Reduced Flame Kinetics Via Rate-Controlled Constrained Equilibrium

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Abstract. The dynamical evolution of a chemically reacting system is governed by the equations of chemical kinetics, which exhibit a wide range of time scales thus giving rise to stiff equations. In the rate-controlled constrained equilibrium method (RCCE), the dynamical evolution of the system is governed by the kinetics of the species associated with the slower timescales (kinetically controlled), while the remaining species are calculated via a constrained minimisation of the Gibbs free energy of the mixture. This permits the derivation of a general set of differential-algebraic equations, which apply to any reduced system given a particular selection of kinetically controlled species. In this paper, it is shown how the differential-algebraic formulation of RCCE can be derived from first principles, in the form of an extension of the computation of chemical equilibrium via miminisation of the free energy. Subsequently, RCCE is employed to reduce a comprehensive combustion mechanism and to calculate the burning velocity of premixed H_2-O_2 and CH_4-air flames under a range of pressures and equivalence ratios.

1 Introduction

Chemical kinetics describes the dynamical evolution of a chemical system via a set of rate equations for all the species and radicals involved, and all possible elementary reactions. Such comprehensive mechanisms often comprise very large numbers of species and reactions, and their integration is additionally hampered by excessive stiffness, due to the presence of a vast range of chemical time scales. Combustion is a classic example, where hundreds of reactions are often included in detailed mechanisms, and in addition they must be coupled with fluid flow. Naturally ways have been sought to describe kinetics via a reduced set of variables, taking advantage of the separation of time scales. In principle, accounting for the kinetics of the species associated with the slow time scales should suffice, if one had a way of calculating the equilibrated ones. Conventional derivation of reduced mechanisms proceeds by examining the detailed mechanism and carefully applying steady-state and partial equilibrium assumptions to individual species and reactions. This laborious procedure must be carried out individually for every reaction mechanism and physical problem. Recently certain mathematical methods have appeared that attempt to identify the time scales separation in a methodical way [9], [8].

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Rate-controlled Constrained Equilibrium (RCCE), first introduced in [7], also discussed in [6], provides a different viewpoint of the problem. As with all methods, the system is guided by the kinetics of the kinetically-controlled species. The remaining ones are then calculated via a minimisation of the Gibbs free energy of the mixture subject to the constraint that the kinetically-controlled species retain their present values. Thus the dynamical evolution is still governed by kinetics alone. One can draw an analogy with the computation of chemical equilibrium via equilibrium constants and via free energy minimisation. Previous work by the author [3] has addressed the formulation of RCCE as a differential-algebraic (DAE) problem, and shown how it can be applied to non-premixed flames. In this work the derivation of the DAE formulation from first principles is discussed, and subsequently RCCE is employed to predict the burning velocity of premixed H_2-O_2 and CH_4-air flames of varying composition and pressure.

2 Derivation of the Constrained Equilibrium Equations

Minimisation of Gibbs free energy
To derive the RCCE equations, we start from the concept of chemical equilibrium via minimisation of the Gibbs free energy. The mixture Gibbs free energy is:

$$g = \sum_{j=1}^{N} \mu_j n_j \tag{1}$$

where n_j is the composition in kmol/kg of mixture, while the chemical potential, μ_j, can be written in terms of the chemical potential in the standard state [2]:

$$\mu_j = \mu_j^o + RTln\frac{n_j}{n} + RTln\frac{P}{P_o} \tag{2}$$

The condition for the minimisation of Gibbs free energy is:

$$\frac{\partial g}{\partial n_j} = 0 \tag{3}$$

subject to the constraints expressing conservation of elements, enthalpy and pressure:

$$E_i = \sum_{j=1}^{N} a_{ij}^e n_j \quad (i = 1, ..., M_e) \tag{4}$$

$$\sum_{i=1}^{N} n_j h_j = h \tag{5}$$

$$\sum_{i=1}^{N} n_j \rho RT = P \tag{6}$$

Full Equilibrium
The computation of the species' concentrations at the equilibrium state is thus reduced to the solution of a constrained optimisation problem that can be solved with the method of Lagrange multipliers. We first introduce introducing the parameters λ_i^e which we call element potentials and form the following function:

$$g' = g + \sum_{i=1}^{M_e} \lambda_i^e \left(E_i - a_{ij}^e n_j\right) \tag{7}$$

According to the method of Lagrange multipliers, the original operation is equivalent to computing the extrema of this function, i.e.:

$$\frac{\partial g'}{\partial n_j} = 0 \tag{8}$$

Substituting eq. 7 and eq. 1 in eq. 8 yields:

$$\mu_j + \sum_{i=1}^{M_e} \lambda_i^e a_{ij}^e = 0 \tag{9}$$

Substituting eq. 2 we obtain:

$$\mu_j^o + RTln\frac{n_j}{n} + RTln\frac{P}{P_o} + \sum_{i=1}^{M_e} \lambda_i^e a_{ij}^e = 0 \tag{10}$$

This system of equations, together with eqs. 4, 5, 6 can be solved to yield the composition, n_j^*, temperature, density and Lagrange multipliers at the equilibrium state - an efficient method is that of Gordon and McBride [2].

Constrained Equilibrium
We now extend the minimisation of free energy to the constrained equilibrium state by adding the following constraints to those defined by eqs. 4, 5, 6:

$$C_i = \sum_{j=1}^{N} a_{ij}^c n_j \quad (i = 1, ..., M_c) \tag{11}$$

In essence, this states that certain species (or linear combinations of) must retain a certain fixed value. Thus, if for instance a system contains C,H,O and N atoms, the full equilibrium may contain certain NO_x species. If, however, we impose the additional constraint that N_2 retains a value such that all of the N atoms must occur in the form of N_2, we would not observe any NO_x species in the constrained equilibrium state. To perform the mimimisation with the method of Lagrange multipliers, we introduce the additional parameters λ_i^c, which we call constraint potentials, and the function to be minimised is now formed as:

$$g' = g + \sum_{i=1}^{M_e} \lambda_i^e \left(E_i - a_{ij}^e n_j\right) + \sum_{i=1}^{M_c} \lambda_i^c \left(C_i - a_{ij}^c n_j\right) \tag{12}$$

Substituting eq. 12 and eq. 11 in eq. 1 yields:

$$\mu_j + \sum_{i=1}^{M_e} \lambda_i^e a_{ij}^e + \sum_{i=1}^{M_c} \lambda_i^c a_{ij}^c = 0 \tag{13}$$

Using eq. 2, we now obtain:

$$\mu_j^o + RTln\frac{n_j}{n} + RTln\frac{P}{P_o} + \sum_{i=1}^{M_e} \lambda_i^e a_{ij}^e + \sum_{i=1}^{M_c} \lambda_i^c a_{ij}^c = 0 \tag{14}$$

This system of equations must be solved together with the constraints, i.e. eqs. 4, 5, 6 and 11. The method of Gordon and McBride [2] can be straightforwardly extended to carry out this calculation.

Rate-Controlled Constrained Equilibrium
The extension to RCCE is now straightforward. Chemical kinetics yields the production rate for each species in terms of the reaction rates of individual reactions, r_k, and the stoichiometric factors, ν_{jk}, as follows:

$$w_j = \sum_{k=1}^{NR} (\nu_{jk} r_k) \quad (j = 1, ..., N) \tag{15}$$

The main idea of RCCE is to allow certain species (or linear combinations of) to evolve according to kinetics, while computing the remaining species via a constrained equilibrium calculation where the kinetically controlled species are the constraints. The selection of kinetically controlled and equilibrated species can be based on criteria for analysing the separation of time scales, e.g. Peters' criteria [10] or Computational Singular Perturbation (CSP) [8]. RCCE is not a criterion itself; instead it provides a system of equations that describe the evolution of the reduced system, and which has the same general form whatever the selection.

The dynamical evolution of the constraints can be computed as follows:

$$\frac{dC_i}{dt} = \sum_{j=1}^{N} \left(a_{ij}^c \sum_{k=1}^{NR} (\nu_{jk} r_k) \right) \quad (i = 1, ..., M_c) \tag{16}$$

These ODEs must be computed together with the algebraic equations of constrained equilibrium, i.e. eqs. 14, 11, 4, 5, 6. A more convenient form of eq. 14 can be obtained by taking exponentials, so that the equation is directly solved in terms of the composition at the constrained equilibrium state (n_j^*):

$$n_j^* = n \, \frac{P}{P_o} \, exp\left(\frac{-\mu_j^o}{RT}\right) \, exp\left[\sum_{i=1}^{M_e} \left(a_{ij}^e \lambda_i^e\right)\right] \, exp\left[\sum_{i=1}^{M_c} \left(a_{ij}^c \lambda_i^c\right)\right] \quad (j = 1, ..., N) \tag{17}$$

Therefore the basic formulation of RCCE is a differential-algebraic system comprising the ODEs (16) for the constraints and the algebraic equations (17),

(11), (4), (5), (6). Solution of this system determines the constrained equilibrium composition, potentials, temperature and density at each time step. Differential-algebraic systems can be solved using programs such as DASSL [1]. An alternative, pure ODE form can be derived using a process called index reduction; this has been presented in [3] and will not be shown here.

3 Results and Discussion

We shall consider a freely propagating, 1-D premixed laminar flame of constant pressure, with equal diffusivities and Lewis numbers equal to unity. Under these conditions the governing equations assume a well-known form:

$$\frac{\partial \rho u}{\partial x} = 0 \tag{18}$$

$$\rho u \frac{\partial Y_i}{\partial x} = \frac{\partial}{\partial x}\left(\rho D \frac{\partial Y_i}{\partial x}\right) + w_i \tag{19}$$

$$\rho u \frac{\partial h}{\partial y} = \frac{\partial}{\partial y}\left(\frac{\lambda}{Cp}\frac{\partial h}{\partial y}\right) \tag{20}$$

where Y_i are the mass fractions of the constrained species; at the same time, the algebraic equations of RCCE must be satisfied.

We will apply RCCE to reduce a comprehensive mechanism of CH_4 combustion due to Lindstedt and co-workers [4] [5] comprising 63 species and 415 reactions. We will calculate a H_2-air flame using the hydrogen part of the mechanism, comprising only 10 species - in which case, the reduction in CPU is not notable - and a CH_4-air flame using the entire mechanism - resulting in a typical

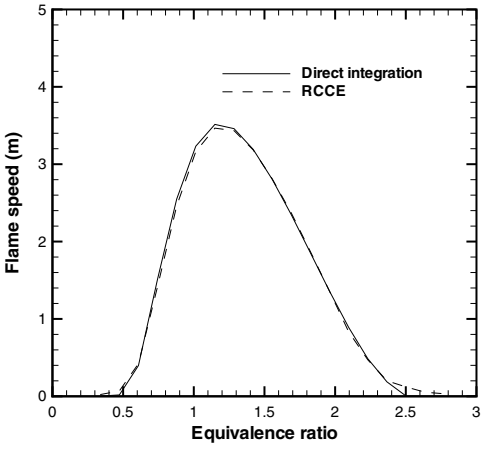

Fig. 1. Burning velocity of stoichiometric H_2 - air flame vs. equivalence ratio, comparison between direct integration and RCCE

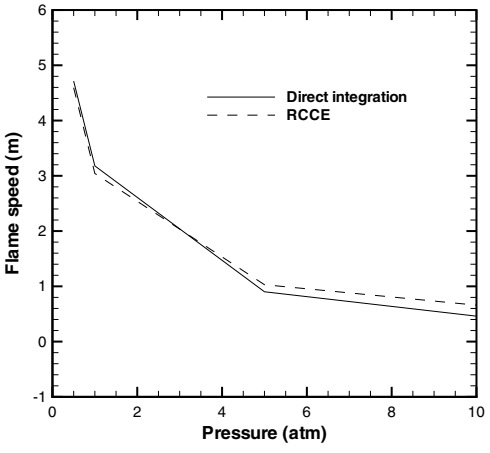

Fig. 2. Burning velocity of stoichiometric H_2 - air flame vs. equivalence ratio, comparison between direct integration and RCCE

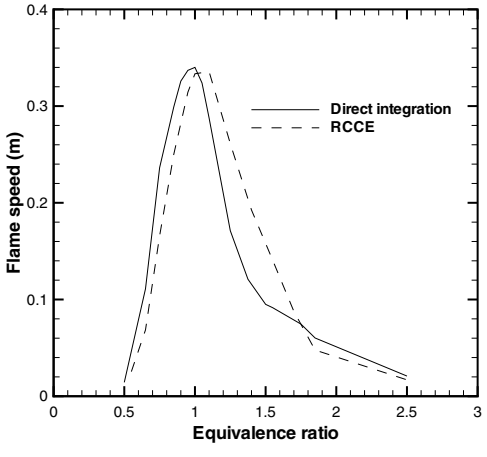

Fig. 3. Burning velocity of stoichiometric CH_4 - air flame vs. equivalence ratio, comparison between direct integration and RCCE

reduction of CPU time from 15 hours to 4. For the H_2 part we constrain H_2, O_2, H_2O, H and OH. For the CH_4 flame we constrain the above plus CH_4, CO_2, CO, O and N_2. These are the most common main species appearing in reduced mechanisms.

Figure 1 shows the predictions of the burning velocity as a function of equivalence ratio for the hydrogen flame. Results are excellent for the entire range of equivalence ratios. Results for different pressures are also shown in fig. 2; these also exhibit good agreement. Figure 3 shows results for the CH_4-air flame over a wide range of equivalence ratios, and good agreement is exhibited in the lean and stoichiometric mixture, with some discrepancy in the rich side. Results for

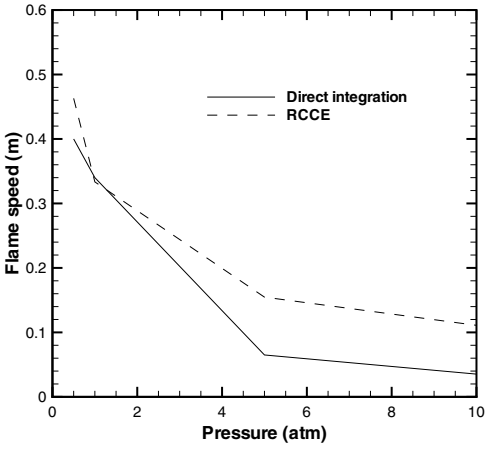

Fig. 4. Burning velocity of stoichiometric CH_4 - air flame vs. pressure, comparison between direct integration and RCCE

different pressures for the CH_4-air flame are also shown in fig. 4, and at elevated pressure the discrepancy is more significant, indicating that more constraints may be necessary to obtain quantitative agreement in that range.

4 Conclusions

In this paper we have presented the derivation of the RCCE equations, starting from the basic equations of chemical equilibrium and chemical kinetics, and shown results for the burning velocity of a laminar premixed flame. RCCE provides a rigorous framework for reduced chemistry computations; the main advantage is that a general differential-algebraic system of equations can be derived that describes the reduced mechanism, irrespective of the choice of kinetically controlled and equilibrated species. Thus once a computer code for solving this system has been set up, investigation of reduced mechanisms is greatly facilitated.

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