are in excellent agreement with the DKM(29,133) results.

The fact that RCCE calculations can be carried out with fewer rate equations than unknowns and always give the correct final chemical-equilibrium state sets the RCCE method apart from all reduction techniques which do not use a constrained-equilibrium manifold for reconstructing the missing species concentrations. This point is illustrated in Fig. 10 where the final equilibrium mole fractions of the most abundant C$_1$ and C$_2$ species calculated using only C$_1$ kinetics in RCCE and DKM are compared with values obtained
using the STANJAN equilibrium code. For C\textsubscript{1} species, all values agree perfectly. However for C\textsubscript{2} species, the RCCE and STANJAN values agree but the DKM values are unchanged from their original assigned values for the obvious reason that the C\textsubscript{1} kinetics used in the DKM does not include any reactions which change C\textsubscript{2} species.

1.5.3 Methanol (CH\textsubscript{3}OH) Oxidation

The same set of basic constraints used for CH\textsubscript{4} can be used for the oxidation of methanol. However in this case, the fuel molecule FU is CH\textsubscript{3}OH and fuel radical constraint, FR, is CH\textsubscript{3}O+CH\textsubscript{2}OH+CH\textsubscript{2}O. In addition, an examination of the kinetics shows that alkylperoxydes reactions are not important and the APO constraint can be eliminated. This results in a reduction of the total number of constraints from 12 to 10. The corresponding reaction diagram is shown in Fig 11.

1.5.4 Reduced CH\textsubscript{3}OH reaction mechanism

A reduced set of 16 reactions for CH\textsubscript{3}OH oxidation is included in Table 3. RCCE calculations using these 16 reactions and the 7 time-dependent constraints included in Table 3 are compared with DKM calculations using 133 reactions and 29 species in figure 1.12. It can be seen that the temperature vs. time plots are in excellent agreement over the entire range of temperature and pressure covered. The agreement for all other variables is similar to that for CH\textsubscript{4}.

1.5.5 Formaldehyde (CH\textsubscript{2}O) Oxidation

The reaction diagram for CH\textsubscript{2}O oxidation is shown in figure 1.13 and a reduced kinetic model is included in Table 3. The reduced kinetic model in this case is even simpler than that for CH\textsubscript{3}OH and only 9 constraints and 12 reactions are required in the RCCE calculations. A comparison of temperature versus time plots is shown in figure 1.14 and again it can be seen that the agreement between RCCE and DKM calculations is
excellent. As in the case of CH$_3$OH, plots of all other variables are also in excellent agreement and are similar to those for CH$_4$.

2.6 Summary and conclusions

RCCE calculations of methane, methanol and formaldehyde oxidation over a wide range of initial temperatures and pressures have been made using up to 12 constraints and 133 reactions and excellent agreement with “detailed”-kinetic-model (DKM) calculations using 29 species and the same reactions have been obtained. In addition, reduced sets of 20 reaction for methane, 12 reactions for methanol and 12 reactions for formaldehyde have been found, which when employed in the RCCE calculations give results identical to those obtained using the full 133 reactions.

Among the important features of the RCCE method for simplifying the kinetics of hydrocarbon oxidation are:

1. It is based on the well established Maximum Entropy Principle of thermodynamics rather than mathematical approximations.

2. The entropy always increases as the system evolves and an approach to the correct final chemical-equilibrium state for the specified elements is guaranteed. This is not true for DKMs where only the listed species are included and all others are missing.

3. The total number of constraints required to describe the state of a complex chemical system can be very much smaller than the number of species in the system resulting in fewer equations.

4. It enables one to obtain a good description of the kinetic behaviour of a complex chemically reacting system using a relatively small number of constraint-controlling reactions without having to start with a DKM.
5. 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 model used.

6. If the only constraints on the system are the elements and the state variables, RCCE calculations reduce to local equilibrium (LTE) calculations.

7. If the species are used as constraints, RCCE calculations simulate DKM calculations with the important distinction that only the listed species can appear in DKM calculations whereas all possible species are implicitly included in RCCE calculations.

8. The accuracy of the results can be systematically improved by adding constraints one at a time.

2.7 Acknowledgment

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2.8 References


[23] Reynolds, W. C., STANJAN Program, Stanford University, ME270, HO#7
Definition of the Constraints

<table>
<thead>
<tr>
<th>Constraint</th>
<th>Definition of the Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 EC</td>
<td>Elemental carbon</td>
</tr>
<tr>
<td>2 EO</td>
<td>Elemental oxygen</td>
</tr>
<tr>
<td>3 EH</td>
<td>Elemental hydrogen</td>
</tr>
<tr>
<td>4 M</td>
<td>Total number of moles</td>
</tr>
<tr>
<td>5 FV</td>
<td>Moles of free valance (any unpaired valence electron)</td>
</tr>
<tr>
<td>6 FO</td>
<td>Moles of free oxygen (any oxygen not directly attached to another oxygen)</td>
</tr>
<tr>
<td>7 OHO</td>
<td>Moles of water radicals (O+OH)</td>
</tr>
<tr>
<td>8 DCO</td>
<td>Moles of HCO+CO</td>
</tr>
<tr>
<td>9 FU</td>
<td>Moles of fuel molecule (CH₄ in the case of Methane)</td>
</tr>
<tr>
<td>10 FR</td>
<td>Moles of fuel radical(s) (CH₃ in the case of Methane)</td>
</tr>
<tr>
<td>11 APO</td>
<td>Moles of AlkyPerOxydes (CH₂OO+CH₂OOH+CH₂OOH)</td>
</tr>
<tr>
<td>12 ALCD</td>
<td>Moles of Alcohols+Aldehydes (CH₂O+CH₂OH+CH₂OH+CH₂O)</td>
</tr>
</tbody>
</table>
Table 1.2a

Constraint Matrix $A$ for the C$_1$ system

|   | 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 |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| EC | 1  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 0  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| EO | 2  | 2  | 0  | 2  | 2  | 1  | 1  | 1  | 0  | 0  | 2  | 1  | 0  | 1  | 1  | 0  | 0  | 1  | 1  | 1  | 2  | 2  | 2  | 2  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  |
| BH | 0  | 0  | 2  | 2  | 1  | 2  | 1  | 0  | 4  | 3  | 4  | 2  | 1  | 3  | 1  | 1  | 2  | 0  | 0  | 3  | 4  | 1  | 2  | 1  | 3  | 3  | 3  | 2  | 1  | 1  | 1  |
| 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  | 1  | 1  | 1  |
| FV | 0  | 0  | 0  | 0  | 1  | 0  | 1  | 0  | 0  | 1  | 0  | 1  | 1  | 1  | 3  | 2  | 4  | 2  | 1  | 0  | 1  | 0  | 1  | 1  | 1  | 0  | 1  | 1  | 0  | 1  | 1  |
| FD | 0  | 0  | 0  | 0  | 1  | 0  | 1  | 0  | 1  | 0  | 0  | 1  | 0  | 1  | 1  | 0  | 0  | 1  | 1  | 1  | 2  | 2  | 2  | 0  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| OHO| 0  | 0  | 0  | 0  | 0  | 0  | 1  | 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  |
| DCO| 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| FU | 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  | 0  | 0  | 0  | 0  | 0  | 0  |
| FR | 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  | 0  | 0  | 0  | 0  | 0  | 0  |
| APO| 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| ALCO| 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 0  | 0  | 0  | 0  | 0  |

Table 1.2b


### Diagonalized $A$ Matrix

|   | 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 |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| CO2 | 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  | 0  | 0  |
| O2  | 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  | 0  | 0  | 0  |
| H2  | 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  | 0  | 0  | 0  |
| H2O2| 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  | 0  | 0  | 0  |
| H2O | 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  | 0  | 0  | 0  |
| HO  | 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  | 0  | 0  | 0  |
| CO  | 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  | 0  | 0  | 0  |
| CH4 | 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  | 0  | 0  | 0  |
| CH3 | 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  | 0  | 0  | 0  |
| CH3OOH| 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 | 0 | 0 |
| H2CO| 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 | 0 | 0 |

Table 1.3
Reaction matrix, $B_{ik}$, for reduced C$_1$ hydrocarbon mechanism (Units: cc, mole, Kcal, sec)

| CH$_3$O | CH$_3$OH | CH$_4$ | REK | CH | CH$_3$O | CH$_3$OH | CH$_2$O | H | F | V | O | HO | HCO | AC | CO | APO | Log(Ar) | $E_r$ | Uncert. Factor |
|--------|--------|-------|-----|---|-----|------|-------|---|---|---|---|---|-----|-----|---|-----|-----|--------|-----|---------------|
| x 1    | CH$_4$+O$_2$=CH$_3$+HO$_2$ | -1 1 0 0 | 0 0 0 0 0 0 0 0 0 0 | 13.6 | 57.3 | 5 |
| x 2    | CH$_4$+HO$_2$=CH$_3$+H$_2$O$_2$ | -1 1 0 0 | 0 0 0 0 0 0 0 0 0 0 | 11.3 | 18.7 | 5 |
| x 3    | CH$_4$+OH=CH$_3$+H$_2$O | -1 1 0 0 | 0 0 0 -1 0 0 0 0 | 13.5 | 2.1 | 1.4 |
| x 4    | CH$_4$+CH$_3$O=CH$_3$+CH$_3$OH | -1 1 0 0 | 0 0 0 0 0 0 0 0 0 | 11.3 | 18.6 | 10 |
| x 5    | CH$_3$+O$_2$+M=CH$_3$O+O$_2$ | 0 -1 0 0 | -1 0 0 0 0 0 1 | 12.0 | 0.0 | 3 |
| x 6    | CH$_3$+O$_2$=CH$_3$O+O | 0 -1 0 0 | 0 2 2 1 0 1 0 | 12.9 | 29.4 | 3 |
| x 7    | CH$_3$+HO$_2$=CH$_3$O+OH | 0 -1 0 0 | 0 0 2 1 0 1 0 | 13.3 | 0.0 | 3 |
| x 8    | CH$_3$+OH=CH$_3$O+H$_2$O | 0 -1 0 0 | 0 0 2 0 2 0 2 -1 | 13.4 | 0.0 | 3 |
| x 9    | CH$_3$O+O$_2$=CH$_3$O+O$_2$ | 0 0 -1 0 | 0 2 0 0 0 0 0 0 | 13.4 | 45.2 | 10 |
| x 10   | CH$_3$O+OH=CH$_3$O+H$_2$O | 0 0 -1 0 | 0 2 0 0 0 0 0 0 | 13.4 | 45.2 | 10 |
| x 11   | CH$_3$O+O$_2$+M=CH$_3$O+O$_2$+M | 0 0 -1 0 | 0 2 0 0 0 0 0 0 | 13.4 | 12.6 | 10 |
| x 12   | CH$_3$O+OH=CH$_3$O+H$_2$O | 0 0 -1 0 | 0 2 0 0 0 0 0 0 | 13.7 | 1.5 | 2 |
| x x x 13 | CH$_2$O+O$_2$=CHO+H$_2$O | 0 0 0 -1 | 0 2 0 0 1 -1 0 | 14.0 | 40.0 | 2 |
| x x x 14 | CH$_2$O+HO$_2$=CHO+H$_2$O | 0 0 0 -1 | 0 0 0 0 1 -1 0 | 13.6 | 12.0 | 3 |
| x x x 15 | CH$_2$O+OH=CHO+H$_2$O | 0 0 0 -1 | 0 0 0 -1 1 1 0 | 13.7 | -0.4 | 2 |
| x x x 16 | H+O$_2$+M=H$_2$O+M | 0 0 0 0 -1 0 0 0 0 0 0 | 15.4 | 0.0 | |
| x x x 17 | OH+H+M=H$_2$O+M | 0 0 0 0 -1 -2 0 -1 0 0 0 | 15.5 | 0.0 | 2 |
| x x x 18 | OH+OH+M=H$_2$O+M | 0 0 0 0 -1 -2 -2 -2 0 0 0 | 12.5 | 0.0 | 2 |
| x x x 19 | H+O$_2$=OH+O | 0 0 0 0 0 2 2 2 0 0 0 | 14.0 | 17.0 | 1.5 |
| x x x 20 | CH$_3$O+O$_2$=CH$_3$O+H$_2$O | 0 0 0 0 -1 0 0 0 0 0 | 13.5 | 4.9 | 5 |
| x x x 21 | H+HO$_2$=H$_2$O+O$_2$ | 0 0 0 0 0 2 0 0 0 0 0 | 11.1 | -1.6 | 3 |
| x x x 22 | CO+HO$_2$=CO$_2$+OH | 0 0 0 0 0 2 1 -1 0 0 | 14.2 | 23.6 | 3 |
| x x x 23 | H+HO$_2$=OH+OH | 0 0 0 0 0 2 2 0 0 0 0 | 14.1 | 0.9 | 2 |
| x x x 24 | CO+OH=CO$_2$+H | 0 0 0 0 0 0 0 -1 -1 0 0 | 11.8 | 0.1 | 1.5 |

12 16 20
Figure 1.1: RCCE reaction flow diagram for CH₄ oxidation.
Figure 1.2: Temperature profiles at different initial pressures for stoichiometric mixture of CH₄/O₂ at initial temperatures of 900 K (a), and 1500 K (b).

Figure 1.3: Temperature profiles for mixtures of CH₄/O₂ at different equivalence ratios at initial pressure and temperature of 100 atm and 900K, (a), and 1 atm and 1500 K (b).
Figure 1.4: RCCE versus DKM predictions of stoichiometric CH₄/O₂ auto-ignition at Tᵢ = 900 K, Pᵢ = 100 atm. Lines represent RCCE and symbols represent detailed kinetics.
Figure 1.5: RCCE versus DKM predictions of stoichiometric CH$_4$/O$_2$ auto-ignition at $T_i = 1500$ K, $P_i = 1$ atm. Lines represent RCCE and symbols represent DKM.
Figure 1.6: Constraint dependence study of ignition delay time predictions for stoichiometric CH\textsubscript{4}/O\textsubscript{2} auto-ignition at different initial temperatures.
Figure 1.7: RCCE predictions of temperature profiles for \( T_i = 900 \) K and 1500 K at different initial pressures using the reduced reaction mechanism listed in Table 3, “RCCE (12,20)”, compared with the detailed kinetics model predictions using the original 133 reactions, “DKM(29,133)”. 
Figure 1.8: RCCE predictions of the temperature profiles for $T_i = 900$ K and $1500$ K using the CH$_4$–reduced reaction mechanism listed in Table 3, “RCCE (12,20)”, compared with the DKM predictions using the original 29 species and 133 reactions, “DKM(29,133)”, and the DKM predictions using the same reduced reaction mechanism, including 15 species and 20 reactions “DKM(15,20)”. The initial pressures are 100 atm and 1 atm for low and high temperature cases respectively.
Figure 1.9: RCCE predictions of the H\textsubscript{2} concentration using the CH4 – reduced reaction list, “RCCE(12,20)”, and the DKM using the full mechanism, “DKM(29,133)”. Note that H\textsubscript{2} is not included in the RCCE (12,20) reaction mechanism.
Figure 1.10: Comparison between final equilibrium calculations of the mole fractions of species, $\log_{10}(X_i)$, using STANJAN, RCCE and DKM with $C_2$ – species used in GRI-Mech3.0 added to species list, while using $C_1$ – kinetic mechanism in kinetic calculations.
Figure 1.11: RCCE reaction flow diagram of CH₃OH/O₂ auto-ignition.
Figure 1.12: RCCE predictions of temperature profiles for $T_i = 900$ K and 1500 K at different pressures using the Methanol – reduced reaction list, (Table 3), compared with the DKM predictions using the original 133 reactions and 29 species.
Figure 1.13: RCCE reaction flow diagram of CH$_2$O/O$_2$ auto-ignition.
Figure 1.14: RCCE predictions of temperature profiles for $T_i = 900$ K and 1500 K at different initial pressures of stoichiometric CH$_2$O/O$_2$ mixtures using the Formaldehyde – reduced reaction list (Table 3), “RCCE (9,12)”, compared with the DKM predictions using the original 29 species and 133 reactions, “DKM(29,133)”. 

$P_i = 1$ atm
$P_i = 10$ atm
$P_i = 50$ atm
$P_i = 100$ atm
Chapter 2

Combustion Modelling of Methane-Air Mixtures Using the Rate-Controlled Constrained-Equilibrium Method
Combustion Modelling of Methane/Air Mixtures Using the Rate-Controlled Constrained-Equilibrium Method

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The method of Rate-Controlled Constrained-Equilibrium (RCCE) has been used to study the ignition of methane/air mixtures. The method is based on local maximization of entropy or minimization of a relevant free energy at any time during the non-equilibrium evolution of the system subject to a set of kinetic constraints. These constraints are imposed by slow rate-limiting reactions. Direct integration of the rate equations for the constraint potentials has been used, once the values of which are known, the concentration of all species can be calculated. The RCCE calculations involve 16 total constraints and the results are in good agreement with those obtained by direct integration of a full set of 60 species rate equations over a wide range of temperatures and pressures. The reactor model is constant volume and constant energy. Also, the recently suggested corrections of Chaos and Dryer, Int. J. of Chem. Kin., 2010, 42: 143–150, have been made to the reactor model and the predictions in ignition delay time have been compared with the shock tube experimental data over initial pressures of 1atm-20atm and initial temperatures of 900K -1500K.

2.1 Introduction

The development of kinetic models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. Such models can easily include several hundred of species and several thousands of reactions for heavy hydrocarbon fuels. The fact that the equations governing the dynamics under such models are highly stiff necessitates the development of tools to reduce the complexity of the model while...
maintaining the degree of detail of predictions. Many approaches for this problem have been proposed over the last two decades among which are the Quasi-Steady State Approximation QSSA [1], Partial Equilibrium Approximation PEA [2], Intrinsic Low Dimensional Manifolds (ILDM) [3], Computational Singular Perturbation [4], Adaptive Chemistry [5], Directed Relation Graph (DRG) [6], ICE-PIC method [7], Slow Inertial Manifolds, SIM [15] and Rate-Controlled Constrained-Equilibrium (RCCE) [8].

In this paper we use the method of RCCE to study the kinetics of Methane/Oxygen under constant volume, constant energy constraints. The model includes the formation of C₂ species from Methane and is in fact the extension of Janbozorgi et. al.’s model [11], in which only C₁ chemistry was considered.

Perhaps the most appealing feature of RCCE, as has also been explained in [11] is that, contrary to all dimension reduction models in which the constrained equilibrium assumption is not used, it is not necessary to start with a detailed kinetic model (DKM) which must then be simplified by various mathematical approximations. Instead, one starts with a small number of constraints, to which more constraints can be added, if necessary, to improve the accuracy of the calculations. The number of constraints needed to describe the dynamic state of the system within experimental accuracy can be very much smaller than the number of species in the system. Therefore fewer reactions are needed to describe the system’s evolution. Given the fact that in the entire body of thousands of chemical reactions perhaps less than hundred have rate constants known better than a factor of two, this feature of RCCE could help remove a great deal of uncertainty from the system by properly invoking the constrained-equilibrium assumption. Reactions which do not change any constraint are in constrained-equilibrium and need not to be specified. Nonetheless, the successful implementation of the RCCE method depends critically on the choice of constraints and knowledge of the rates of the constraints-changing reactions is required. Although several important steps have been taken toward automatic selection of single species as constraints [18-19], the work of Janbozorgi et. al. [11] shows that the optimum set of structural constraints is still a research subject. The aim of this paper is to present a set of structural constraints based on a careful study of the kinetics of the system, which yields good agreements with the corresponding DKM over a wide range of initial temperatures, pressures...
and equivalence ratios. Also, the ignition delay time predictions are compared with the RCM and Shock Tube experimental data.

2.2 Rate-Controlled Constrained-Equilibrium

An excellent presentation of the theoretical foundations of RCCE can be found in [9]. Also, the working equations and initialization of the calculations are presented in [11, 16, and 17]. One major area of research in RCCE is selection of RCCE constraints. Constraints could be either linear combinations of species or single species. Methodologies based on the greedy algorithm [19] and index of importance, IOI, have been developed to select the single species as constraints, although the greedy algorithm could in principle be used for group of species as well. The algorithm presented in [17] and studies based on careful considerations of chemistry [11] aim at determining the constrained-equilibrium paths, which may or may not result in linear combination of species.

The main aim of our studies in RCCE is directed toward identifying the pattern of conversion of heavy hydrocarbons to smaller ones and ultimately to combustion products. Given the importance of the C₁ chemistry in combustion of all heavy hydrocarbons, we continue our efforts by building upon the C₁ RCCE model developed in [11] to account for C₁/C₂ interactions. The C₁ mechanism is taken from [11], which includes the C₁/H/O from GRI-mech3.0 [10] plus additional peroxide species and reactions, enabling the model to be used at high pressures and low temperatures. The C₂ sub-mechanism is taken from GRI-mech3.0. The constraints identified through studies of chemistry and also the RCCE reaction flow diagrams are shown in table 2.1 and figure 2.1 respectively.

Table 2.1: C₁/C₂ constraints

<table>
<thead>
<tr>
<th>Constraint</th>
<th>Definition of the constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EN Elemental Nitrogen</td>
</tr>
<tr>
<td>2</td>
<td>EC Elemental Carbon</td>
</tr>
<tr>
<td>3</td>
<td>EH Elemental Hydrogen</td>
</tr>
<tr>
<td>4</td>
<td>EO Elemental Oxygen</td>
</tr>
<tr>
<td>5</td>
<td>M Total number of moles</td>
</tr>
<tr>
<td>6</td>
<td>FV Moles of free valence(any unpaired valence electron)</td>
</tr>
<tr>
<td>7</td>
<td>FO Moles of free oxygen(any oxygen not directly attached to another oxygen)</td>
</tr>
<tr>
<td>8</td>
<td>FU Moles of fuel molecules</td>
</tr>
<tr>
<td>9</td>
<td>FR Moles of fuel radicals</td>
</tr>
<tr>
<td>10</td>
<td>DCO Moles of HCO+CO</td>
</tr>
<tr>
<td>11</td>
<td>OHO Moles of water radicals (OH+O)</td>
</tr>
<tr>
<td>12</td>
<td>APO Moles of alkyl peroxides(CH₃OO+CH₃OOH+CH₃OOH)</td>
</tr>
<tr>
<td>13</td>
<td>ALCD Moles of alcohols + aldehydes(CH₂O+CH₂OH+CH₂O+CH₂OH)</td>
</tr>
<tr>
<td>14</td>
<td>C-C Moles of C-C Bond</td>
</tr>
<tr>
<td>15</td>
<td>C₂H₆   Moles of C₂H₆</td>
</tr>
<tr>
<td>16</td>
<td>C₃H₆ + C₄H₄ Moles of C₃H₆ + C₄H₄</td>
</tr>
</tbody>
</table>
The discussion pertinent to the first 13 constraints can be found in [11]. The extra three constraints, namely C-C, C_2H_6 and C_2H_5+C_2H_4 were identified in this work. The aim has been to identify a set which results in equally good agreements with the corresponding DKM over a wide range of initial temperatures, pressures and equivalence ratios.

2.3 Results and discussions

Ignition of CH_4/O_2/N_2 in an adiabatic constant volume reactor has been studied over a wide range of initial temperatures (900K-1500K), initial pressures (1atm-20atm) and stoichiometric ratios (0.6-1.2). The 16 constraints showed in Table 2.1 were used in the RCCE calculations. RCCE calculations were compared with those of DKM involving C_1/C_2 chemistry that includes 17 Nitrogen species and 43 C/H/O species.

2.3.1 C_1/C_2 oxidation

As stated earlier, discussions related to the first 13 constraints can be found in [11] in which only C1 chemistry was considered. In the case of close to stoichiometric or rich conditions the path from C_1 to C_2 becomes important, which introduces an important structural constraint on the C-C bonds. A change in the value of this constraint is a necessary and sufficient condition for formation or consumption of heavier hydrocarbons, in this case C_2 and C_3 species. The next constraint identified is C_2H_6, which in a species map is directly connected to C_2H_5. The calculations of the rate of formation and consumption of C_2H_6 compared to the rate of consumption of C_2H_5 show that C_2H_6 is an important rate-controlling constraint over a wide range of thermodynamic conditions. Such calculations further show that the path from C_2H_5 to C_2H_4 can be assumed equilibrated subject to formation of C_2H_5 and consumption of C_2H_4, that is C_2H_5 + O ⇌ CH_3 + CH_2O and C_2H_4 + HO_2 ⇌ C_2H_3 + H_2O_2 coupled with the constrained equilibrium reaction C_2H_5 + O_2 ⇌ C_2H_5 + HO_2 define C_2H_5 + C_2H_4. This number of constraints is enough to put the predictions of RCCE within, in the worst case, 5% of accuracy with respect to DKM. The model consistency demonstrates the same level of agreement over the entire range of (p,T,\phi). Illustrative results including
dependence studies are shown in figure 2.2. Also, concentrations are in good agreement with their corresponding DKM.

2.3.2 Comparison with Shock Tube Data

As stated in the previous section, the predictions of the RCCE model consistently fall within, in the worst case, 5% of the DKM predictions. In order to check whether this level of accuracy is acceptable or not, comparisons were made against the experimental data of Shock tube [14]. However, it is well known that making comparisons to Shock Tube data, especially at low temperatures, requires modifications in the reactor model, since the constant volume - constant energy model does not hold due to pressure changes during the delay time, [12, and 13]. Two methods have been suggested for considering pressure corrections; CHEMSHOCK [20] and the isentropic compression [21]. The isentropic assumption implies non-reacting gas, while the delay time is certainly not isentropic. In this study we considered a third possibility, i.e. the prescribed pressure, in which volume is obtained as part of the solution of the reacting system, given the experimental pressure curve during the delay time which is typically similar to figure 2.3. Dryer et al. [12] suggested a pressure profile approximation as having a constant pressure for a finite amount of time and then increasing linearly until the moment of ignition. Values of 1 – 5 ms and 1~10%/ms were considered for the constant pressure duration and dP/dt respectively. Figure 2.4 demonstrates the results before and after making the modification. Obviously, predictions show a consistent improvement after implementing the correction. Since, in principle, predictions at high enough temperatures were not expected to require modifications, it means that the DKM model is not predictive at this range of temperature in the first place, although pressure corrections make great improvements in the predictions of the model.

2.4 Summary and conclusions

RCCE calculations of CH₄/O₂/N₂ have been made over a wide range of initial temperatures, pressures and equivalence ratios using up to 16 constraints and 352 reactions
and good agreements with “Detailed kinetic Model” (DKM) calculations using 60 species were obtained. The model RCCE demonstrates consistent accuracies, ranging from 0.05-1.5%, with respect to the corresponding DKM. Such predictions are also in good agreement with the Shock Tube data after considering the variable pressure effects in ignition delay period.

Important features of RCCE are:

1. It is based on the well-established Maximum Entropy Principle of Thermodynamics rather than mathematical approximations.

2. The total number of constraints required to determine the equilibrium state of a system can be much smaller than the number of species in the system so fewer rate equations are required to describe its evolution.

3. Every species for which the thermodynamic data is available can evolve dynamically based on the constrained-equilibrium requirement. This feature could be used to investigate whether a species, which is not explicitly included in the kinetic model, may be kinetically important or not.
Figure 2.1: RCCE reaction flow diagram
Figure 2.2. (a) $T_i$-dependence, (b) $P_i$-dependence and (c) $\phi$ - dependence studies, (d,e,f) species concentrations
2.5 References


Chapter 3

Rate-Controlled Constrained-Equilibrium Theory Applied to Expansion of Combustion Products in the Power Stroke of an Internal Combustion Engine

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Rate-Controlled Constrained-Equilibrium Theory Applied to Expansion of Combustion Products in the Power Stroke of an Internal Combustion Engine

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Rate-controlled constrained-equilibrium method, firmly based on the second law of thermodynamics, is applied to the expansion of combustion products of methane during the power stroke of an internal combustion engine. The constraints used in this study are the elemental oxygen, hydrogen, carbon and nitrogen together with other four dynamic constraints of total number of moles, moles of DCO (CO+HCO), moles of free valence and moles of free oxygen. Since at chemical equilibrium, the mixture composition is dominated by H/O, CO/CO₂, and a few other carbon-containing species, almost independent of the fuel molecule, the set results in accurate predictions of the kinetic effects observed in all H/O and CO/CO₂ compounds and temperature history. It is shown that the constrained-equilibrium predictions of all the species composed of the specified atomic elements can be obtained independent of a kinetic path, provided their Gibbs free energies are known.

Keywords: Second law of thermodynamics, The Rate-controlled constrained-Equilibrium (RCCE) method, Constraints, Chemical kinetics, Internal combustion engine, Power stroke.

3.1 Introduction

Equilibrium gas dynamics is based on the assumption that when a system undergoes an either heat or work interaction with the surrounding environment, the internal molecular relaxation processes are faster than changes brought about in system’s thermodynamic states due to interaction. Under this assumption the condition of local thermodynamic equilibrium (LTE) is valid. LTE leads to thermal equilibrium among various molecular degrees of freedom, enabling the definition of a single temperature. However, this is not generally the case, as energy re-distribution among internal degrees of freedom (translation, rotation, vibration, and electronics) requires definite lengths of time, known as relaxation times (Vincenti, Kruger, 1965). If the interaction occurs on a time scale shorter or comparable with molecular relaxation, the internal dynamics of the system lags behind in re-establishing local thermodynamic equilibrium and the slow degree of freedom has to be treated by means of non-equilibrium thermodynamics.

This study is focused on gas phase chemical relaxation, where a chemically reacting system undergoes work interaction with the environment and is initially in a chemical equilibrium state. As pointed out by Keck (1990), an equilibrium state is meaningful only when the constraints, subject to which such a state is attained, are carefully determined and all equilibrium states are in fact constrained equilibrium states. At temperatures of interest to combustion, nuclear and ionization reactions can be assumed frozen and the fundamental constraints imposed on the system are conservation of neutral atoms. The cascade of
constraints can be easily extended based on the existence of classes of slow chemical or energy-exchange reactions, which if completely inhibited would prevent the relaxation of the system to complete equilibrium. For instance, total number of moles in a reacting system does not change unless a three body reaction occurs, radicals are not generated in the absence of chain branching reactions and the definition of a single temperature in a chemically reacting system is based on the observation that thermal equilibration among translation, rotation and vibration is in general faster than chemical reactions.

Based on the most profound law of nature, i.e. second law of thermodynamics, Rate-Controlled Constrained-Equilibrium (RCCE) method was originally developed by Keck and Gillespie (1971) and later by Keck and coworkers (Bishnu, Hamiroune, Metghalchi, Keck, 1997 and Hamiroune, Bishnu, Metghalchi, Keck, 1998), Tang and Pope (2004) and Jones and Rigopoulos (2005) to estimate the state of a nonequilibrium system by maximizing entropy at any time during the nonequilibrium evolution subject to the known constraints imposed on the system. The dynamics of the unrepresented part of the system is then determined by the requirement of constrained equilibrium.

According to the fundamental premise of RCCE, 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 (Keck, 1990).

Morr and Heywood (1974) considered the problem of sudden cooling of the combustion products of aviation kerosene, by passing the combustion products through an energy exchanger at constant pressure as a model for gas turbine. They compiled a model for CO oxidation chemistry based on the fact that three body and CO oxidizing reactions are generally slower than other reactions and confirmed the notion through comparison against experimental data. In this paper we look at the expansion of (CH₄/O₂/N₂) combustion products in the power stroke of an internal combustion engine, when N₂ is assumed to be inert, using the RCCE method. This method enables a systematic analysis of the underlying kinetics through testing different constraints with the least amount of effort.

3.2 Physical Model

The physical model is shown in figure 3.1. It is assumed that power stroke begins with the combustion products at a complete chemical equilibrium state and that expansion occurs so rapidly that heat conduction does not occur through the piston wall. It is further assumed that the gas composition is homogeneous at any time during expansion. Volume is assumed to be a prescribed function of time (Heywood, 1988):

\[
\frac{V(t)}{V_c} = 1 + \frac{1}{2} (r_c - 1) \times f(\theta),
\]

where
\[ f(\theta) = [R + 1 - \cos(\theta(t)) - \sqrt{R^2 - \sin^2(\theta(t))}], \quad R = \frac{l}{a} \]

and \( V(t), V_c, r_c, \) and \( \theta \) represent the instantaneous volume of the cylinder, clearance volume, compression ratio and the instantaneous crank angle respectively. The numerical values used in this study are \( V_c = 125 \text{ mlit}, \) \( r_c = 11, \) and \( R = 3. \) The power stroke is also identified by \( 0 \leq \theta \leq 180. \)

![Figure 3.1: Schematic of the physical model](image)

### 3.3 Governing Equations in RCCE Form

The detailed formulation of RCCE in constrained-potential form can be found in earlier works (Janbozorgi, Gao, Metghalchi, Keck, 2006), so we avoid repeating the procedure in detail here and address the important points. Consistent with the perfect gas assumption, the constraints imposed on the system by the reactions are assumed to be a linear combination of the mole number of the species present in the system, \( C_i = \sum_{j=1}^{N_i} a_{ij} N_j, \quad i = 1, K N_c \) \hfill (3.2)

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 (Keck, 1990):

\[ N_j = Q_j \exp(-\sum_{i=1}^{m_c} a_{ij} \gamma_i), \quad j = 1, K N_s \] \hfill (3.3)

where,
Clearly, the partition function of each species depends on temperature, volume and the standard Gibbs free energy of the species. The time rate of change of constraints or equivalently, constraint potentials, can be obtained by taking the time derivative of equation (3.2) as:

$$\mathbf{c}^\& = \sum_{j=1}^{N_r} a_j N_j$$  \hspace{1cm} (3.4)

It is assumed that changes in the chemical composition are the results of chemical reactions of the form

$$\sum_{j=1}^{N_r} v_{jk}^- X_j \leftrightarrow \sum_{j=1}^{N_r} v_{jk}^+ X_j, \quad k = 1, K, N_r$$ \hspace{1cm} (3.5)

The phenomenological expression of chemical kinetics can be used to replace $N_j$ in equation (3.4)

$$N_j = \sum_{k=1}^{N_r} v_{jk} r_k$$ \hspace{1cm} (3.6)

where

$$r_k = r_k^+ - r_k^-$$ \hspace{1cm} (3.6a)

$$v_{jk} = v_{jk}^- - v_{jk}^+$$ \hspace{1cm} (3.6b)

Substituting equation (3.6) into (3.4) results in the required time rate of change of the constraint $C_i$:

$$\mathbf{c}^\& = \sum_{k=1}^{N_r} b_{ik} r_k$$ \hspace{1cm} (3.7)

$$b_{ik} = \sum_{j=1}^{N_r} a_j v_{jk}$$ \hspace{1cm} (3.7a)

Clearly, a reaction $k$ for which the value of $b_{ik}$ is zero for all constraints $i$ is in constrained equilibrium. All reactions in the mechanism must satisfy this condition for elemental constraints. In the absence of any spatial nonhomogeneity, the implicit differential equations governing the constraint potentials can be obtained by substituting equation (3.7) and the time derivative of equation (3.3) into equation (3.4), the final result of which is:
\[
\sum_{n=1}^{N_r} C_{n} \gamma_{n} \frac{\nu}{V} - C_{iv} \frac{\nu}{V} - C_{iT} \frac{\Phi}{T} + \sum_{k=1}^{N_{r}} b_{k} r_{k} = 0
\]

where

\[
C_{n} = \sum_{j=1}^{N_{r}} a_{j} a_{n} [N_{j}]
\]

\[
C_{iv} = \sum_{j=1}^{N_{r}} a_{j} [N_{j}]
\]

\[
C_{iT} = \sum_{j=1}^{N_{r}} a_{j} \frac{E_{j}}{RT} [N_{j}]
\]

In cases where state variables other than \(T\) and \(V\) are used, additional equations for these are required. In the present work, the energy of the system

\[
E = \sum_{j=1}^{N_{r}} E_{j} N_{j}
\]

is used to replace \(T\). The required energy equation can be obtained from the first law of thermodynamics. As stated in section 3, we assume that expansion occurs so rapidly that heat conduction through the piston wall is frozen and that the work term is due only to volume change. Differentiating equation (3.9) with respect to time and using the differential form of equation (3.3) results in the required energy equation:

\[
\sum_{n=1}^{N_{r}} D_{n} \gamma_{n} \frac{\nu}{V} + D_{iv} \frac{\nu}{V} + D_{iT} \frac{\Phi}{T} - \Phi = 0
\]

where

\[
D_{n} = -\sum_{j=1}^{N_{r}} E_{j} a_{n} [N_{j}]
\]

\[
D_{iv} = \sum_{j=1}^{N_{r}} E_{j} [N_{j}]
\]

\[
D_{iT} = \sum_{j=1}^{N_{r}} \left( c_{j} T + \frac{E_{j}^{2}}{RT} \right) [N_{j}]
\]

\[
\Phi = -p \Phi
\]

Upon solving the differential equations for the \(\gamma_{i}\) vector, the constrained-equilibrium composition of the system can be found at each time step from equation (3.3). Of particular importance at this point is to notice that every species for which the Gibbs free energy is known can be included in the model, even though they may not explicitly participate in the kinetic mechanism, and an estimation of its dynamic evolution can be obtained based on the
value of the known constraints. Such dynamic evolution is dictated by the requirement of constrained-equilibrium. In the limit of local chemical equilibrium, where all reactions are in constrained-equilibrium, the constraints imposed by the conservation of neutral atoms enables determining the concentration of every possible species made up of the same elements. Such an approach is the basis of the widely used STANJAN and NASA equilibrium codes (Reynolds, Gordon, McBride, 1971). Evidently, different sets of constraints can be handled with the same ease using the above formulations.

3.4 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. The constraints used in this study are listed in Table 3.1.

According to the Le Châtelier principle, when a highly dissociated mixture undergoes an interaction with the environment which lowers the gas temperature and density, the internal dynamics shift in the exothermic direction to minimize the cooling effect of interaction. As a result, three body recombination reactions become an important part of the energy restoration process. The total number of particles in the system does not change unless one such reaction occurs. This is the rationale for putting a constraint on total number of moles; M. Among the reactions changing this constraint is:

\[
\begin{align*}
H+H+M &= H_2+M \\
O+H+M &= OH+M \\
O+O+M &= O_2+M \\
H+OH+M &= H_2O+M
\end{align*}
\]

Oxidation of CO to CO\(_2\) constitutes an important part of the exothermic relaxation which is dominated by several reactions, such as:

\[
\begin{align*}
\text{HCO}+X &= \text{CO}+HX, \ X = \text{radical pool} \quad (\text{R3}) \\
\text{HCO}+O_2 &= \text{CO}+\text{HO}_2 \quad (\text{R2}) \\
\text{CO}+\text{OH} &= \text{CO}_2+\text{H} \quad (\text{R3})
\end{align*}
\]

Figure 3.2: Chemical equilibrium composition of stoichiometric CH\(_4\)/O\(_2\)/N\(_2\) mixture.
CO+HO_2 = CO_2+OH \quad \text{(R4)}

(R1) is a generic reaction that involves interaction with the radical pool, which is in this case dominated by H/O radicals, and is generally faster than others because it involves small or zero activation energy. In order to allow these reactions to be in constrained equilibrium, a constraint on HCO+CO is introduced. This constraint further controls the exothermic path from CO to CO_2. The energy restoration process also requires chain branching reactions that act to produce more OH radicals, which itself feeds exothermic water and CO_2 formation reactions. This condition requires constraints on both free valance, FV, and free oxygen, FO. The most important reaction belonging to these constraints is

H+O_2 = OH+O \quad \text{(R5)}

3.5 Results and Discussion

Equations (3.8) and (3.10) were integrated using DASSL (Petzold 1982). A mixture of (CH_4/O_2/N_2) is compressed to an initial temperature of 735 K and initial pressure of 15 atm. It is further assumed that compression occurs so rapidly that chemical reactions are frozen. Power stroke is then assumed to start with the combustion products, corresponding to instantaneous conversion of fuel/oxidizer under a constant-volume, constant energy combustion process at the clearance volume. Initial conditions for expansion can be obtained from STANJAN. The chemical equilibrium composition for all 30 species corresponding to an initially stoichiometric mixture of (CH_4/O_2/N_2) is shown in Figure 3.2. The equilibrium temperature and pressure are $T_{eq}=2869K$ and $P_{eq}=59.5atm$. Clearly, it is dominated by H/O and CO/CO_2 components followed by HOCO, HCO, CH_2O, and HOCHO as the next important carbon-containing compounds. Such an equilibrium mixture is almost fuel independent.

From kinetics standpoint, three body reactions have small or zero activation energies, making them almost temperature insensitive and rather highly pressure (density) sensitive, whereas the rate of bimolecular reactions which involve activation energies are temperature sensitive. Therefore, sudden cooling to low temperatures and lowering density depress the rate of recombination and exothermic bimolecular reactions markedly and the exothermic processes lag in their attempt to restore the equilibrium. A failure to release latent energy of molecule formation enhances the cooling and puts the system farther out of equilibrium. If

<p>| | | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>1</td>
<td>EN</td>
<td>Elemental nitrogen</td>
</tr>
<tr>
<td>2</td>
<td>EC</td>
<td>Elemental carbon</td>
</tr>
<tr>
<td>3</td>
<td>EO</td>
<td>Elemental oxygen</td>
</tr>
<tr>
<td>4</td>
<td>EH</td>
<td>Elemental hydrogen</td>
</tr>
<tr>
<td>5</td>
<td>M</td>
<td>Total number of moles</td>
</tr>
<tr>
<td>6</td>
<td>DCO</td>
<td>Moles of HCO+CO</td>
</tr>
<tr>
<td>7</td>
<td>FV</td>
<td>Moles of free valence (any unpaired valence electron)</td>
</tr>
<tr>
<td>8</td>
<td>FO</td>
<td>Moles of free oxygen (any oxygen not directly bound to another oxygen)</td>
</tr>
</tbody>
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expansion is fast enough, the exothermic lag grows indefinitely and the composition becomes frozen.

Figure 3.3 and figure 3.4 represent the frozen, local thermodynamic equilibrium (L.T.E.) and non-equilibrium temperature and CO profiles during expansion of combustion products of an initially stoichiometric mixture of (CH\textsubscript{4}/O\textsubscript{2}/N\textsubscript{2}). It should be mentioned that since the mixture is assumed to be spatially homogeneous at each instant of time, local chemical equilibrium is equivalent with L.T.E. Physically, frozen chemistry corresponds to the case in which expansion occurs so rapidly that chemistry is completely frozen, whereas L.T.E. is the case when expansion occurs extremely slowly so that all the kinetic processes are instantaneously equilibrated. L.T.E. calculations are carried out using the general formulations but using only elemental constraints. In both cases the expansion is isentropic but in the former the species are the fixed constraints, whereas in the latter neutral atoms are the fixed constraints and the chemical composition of the system changes according to the requirement of L.T.E. in response to changes in the state variables.

Obviously, L.T.E. calculations result in the highest temperature and highest conversion of CO to CO\textsubscript{2}. The opposite is true for the frozen chemistry. Predictions of the finite-rate chemistry are bounded by these two extremes. The results of such predictions using a mechanism comprising 133 reactions and 30 species, designated by “detailed kinetics”, are compared with RCCE results when constraints are added one at a time. All RCCE results include elemental constraints. Thus labels refer to constraints in addition to elementals.

The slowest constraint is imposed by three-body recombination/dissociation reactions. The effect of all such reactions is captured by putting a constraint on the total number of moles (M).
Figure 3.5: Engine-speed dependence of temperature profiles compared with the predictions of detailed kinetics at the equivalence ratio of 1.0

Figure 3.6: Engine-speed dependence of CO profiles compared with the predictions of detailed kinetics at the equivalence ratio of 1.0

Figure 3.7: Temperature and pressure profiles under different conditions at an engine speed of 3000 rpm, initial temperature of $T_i=2673$ K, initial pressure of $P_i=54.83$ atm and equivalence ratio of 0.8

Figure 3.8: CO profiles under different sets of constraints at an engine speed of 3000 rpm, initial temperature of $T_i=2673$ K, initial pressure of $P_i=54.83$ atm and equivalence ratio of 0.8
Figure 3.9: Temperature profiles under different sets of constraints at an engine speed of 3000 rpm, initial temperature of $T_i=2846.8$ K, initial pressure of $T_i=60.5$ atm and equivalence ratio of 1.2

Evidently adding to the list a constraint on $DCO=HCO+CO$ does not change the predictions noticeably, meaning that these reactions (reactions similar to R3 and R4) are nearly in constrained equilibrium. However, the collective effect of $DCO$, $FV$, and $FO$ results in perfect match between RCCE using 8 constraints and detailed kinetics using 30 species.

It is also interesting to notice that the state of the gas follows exactly the predictions of L.T.E. during the early stage of expansion, when the piston speed is very slow. Departures from local thermodynamic equilibrium emerge as the piston speed increases.

In order to check the validity of the identified constraints under faster expansions, engine speed is increased to 6000 rpm and 12000 rpm. In this case the kinetic effects are only observed in species profiles and not in temperature. Figures 3.5 and 3.6 demonstrate these observations. Figures 3.7 and 3.8 show the same set of results for expansion of combustion products of a mixture of $(CH_4/O_2/N_2)$ with an initial equivalence ratio of 0.8. Progressive improvements of the results by adding constraints one at a time is evident. Pressure at the end of the stroke is 3 atm. Figures 3.9 and 3.10 show the same result for the case in which the initial equivalence ratio is 1.2. Contrary to the results corresponding to a stoichiometric mixture, Figure 3.4, in this case three body reactions are in constrained equilibrium and $DCO$-changing reactions are rate limiting.

Figure 3.11(a,b,c,d) represents the profiles of $H_2O$, $CO_2$, $H$, $O$, $HO_2$, $H_2O_2$, HOCO, HCO, HOCHO, $CH_2O$, $CO$, $O_2$, $H_2$, $OH$ corresponding to an equivalence ratio of 1.0 at an engine speed of 3000 rpm. Comparison has been made between RCCE calculations using 8 constraints against detailed kinetics using 30 species and 133 reactions. It should be noticed that HOCHO, $CH_2O$ and HOCO are not directly constrained and their evolution is determined based on the requirement of constrained equilibrium. This demonstrates one of the most important features of RCCE that with a few constraints the concentrations of all possible species composed of the specified elements can be readily obtained, provided their Gibbs free energies are known. Having defined the constraint $DCO=HCO+CO$, the
concentration of HCO is also determined based on an internal equilibrium with CO. Clearly, the single constraint DCO is able to give quite acceptable predictions for CO, figure 3.11d and HCO, figure 3.11c, which confirms the partial equilibrium between them.

3.6 Concluding Remarks

Local thermodynamic equilibrium (L.T.E.), frozen chemistry, detailed kinetics and Rate-controlled constrained-equilibrium calculations of the expansion of (CH\textsubscript{4}/O\textsubscript{2}/N\textsubscript{2}) combustion products during the power stroke of an internal combustion engine were conducted. Looking at the dynamic of the expansion process, a set of 8 generalized constraints was identified. The set gives perfect matches with the results of detailed kinetics. The constraints identified are quite general and are able to handle relaxation from an initial equilibrium state of the combustion product of any hydrocarbon fuels. Under stoichiometric conditions, DCO-changing reactions are in constrained equilibrium and \textit{M}-changing reactions are rate limiting, whereas, making the mixture richer, puts \textit{M}-changing reactions in equilibrium and DCO-changing reactions out of equilibrium.

Of the salient features of the RCCE technique is that it is based on the most profound law of thermodynamics, Maximum Entropy Principle. Every species made up of the specified elements can be included in the model, provided its Gibbs free energy is known. In the absence of any direct constraint on a species or group of species, they will evolve according to the requirement of constrained-equilibrium. RCCE has the dazzling ability to carry out local thermodynamic equilibrium, frozen equilibrium and rate-controlled constrained-equilibrium calculations with the same ease, by implementing different classes of constraints. In the limit where the number of constraints equals the number of species, the method becomes exact.

Acknowledgments

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3.7 Nomenclature

- \( C_i \) Value of constraint \( i \)
- \( a_{ij} \) Value of constraint \( i \) in species \( j \)
- \( N_j \) Number of moles of species \( j \)
- \([N_j]\) Concentration of species \( j \)
- \( Q_j \) Partition function of species \( j \)
- \( \gamma_i \) Constraint potential (Lagrange multiplier) conjugate to constraint \( i \)
- \( \mu_j^o \) Nondimensional standard Gibbs free energy of species \( j \), 
  \[ (\mu_j^o - T \epsilon_j^o) / RT \]

Figure 3.11: Profile of different species for \( T_i = 2869 \) K, \( P_i = 59.5 \) atm at \( \phi = 1 \) and \( \omega = 3000 \) rpm
$E_j$  Molar energy of species $j$

$b_{ik}$  Change in constraint $i$ by reaction $k$

$r_k$  Net rate of reaction $k$

$r_k^+$  Forward rate of reaction $k$

$r_k^-$  Reverse rate of reaction $k$

$\nu_{ij}^+$  Stoichiometric coefficient of product species $j$ in reaction $i$

$\nu_{ij}^-$  Stoichiometric coefficient of reactant species $j$ in reaction $i$

$N_s$  Number of species

$N_c$  Number of constraints

$N_r$  Number of reactions

$c_{ij}$  Frozen molar heat capacity of species $j$ at constant volume

$T$  Temperature

$V$  Volume

$P$  Pressure

$p_o$  Standard (atmospheric) pressure

$E$  Total energy

$R$  Universal gas constant

### 5.3 References


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Chapter 4

Rate-Controlled Constrained-Equilibrium Modelling of Expansion of Combustion Products in a Supersonic Nozzle

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Organized by the Eastern States Section of the Combustion Institute
and Hosted by the Georgia Institute of Technology, Atlanta, GA
March 20-23, 2011
4.1 Introduction

Under a broad range of conditions encountered in chemical nozzles, departures from Boltzmann distribution among private molecular degrees of freedom can be neglected. Under this condition the gas can be assumed in thermal equilibrium, which enables definition of a single temperature and, therefore, the only major non-equilibrium phenomenon is associated with chemical reactions. This part of research was focused on the gas phase chemical relaxation in a supersonic diverging nozzle using the RCCE method. The system is considered to be initially at equilibrium at a Mach number of 1.0, which subsequently expands to lower densities and higher Mach numbers. Depending on how fast the expansion occurs the system could relax through a series of shifting chemical equilibrium, chemical non-equilibrium or frozen chemical equilibrium states, each of which implies different sets of controlling constraints. At temperatures and time scales of interest to combustion, nuclear and ionization reactions can be assumed frozen and the conservation of neutral atoms forms the constant of chemical kinetics under homogeneous conditions. The cascade of kinetic constraints can then be refined based on the existence of classes of fast and slow reactions that are responsible for defining and evolving the state of the system, respectively, in such a way that the entropy (an appropriate form of free energy) is maximized (minimized) subject to a set of constraints [1-6]. A major difficulty with RCCE has been the lack of an automated algorithm to select the constraints. The method was used [7] with much success in a way which is heavily based on deep insight into the mechanism, as a result of which some patterns have started to reveal about the rate limiting steps. This approach has resulted in a successful set of structurally valid constraints for C1 hydrocarbon fuels. Yousefian [8] was first to demonstrate an automated algorithm with certain degree of success for selecting constraints. Recently an algorithm, called greedy algorithm, was also developed [9] to select, one at a time, the most effective single-species constraints based on the least kinetic couplings among species. Although may prove costly, the algorithm has potentials to be extended to select groups of species as constraints as well.

A new algorithm was presented in this part of research based on the degree of disequilibrium (DOD) of chemical reactions. It was demonstrated for systems initially at
equilibrium and it were shown that under the conditions considered, the generalized constraints can be analytically deduced from this algorithm.

4.2 Model
Consistent with the reasoning of Bray, [10], the quasi one dimension, steady, adiabatic, inviscid and nondiffusive flow assumptions are used for studying the chemical relaxation within the nozzle. Under these assumptions the stagnation enthalpy of the reacting flow is conserved and the governing equations take the following form:

\[
\frac{1}{\rho} \frac{d\rho}{dx} + \frac{1}{u} \frac{du}{dx} + \frac{1}{A} \frac{dA}{dx} = 0
\] (4.1)

\[
\rho u \frac{du}{dx} + \frac{dp}{dx} = 0
\] (4.2)

\[
[N_j] \frac{du}{dx} + u \frac{d[N_j]}{dx} + \frac{u[N_j]}{A} \frac{dA}{dx} = \partial_j
\] (4.3)

\[
\rho u C_p \frac{dT}{dx} + \sum_{j=1}^{N_s} h_j M_j \partial_j + \frac{d[N_j]}{dx} + \rho u^2 \frac{du}{dx} = 0
\] (4.4)

\[
p = NR_u T.
\] (4.5)

where \( C_p = \sum_{j} C_{p_j} Y_j j \) is the mixture heat capacity. Notice that the density and the concentrations are related through \( \rho = \sum_{j} M_j [N_j] \). Also, \( \partial_j \) is the net molar rate of consumption of species \( j \) and is defined as

\[
\partial_j = \sum_{k=1}^{n_r} \nu_{jk} (r_k^+ - r_k^-)
\] (4.6)

where

\[
r_k^+ = k^+ \prod_{j=1}^{n_r} [N_j]^{\nu_{jk}^+}, \quad r_k^- = k^- \prod_{j=1}^{n_r} [N_j]^{\nu_{jk}^-}, \quad \nu_{jk} = \nu_{jk}^+ - \nu_{jk}^-
\] (4.7)

are the forward and reverse reaction rates of reaction \( k \) and the net stoichiometric coefficient of species \( j \) in reaction \( k \).
4.3 RCCE Form of the Equations

It can be shown that equations (4.3), (4.4) and (4.5) can be expressed in terms of constraint potentials as follows:

\[
\begin{align*}
&u \sum_{j=1}^{n} f_{jk} \frac{d\gamma_j}{dx} - u \frac{h_k}{T} \frac{dT}{dx} - C_k \frac{du}{dx} - \frac{u C_k}{A} \frac{dA}{dx} + \sum_{i=1}^{n} a_{ik} \frac{\delta_k}{A} = 0, \\
&- \sum_{j=1}^{n} E_{jk} \frac{d\gamma_k}{dx} + E_T \frac{dT}{dx} + E_u \frac{du}{dx} + E_A \frac{dA}{dx} = 0, \\
&\frac{1}{p} \frac{dp}{dx} - S_T \frac{dT}{dx} + \sum_{k=1}^{n} S_{jk} \frac{d\gamma_k}{dx} = 0.
\end{align*}
\]

where

\[
\begin{align*}
f_{jk} &= \sum_{i=1}^{n} a_{jk} [N_i], & \lambda_k &= \sum_{i=1}^{n} a_{ik} [N_i] \frac{E_i}{R_n T}, \\
C_k &= \sum_{i=1}^{n} a_{ik} [N_i], & E_k &= \sum_{i=1}^{n} a_{ki} [N_i] M_i h_i, \\
E_T &= \sum_{i=1}^{n} [N_i] M_i h_i \frac{E_i}{R_n T}, & E_u &= \sum_{i=1}^{n} [N_i] M_i h_i + n \delta u, \\
E_u &= \sum_{i=1}^{n} [N_i] M_i h_i, & S_T &= \frac{1}{N} \sum_{i=1}^{n} \frac{[N_i] E_i}{R_n T} + 1, \\
S_{jk} &= \frac{1}{N} \sum_{i=1}^{n} a_{ki} [N_i], & N &= \sum_{i=1}^{n} [N_i].
\end{align*}
\]

4.4 Area Profile

\[
\frac{A(x)}{A_{th}} = -2(A_r - 1) \left( \frac{x}{L} \right)^3 + 3(A_r - 1) \left( \frac{x}{L} \right)^2 + 1
\]

(4.11)

The diverging nozzle area profile is considered to be
where

\[ A_r = \frac{A_{\text{end}}}{A_{\text{th}}} \]

The length of the nozzle, \( L \), has been non-dimensionalized with respect to the height of the throat section.

### 4.5 Constraints

Selection of constraints is certainly the most important aspect of RCCE, on which a successful application of the method depends. Among the general requirements for the constraints are that they must (a) be linearly independent combinations of the species mole numbers, (b) hold the system in the specified initial state, (c) prevent global reactions in which reactants or intermediates go directly to products, and (d) determine the energy and entropy of the system within experimental accuracy. In addition, they should reflect whatever information is available about rate-limiting reactions which control the evolution of the system on the time scale of interest.

A new algorithm based on the degree of disequilibrium (DOD) of chemical reactions has been proposed to select constraints. The DOD of reaction \( k \) is defined as

\[ \phi_k = \ln \frac{r_k^+}{r_k^-} \]  

(4.12)

This physical quantity serves as the driving force for reaction \( k \) and generates the reaction flux \( r_k = r_k^+ - r_k^- \). The quantity \( r_k \phi_k \) determines the amount of entropy produced by reaction \( k \), which is obviously non-negative. If a reaction has a DOD equal or close to zero, depending on the value of either forward or reverse reaction rates, it can be either very slow or at partial equilibrium.

As stated earlier in the previous section, a reaction is in constrained equilibrium only if it does not change any of the constraints. Equivalently, if a reaction or classes of reactions are judged to be in constrained equilibrium, either by user's knowledge of chemistry or by a mathematical algorithm, they imply one or several constraints of varying degrees of effectiveness. The conjecture here is that the smaller the DOD of a reaction or groups of reactions, the more valid the assumption of constrained equilibrium for such reactions.
This assumption subsequently implies a set of constraints, *it a subset or all of which may be sufficient to describe the system to within the accuracy of experimental data or a DKM*. So far this conjecture has been tested for relaxations away from an equilibrium state.

4.6 Results and discussions

4.6.1 H/O Reacting System

The nozzle considered is a diverging nozzle and has an exit-to-throat area ratio of 50. The length of the nozzle is assumed to be ten times the height of the throat section. The initial condition corresponds to a Mach number of 1.01 and temperature and pressure of 3200K and 25atm, respectively. The kinetic mechanism involves 8 species and 24 reactions. Figure 4.1 presents the DOD for reactions in the mechanism.

![Figure 4.1: Degree of disequilibrium (DOD) for reactions involved in the kinetics](image)

Several interesting observations can be made in figure 4.1. The first observation is that *all* three-body reactions are far from equilibrium, confirming the previously
discovered *structural* constraint on total number of moles, which controls the dynamics of molecule formation and the change in the total number of particles in the system [7]. It is also compatible with the physics of expansion that when a highly dissociated mixture expands to lower gas temperatures and densities three body recombination dynamics becomes an important part of the restoration process, in accordance with the Le Chatelier principle. The second observation is that the three body reactions can further be divided in to two groups based on their DOD’s. This suggests that the group with lower DOD may be of secondary importance within the three-body dynamics. Three body reactions are listed below:

R1. O+O+M=O₂+M  
R2. O+H+M=OH+M  
R3. H+H+M=H₂+M  
R4. H+H+H₂=H₂+H₂  
R5. H+H+H₂O=H₂+H₂O  
R6. H+OH+M=H₂O+M  
R7. O+O₂+M=HO₂+M  
R8. O+O₂+O₂=HO₂+O₂  
R9. O+O₂+H₂O=HO₂+H₂O  
R10. OH+OH+M=H₂O₂+M

The first 6 reactions are obviously the most important ones in molecule formation, which are directly related to the major species. Given the importance of the H/O dynamics in all starting-from-equilibrium relaxations, it is anticipated that the same set of reactions, R1-R6, would control the major dynamics under total number of moles, if M were proved to be a rate-controlling constraint. The third interesting observation made in figure 4.1 is that a subset of bi-molecular reaction dynamics remains close to *constrained equilibrium* throughout the relaxation. These reactions are listed below:

R11. O+H₂=H+OH  
R13. O+H₂O₂=OH+HO₂  
R14. H+O₂=O+OH  
R18. H+H₂O₂=HO₂+H₂  
R20. OH+H₂ =H+H₂O  
R21. OH+OH =O+H₂O  
R23. OH+H₂O₂=HO₂+H₂O

These reactions are the ones assumed in constrained equilibrium. As explained under section 2.2, the assumption of constrained equilibrium implies constraints which are unchanged by these reactions. A little scrutiny reveals the following groupings: \( c_1 \equiv \)
H+H₂ based on R11, R18, R20, c₂ ≡ O+OH based on R11, R13, c₃ ≡ HO₂+H₂O₂ based on R13, R18 and R23 and c₄ ≡ OH+H₂O based on R20, R23. Interestingly, combining c₂ and c₄ and forming c₅ ≡ O+OH+H₂O leaves their corresponding reactions intact, yet puts reactions R21 in constrained-equilibrium as well, which further means reduction of the number of constraints by one!

Based on the foregoing analysis the following table of constraints is suggested by constrained-equilibrium reactions:

<table>
<thead>
<tr>
<th>Constraints Based on reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁ ≡ H+H₂</td>
</tr>
<tr>
<td>R₁₁, R₁₈, R₂₀</td>
</tr>
<tr>
<td>C₂ ≡ O+OH+H₂O</td>
</tr>
<tr>
<td>R₁₁, R₁₃, R₂₀, R₂₃</td>
</tr>
<tr>
<td>C₃ ≡ HO₂+H₂O₂</td>
</tr>
<tr>
<td>R₁₃, R₁₈ and R₂₃</td>
</tr>
</tbody>
</table>

Two yet more interesting observations can be made from Table 4.1 and the constrained-equilibrium reactions. The C₂ group is the previously discovered structural constraint of Free Oxygen and all constrained-equilibrium reactions, except reaction R₁₄, conserve another not-easy-to-observe structural constraint, namely Free Valence. One extra observation is that Reaction R₁₄ not only does not suggest any consistent constraint, it further does not conserve any of the constraints in Table 4.1. Calculations, as presented in figure 4.2, show that, although known to be important, elimination of this reaction results in agreements with DKM to within 0.2% of accuracy throughout. Obviously this elimination is only valid over the range of thermodynamic conditions that the reaction shows the behavior of a constrained-equilibrium reaction. In figure 4.2, the RCCE (DOD) designates the calculations under Table 4.1 in addition to elemental constraints. RCCE-Shifting Equilibrium corresponds to local thermodynamic calculations subject to elemental constraints only and RCCE - Frozen Equilibrium designates calculations in which each species forms a conserved constraints. The difference between RCCE(DOD) and DKM is consistently less than 0.06% throughout.
An important question at this stage is the relation between the set presented in Table 4.1 and the structural constraints, M and FV. In what follows we show that these are not linearly independent. By definition the elemental oxygen can be written as:

\[ \text{EO} = \text{FO} + 2(\text{H}_2\text{O}_2 + \text{HO}_2) + 2\text{O}_2 = \text{C}_2 + 2\text{C}_3 + 2\text{O}_2 \]  

(4.13)

In which FO is free oxygen. Also, the total number of moles, M, is defined as:

\[ M = (\text{H} + \text{H}_2) + (\text{O} + \text{OH} + \text{H}_2\text{O}) + (\text{HO}_2 + \text{H}_2\text{O}_2) + \text{O}_2 = \text{C}_1 + \text{C}_2 + \text{C}_3 + \text{O}_2 \]  

(4.14)

Substituting similar terms from (2) into (3), one gets:

\[ M = \text{C}_1 + 1/2(\text{EO} + \text{C}_2) \]  

(4.15)

Figure 4.2: RCCE predictions under Table 4.1 compared with DKM, shifting equilibrium and frozen equilibrium.
Relations (4.13) and (4.15) clearly establish the linear dependence of \( M \) and \( O_2 \) on constraints in Table 4.1. It can also be shown that \( M \) and \( FV \) are related to \( O_2 \) and elemental Hydrogen, \( EH \), in the following form:

\[
(M-O_2) - \frac{FV}{2} = \frac{EH}{2} \tag{4.16}
\]

Substituting from the second equality of relation (49) into (51), one obtains:

\[
2(C_1+C_2+C_3) - EH = FV \tag{4.17}
\]
Relations (4.15) and (4.17) mathematically demonstrate that $M$ and $FV$ can substitute $C_1$ and $C_2$ with no change in predictions at all. All calculations show exact same predictions for the set $(M, C_2, FV)$ which is basically the generalized set $(M, FO, FV)$.

### 4.7 RDX Reacting System

The same methodology was applied to expansion of RDX combustion products through a supersonic nozzle. Calculations show that the high pressure keeps the mixture at the corresponding local thermodynamic equilibrium at each point up to the throat section, beyond which kinetic effects emerge. Therefore, the boundary condition at the throat section corresponds to an equilibrium mixture at a Mach number of 1.0. The corresponding temperature profiles are shown for different constraints in figure 4.3.

![Figure 4.4: The RCCE prediction of temperature profile during expansion of combustion products through a supersonic nozzle.](image)

As is evident from figure 4.4, the only kinetic constraint required in this case is $DCO$ to match the predictions of the detailed kinetic model. This means only one differential rate equation for the kinetic constraints, a considerable reduction in the number of differential
rate equations to be solved! An interesting observation is that the recombination dynamics is completely in equilibrium. Contrary to the consensus in the community, when taking into account the residence time of $1.2 \times 10^{-4}$ sec within the nozzle, it demonstrates that all three body reactions are equilibrated.

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4.8 References

Chapter 5
Conclusions and Future Works
5.1 Conclusions

The RCCE method was developed to study the oxidations of methane, methanol and formaldehyde over a wide range of initial temperatures and pressures. In this regard, a set of up to 12 total constraints (elemental + kinetic) were identified, which result in excellent agreements with “detailed”-kinetic-model (DKM) calculations using 29 species and the same set of 133 reactions. In addition, reduced sets of 20 reaction for methane, 12 reactions for methanol and 12 reactions for formaldehyde have been found, which when employed in the RCCE calculations give results identical to those obtained using the full 133 reactions. Also, it was shown that a subset of these constraints, termed as generalized or universal constraints, is able to reproduce the chemical kinetic features of the expansion dynamics in an internal combustion engine and in a supersonic nozzle.

Among the important features of the RCCE method for simplifying the kinetics of hydrocarbon oxidation are:

1. It is based on the well established Maximum Entropy Principle of thermodynamics rather than mathematical approximations.
2. The entropy always increases as the system evolves and an approach to the correct final chemical-equilibrium state for the specified elements is guaranteed. This is not true for DKMs where only the listed species are included and all others are missing.
3. The total number of constraints required to describe the state of a complex chemical system can be very much smaller than the number of species in the system resulting in fewer equations.
4. It enables one to obtain a good description of the kinetic behaviour of a complex chemically reacting system using a relatively small number of constraint-controlling reactions without having to start with a DKM.
5. 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 model used.

6. If the only constraints on the system are the elements and the state variables, 
RCCE calculations reduce to local equilibrium (LTE) calculations.

7. If the species are used as constraints, RCCE calculations simulate DKM 
calculations with the important distinction that only the listed species can 
appear in DKM calculations whereas all possible species are implicitly 
included in RCCE calculations.

8. The accuracy of the results can be systematically improved by adding 
constraints one at a time.
5.2 Future Works

Future works on RCCE could be carried out in two very exciting and currently demanding fields: a) inclusion of diffusion fluxes and studying the RCCE structure of laminar and turbulent flames, b) using RCCE in a bottom-up approach to build kinetic models for heavy hydrocarbon fuels. Furthermore, an important observation throughout the course of this thesis was that using groups of species as constraints results in sometimes stiff RCCE calculations, such that the overall time saving is minimal. From the modelling standpoint, which has been the focus of this thesis, grouping species as constraints offers the exceptional feature of identifying the oxidation pattern that could be further extended to heavy hydrocarbons. However, optimized numerical algorithms must be developed to further reduce the CPU time. A reduction in the CPU time proportional with the considerable reduction in the number of equations would make the RCCE a very promising method for kinetic simplification.