A REDUCED-ORDER METHANE-AIR COMBUSTION MECHANISM
THAT SATISFIES THE DIFFERENTIAL ENTROPY INEQUALITY

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Abstract. This paper presents a new method for determining the Arrhenius parameters of a reduced chemical mechanism such that it satisfies the second law of thermodynamics. The strategy is to approximate the progress of each reaction in the reduced mechanism from the species production rates of a detailed mechanism by using a linear least squares method. A series of non-linear least squares curve fittings are then carried out to find the optimal Arrhenius parameters for each reaction. At this step, the molar rates of production are written such that they comply with a theorem that provides the sufficient conditions for satisfying the second law of thermodynamics. This methodology was used to modify the Arrhenius parameters for the Westbrook and Dryer two-step mechanism for methane combustion. The optimized mechanism showed good agreement with the detailed mechanism for species mole fractions and production rates of most major species. The optimized mechanisms produced no violations of the second law of thermodynamics.

Key words: Second law of thermodynamics, Methane combustion, Differential entropy inequality, Laminar flame, Chemically reacting flows.

1. INTRODUCTION

The differential entropy inequality, while not entirely unknown, is always ignored in simulating chemically reacting flows. In addition to satisfying the differential mass, momentum, and energy balances, simulations of chemically/biochemically reacting systems must satisfy the entropy inequality (the second law of thermodynamics). Common types of material behavior (Newton's law of viscosity, Fourier's law, Fick's first law) satisfy the differential entropy inequality automatically, but common empirical descriptions of chemical/biochemical reactions do not.

To simulate methane flame combustion, or any reacting fluid flow, it is necessary to incorporate a reaction mechanism that describes the incremental steps and associated rates leading from reactant species to products. Detailed mechanisms include all possible species and elementary reactions so as to provide accurate solutions in a wide range of simulation conditions. Unfortunately, there is a large computational cost associated with the complexity of detailed mechanisms. Therefore, reduced mechanisms are created for specific conditions where simplifying assumptions can be made to decrease the complexity of detailed mechanisms. It has been shown, however, that common reduced mechanisms produce violations of the differential entropy inequality (DEI)

$$-\text{tr}\left[(\mathbf{T}+P\mathbf{I})\cdot\mathbf{D}\right]+\frac{1}{T}\varepsilon\cdot\nabla T+cRT\sum_{n=1}^{N_S}j_{(n)}\cdot\frac{d_{(n)}}{\rho_{(n)}}+\sum_{r=1}^{N_r}\sum_{n=1}^{N_S}\mu_{(n)}R_{(n)(r)}\leq 0, \qquad (1)$$

a local form of the second law of thermodynamics [1]. Here $\mathbf{T}$ is the stress tensor, P the thermodynamic pressure, I the identity tensor, $\mathbf{D}$ the rate of deformation tensor, c the total molar density, R the gas law constant, T the temperature, N_s the number of species, $j_{(n)}$ the mass flux of species n relative to v, $\rho_{(n)}$ the mass density of species n, N_r the number of reactions, $\mu_{(n)}$ the chemical potential for species n on a molar

basis, and $R_{(n)(r)}$ the rate of production of moles of species n per unit volume by homogeneous chemical reaction r. ε is the energy flux corrected for the effects of mass transfer [2, p. 449]; $d_{(n)}$ is the driving force for mass transfer corrected for temperature gradients and pressure gradients [2, p. 450].

A theorem was introduced in [1], which states that (1) is automatically satisfied for dilute gases if all reactions are reversible and conform to the law of mass action. Using this theorem, a least squares method was proposed to modify a reduced chemical kinetics model to automatically satisfy the DEI [1].

This paper presents an improved method developed to determine rate parameters for reduced mechanisms such that they satisfy the DEI. This method builds on the least squares method that was used to create reduced kinetics models that satisfy the second law of thermodynamics [3]. The next section discusses the approach proposed herein followed by details of the method. The results section presents the new reduced kinetics model and examines whether it satisfy the DEI.

2. APPROACH

The basic idea of this method is to find the Arrhenius rate parameters for a reduced mechanism through a series of curve fittings. Starting with a data set of species production rates as a function of temperature and composition, the progresses of each reaction in the reduced mechanism are estimated using a linear least squares method. The progresses of reaction are then used in a series of non-linear least squares curve fittings to find the Arrhenius rate parameters for each reaction. The original data set can either come from experimentation or from a simulation using a detailed mechanism. For this work, a one-dimensional simulation was carried out using the GRI 3.0 mechanism. The method presented herein makes heavy use of least squares curve fitting techniques so the next section briefly presents a summary of useful relations.

2.1. Least Squares Curve Fitting

Least squares method seeks to minimize the sum of the squares of the difference between the dependent variable data and the function to be fit. This difference is termed the residual and is defined as

$$r_i = y_i - f(x_i, \vec{\eta}), \; i = 1 \ldots N_p. \tag{2}$$

Here r_i is the residual at point i of a data set containing N_p points. The associated independent and dependent coordinates are x_i and y_i, respectively. The equation to fit the data to is f which is a function of the independent variable and the solution vector $\vec{\eta}$; $\vec{\eta} \in \mathbf{R}^{N_\eta}$ where N_η is the number of parameters. Written in vector form the residual becomes

$$\vec{r} = \vec{y} - \vec{f}(\vec{x}, \vec{\eta}). \tag{3}$$

For a linear function of the parameters η_j, the minimization of the square of the residual over all the data points yields [4]

$$\overline{\overline{J}}^T \overline{\overline{J}} \vec{\eta} = \overline{\overline{J}}^T \vec{y}, \tag{4}$$

where the elements of the Jacobian $\overline{\overline{J}}$ are

$$J_{ij} = -\frac{\partial r_i}{\partial \eta_j} = \frac{\partial f(x_i, \vec{\eta})}{\partial \eta_j}, \qquad \begin{matrix} i = 1, \ldots, N_p \\ j = 1, \ldots, N_\eta. \end{matrix} \tag{5}$$

For a non-linear function of the parameters η_j, an iterative method is used to calculate the parameters $\vec{\eta}^{k+1}$
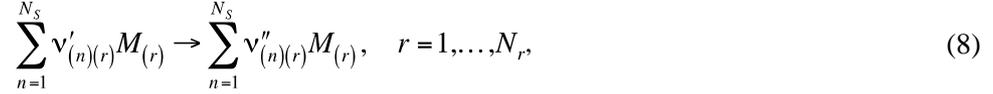
$$\vec{\eta}^{k+1} = \vec{\eta}^k + \Delta \vec{\eta}^k, \tag{6}$$

where k is the index of the iterative process. The correction $\Delta \vec{\eta}$ is calculated by solving

$$\overline{\overline{J}}^{T,k}\overline{\overline{J}}^{k}\vec{\eta}^{k} = \overline{\overline{J}}^{T,k}\vec{k}^{k}. \tag{7}$$

2.2. Finite Rate Chemistry

In a reactive system with N_S chemical species, any arbitrary reaction out of the N_r possibilities can be written as [5, pp. 554–94]

$$\sum_{n=1}^{N_S}\nu'_{(n)(r)}M_{(r)} \rightarrow \sum_{n=1}^{N_S}\nu''_{(n)(r)}M_{(r)}, \quad r=1,\dots,N_r, \tag{8}$$

where $M_{(r)}$ is the chemical symbol for species n and $\nu'_{(n)(r)}$ and $\nu''_{(n)(r)}$ are the stoichiometric coefficients for species n in reaction r as a reactant and a product, respectively. The progress of reaction $r,$ only considering the forward reaction and allowing for non-stoichiometric concentration exponents, is given by

$$\omega_{(r)} = k_{(r)}\prod_{n=1}^{N_S}c_{(n)}^{q'_{(n)(r)}}, \quad r=1,\rightleftharpoons,N_r, \tag{9}$$

where $c_{(n)}$ is the molar concentration of species n.

To evaluate the progress of reaction, the reaction-rate constant $k_{(r)}$ is given by the empirical Arrhenius expression

$$k_{(r)} = A_{(r)}T^{\beta_{(r)}}\exp\left[\frac{-E_{a,(r)}}{\hat{R}T}\right], \quad r=1,\rightleftharpoons,N_r, \tag{10}$$

where $\hat{R}$ is the universal gas law constant and $E_{a,(r)}$ is the activation energy of reaction r.

The net molar production rate of species n is found by simply summing the contributions from each reaction

$$R_{(n)} = \sum_{r=1}^{N_r}R_{(n)(r)} = \sum_{r=1}^{N_r}\left(\nu''_{(n)(r)} - \nu'_{(n)(r)}\right)\omega_{(r)}, \quad n=1,\rightleftharpoons,N_S. \tag{11}$$

2.3. Least Squares Method for Fitting Arrhenius Parameters

The method presented herein distinguishes itself from other methods by first solving for the progress of each reaction, $\omega_{(r)}$ in the reduced mechanism before curve fitting the Arrhenius parameters. In most cases (11) is an over-constrained linear system, which can be represented in matrix form as

$$\vec{R} = \overline{\overline{\nu}}\vec{\omega}. \tag{12}$$

The size of $\overline{\overline{\nu}}$ is $N_S \times N_r$, where N_S and N_r are the number of species and reactions in the reduced mechanism, respectively. Since $\overline{\overline{\nu}}$ is generally non-square, $\vec{\omega}$ must be obtained by solving an optimization problem as in (4). Rewriting in the form of (4) and solving for the reaction progress rates results in

$$\vec{\omega} = \left(\overline{\overline{\nu}}^{T}\overline{\overline{\nu}}\right)^{-1}\overline{\overline{\nu}}^{T}\vec{R}. \tag{13}$$

The solution to (13) gives the progress of each reaction r at every temperature T_i of the one-dimensional flow simulation.

The next step is to perform a set of non-linear least squares curve fits to find the Arrhenius parameters for each reaction. The temperature is the independent variable and the progresses of each reaction just solved for are the dependent variable data. This leads to the residual from (2) being calculated as

$$r_{(r),i} = \omega_{(r),i} - f_{(r),i}\left(T_i, \vec{\eta}_{(r)}\right), \, i = 1 \ldots N_p. \tag{14}$$

Since each progress of reaction is independent, a separate non-linear least squares curve fit must be performed for each reaction. Each curve fit will produce the Arrhenius parameters for one reaction.

The form of the function in the residual is found by substituting the Arrhenius rate equation (10) into the progress of reaction equation (9)

$$f_{(r),i}\left(T_i, \vec{\eta}_{(r)}\right) = A_{(r)} T_i^{\beta_{(r)}} \exp\left[\frac{-E_{a,(r)}}{\hat{R}T}\right] \prod_{n=1}^{N_S} c_{(n),i}^{q'_{(n)(r)}}, \qquad \begin{matrix} i = 1, \ldots, N_p \\ j = 1, \ldots, N_r. \end{matrix} \tag{15}$$

To conform to the law of mass action the exponent $q'_{(n)(r)}$ is taken to be $v'_{(n)(r)}$, the reactant stoichiometric coefficient of species n in reaction r. The solution vector is composed of the Arrhenius parameters for reaction r

$$\eta_{(r)} = \begin{bmatrix} A_{(r)} & \beta_{(r)} & E_{a,(r)} \end{bmatrix}, \quad r = 1, \overset{\rightharpoonup}{\leftharpoondown}, N_r. \tag{16}$$

To summarize, the method consists of the following steps:
1. A detailed mechanism simulation is run to generate a data set containing temperature, species concentration, and species production rate through a flame front.

2. Progresses of reaction are approximated at each data point from the species production rates using linear least squares as in (13).

3. The Arrhenius parameters are found for each reaction by performing a non-linear least squares curve fit of the approximated progresses of reaction.

3. RESULTS

The Arrhenius parameter fitting algorithm presented in section 2 was used to find optimized parameters for the reaction steps of the Westbrook and Dryer two-step mechanism [6]. The newly created mechanism will be called the optimized two-step mechanism. The values of the parameters are given in Table 1.

Table 1

Optimized two-step mechanism Arrhenius parameters

Reaction	Equation	A	β	E
1	$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	3.1623×10^{14}	0.8308	2.3855×10^4
2_f	$CO + 0.5O_2 \rightarrow CO_2$	4.2094×10^6	0.1251	7.3969×10^3
2_b	$CO_2 \rightarrow CO + 0.5O_2$	1.4286×10^9	0.2851	1.7072×10^5

Units are cm, mol, cal, s, and K.

Table 2 gives a comparison of the flame speeds for the optimized two-step mechanism and the detailed GRI 3.0 mechanism [7]. These were all calculated using Cantera [8] for standard atmospheric conditions and a stoichiometric mixture of methane and air.

Table 2

Flame speed comparison of various mechanisms

Mechanism	Flame Speed [cm/s]	Error [%]
GRI 3.0	38.05	—
Optimized 2-step	28.43	25.28

Up to this point all of the discussion of the created mechanism has centered around the Cantera one-dimensional flame simulations. Comparisons of all mechanisms when applied to the axisymmetric FLUENT model of Sandia flame A, including violations of the DEI, will be discussed in the following paragraphs.

A numerical simulation of Sandia flame A using Fluent with the Westbrook and Dryer reduced kinetics model showed that the DEI is violated at 22,014 cells out of 167,523 cells [1]. These violations were due to the fourth term of the left-hand side of (1) becoming positive and exceeding the sum of the other three terms. This section will reassess the entropy violations of Sandia flame A using Fluent with the following kinetics models: GRI 3.0, Westbrook and Dryer, and the model proposed herein.

Table 3 summarizes the violations of the DEI found for each chemical mechanism. The optimized two-step mechanism performed exactly as it was intended, producing no violations of the DEI. The detailed GRI 3.0 mechanism contained a small number of violating cells while the Westbrook and Dryer two-step mechanism contained the most, and largest magnitude, violating cells. The Westbrook and Dryer mechanism was expected to produce the greatest number of violations since it met none of the criteria of the theorem [1].

Table 3

Violations of the DEI for various mechanisms

Mechanism	Number of Cells	Volume Fraction [%]	Maximum Value
GRI 3.0	3513	3.98×10^{-3}	5.72×10^{7}
Westbrook & Dryer	20653	3.62×10^{-2}	1.40×10^{9}
Optimized 2-step	0	0	—

Figure 1 shows contours of violations of the DEI for the two violating mechanisms. For each of the mechanisms there is a channel, centrally located in the flame, where violations do not occur. Violations occur much more prevalently where reactions are occurring, or in other words, where the global reaction has not moved completely to product species. This could also support the theory that violations of the GRI 3.0 mechanism are due to the inaccurate rate parameters for the minor species reactions. However, more analysis is required to verify this claim.
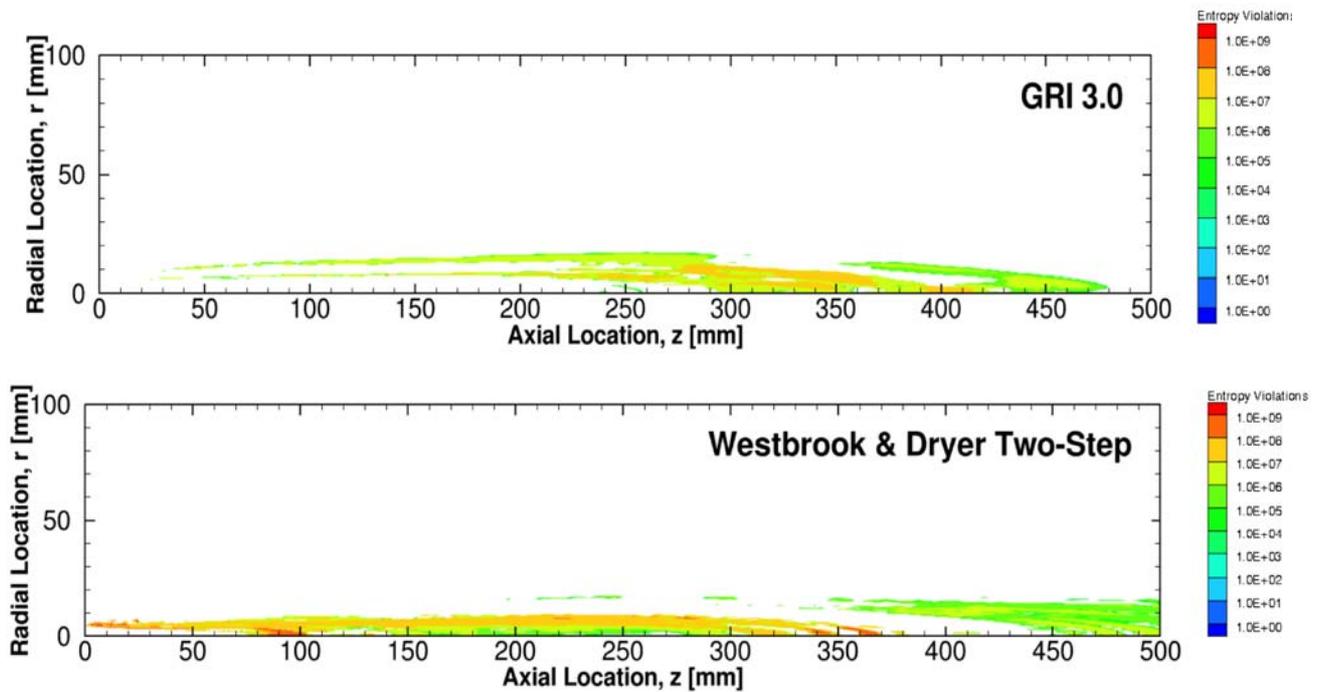

Fig. 1 — Profile of entropy violations for two mechanisms: GRI 3.0 (top) and Westbrook and Dryer two-step (bottom). The optimized two-step mechanism had no violations.

4. CONCLUSIONS

A new method for determining the Arrhenius parameters of a reduced chemical mechanism was developed herein. This method seeks to find an optimal set of parameters for a specific operating condition. The basic strategy is to approximate the progress of each reaction in a reduced mechanism from the species production rates of a detailed mechanism. A series of non-linear least squares curve fittings are then carried out to find the optimal Arrhenius parameters for each reaction. This process was used to find parameters for the reaction steps of the Westbrook and Dryer two-step mechanism. The optimized mechanism showed good agreement with the detailed mechanism for species mole fractions and production rates of most major species. The optimized mechanisms produced no violations of the DEI.

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