

**VALIDATION OF THE ASVDADD CONSTRAINT SELECTION ALGORITHM FOR EFFECTIVE RCCE
MODELING OF NATURAL GAS IGNITION IN AIR**

Luca Rivadossi and Gian Paolo Beretta

Department of Mechanical and Industrial Engineering
Università di Brescia
Via Branze 38, 25123 Brescia, Italy

ABSTRACT

The Rate-Controlled Constrained-Equilibrium (RCCE) model reduction scheme for chemical kinetics provides acceptable accuracies in predicting hydrocarbon ignition delays by solving a smaller number of differential equations than the number of species in the underlying Detailed Kinetic Model (DKM). To yield good approximations, the method requires accurate identification of the rate controlling constraints. Until recently, a drawback of the RCCE scheme has been the absence of a fully automatable and systematic procedure capable of identifying the best constraints for a given range of thermodynamic conditions and a required level of approximation. A recent paper [1] has proposed a new methodology for such identification based on a simple algebraic analysis of the results of a preliminary simulation of the underlying DKM, focused on the behaviour of the degrees of disequilibrium (DoD) of the individual chemical reactions. The new methodology is based on computing an Approximate Singular Value Decomposition of the Actual Degrees of Disequilibrium (ASVDADD) obtained from the DKM simulation. The effectiveness and robustness of the method has been demonstrated in [1] for some cases of methane/oxygen ignition by considering a C1/H/O (29 species/133 reactions) sub-mechanism of the GRI-Mech 3.0 scheme and comparing the results of a DKM simulation with those of RCCE simulations based on increasing numbers of ASVDADD constraints. The RCCE results are in excellent agreement with DKM predictions for relatively small numbers of RCCE constraints. Here we provide a demonstration of the new method for some cases of shock-tube ignition of a natural gas/air mixture, with higher hydrocarbons approximately represented by propane according to the full (53 species/325 reactions) GRI-Mech 3.0 scheme.

1 INTRODUCTION

In the framework of modeling the ignition of a homogeneous methane/air mixture, the purpose of this paper is to present a validation of the recently proposed [1] ASVDADD method (Approximate Singular Value Decomposition of the

Actual Degrees of Disequilibrium) for automatic constraint selection for use in the RCCE (Rate-Controlled Constrained-Equilibrium) method of model order reduction [2-14]. The ASVDADD method requires a preliminary full DKM (Detailed Kinetic Model) simulation aimed at computing the time dependence of the DoD (Degree of Disequilibrium) of every individual chemical reaction in the scheme. It then extracts the selection of RCCE constraints from the Singular Value Decomposition (SVD) of a matrix that contains the information about the DoD-time traces of all reactions.

In Section 2, we review the assumptions of a typical DKM for gas-phase combustion. In Section 3, we recall the meaning of DoD-time trace analysis. In Section 4, we review the RCCE fundamentals. In Section 5, we outline the general logic of automatic constraint selection and in Section 6, the particular logic of the ASVDADD algorithm based on DoD analysis. In Section 7, we present the results of the numerical validation and in Section 8 our conclusions.

2 STANDARD DKM FORMULATION

A Detailed Kinetic Model for gas-phase combustion is typically defined by:

- A list of n_s chemical species.
- A kinetic scheme with r chemical reactions (we denote the forward and reverse stoichiometric coefficients of the ℓ -th reaction by $\nu_{j\ell}^+$ and $\nu_{j\ell}^-$, respectively).
- The kinetic parameters that determine the forward reaction rate constants

$$k_{\ell}^+(T) = A_{\ell}^+ T^{b_{\ell}^+} \exp(-E_{\ell}^+/RT) \quad (1)$$

(typically in mol-cm-s-K units with the forward activation energy E_{ℓ}^+ in cal/mol).

- The principle of detailed balance to determine the backward reaction rate constants according to

$$k_{\ell}^-(T) = k_{\ell}^+(T)/K_{\ell}^{co}(T) \quad (2)$$

where the equilibrium constant based on concentrations is

$$K_{\ell}^{co}(T) = (p_o/RT)^{\nu_{\ell}} \exp(-\Delta g_{\ell}^o(T)/RT) \quad (3)$$

where $v_\ell = \sum_j (v_{j\ell}^- - v_{j\ell}^+)$ and $\Delta g_\ell^o(T) = \sum_{j=1}^{n_s} v_{j\ell} g_{jj}(T, p_o)$ is the Gibbs free energy of the ℓ -th reaction at standard pressure p_o and temperature T . In the present paper, we use the notation of [11], which differs only slightly from that of [15], whereby $g_{jj} = \mu_{jj}$ (with the double subscript) refers to the Gibbs free energy of pure substance j , whereas the symbol $g_j = \mu_i$ (with a single subscript), used below, represents instead the partial Gibbs free energy, i.e., the chemical potential, of species j in the mixture.

- The relation

$$r_\ell^\pm = k_\ell^\pm(T) \prod_{j=1}^{n_s} [N_j]^{v_{j\ell}^\pm} \quad (4)$$

to compute the forward and reverse reaction rates, r_ℓ^+ and r_ℓ^- , respectively, where $[N_j]$ is the concentration of species j . From these we compute the chemical production density terms in the species balance equations (consumption density if negative)

$$\dot{\omega}_j = \sum_{\ell=1}^{n_r} v_{j\ell} (r_\ell^+ - r_\ell^-) \quad (5)$$

and the chemical contribution to the entropy production density

$$\sigma_{\text{chem}} = R \sum_{\ell=1}^{n_r} (r_\ell^+ - r_\ell^-) \ln (r_\ell^+ / r_\ell^-) \quad (6)$$

- The local equilibrium assumption whereby the so-called "surrogate system" [16-17] obtained by instantaneously "freezing" all reactions can be assumed to have the properties of a stable thermodynamic equilibrium at temperature T and pressure p of the non-reacting mixture (hence the "off" subscript, below) with mole fractions

$$X_j = [N_j]/[N], \quad \text{where } [N] = \sum_{j=1}^{n_s} [N_j] \quad (7)$$

For convenience, we introduce the vector of mole fractions

$$\mathbf{X} = [X_1 \dots X_{n_s}] \quad (8)$$

- The assumption of ideal Gibbs-Dalton mixture of ideal gases whereby $p = [N]RT$ and the chemical potential of species j in the "surrogate system" is given by

$$\mu_{j,\text{off}}(T, p, \mathbf{X}) = g_{jj}(T, p_o) + RT \ln(p/p_o) + RT \ln(X_j) \quad (9)$$

For convenience, we introduce the *entropic chemical potentials*

$$\lambda_j = \lambda_{j,\text{off}}(T, p, \mathbf{X}) = -\mu_{j,\text{off}}(T, p, \mathbf{X})/RT \quad (10)$$

and, for shorthand, the vectors

$$\mathbf{A} = [\lambda_1 \dots \lambda_{n_s}] \quad (11)$$

$$\mathbf{A}_{\text{pure}} = [\lambda_{11} \dots \lambda_{n_s n_s}] \quad (12)$$

$$\ln \mathbf{X} = [\ln X_1 \dots \ln X_{n_s}] \quad (13)$$

so that Eq. (9) rewrites in either of the following forms

$$\mathbf{A} = \mathbf{A}_{\text{pure}}(T, p_o) - \ln(p/p_o) - \ln \mathbf{X} \quad (14)$$

$$\mathbf{A} = \mathbf{A}_{\text{pure}}(T, p) - \ln \mathbf{X} \quad (15)$$

3 DEGREES OF DISEQUILIBRIUM

The degree of disequilibrium (DoD) of reaction ℓ is defined as

$$\phi_\ell = \ln(r_\ell^+ / r_\ell^-) \quad (16)$$

For convenience of discussion, below we refer to the degree of disequilibrium of reaction ℓ also by DoD_ℓ . Under the set of

assumptions outlined in the preceding sections, it is easy to verify that DoD_ℓ is related to T, p, \mathbf{X} via the equation

$$\phi_\ell = \sum_{j=1}^{n_s} v_{j\ell} \lambda_{j,\text{off}}(T, p, \mathbf{X}) \quad (17)$$

and to $T, [N]$ via the non-equilibrium law of mass action

$$\prod_{j=1}^{n_s} [N_j]^{v_{j\ell}} = K_\ell^{\text{co}}(T) \exp(-\phi_\ell) \quad (18)$$

In view of Eqs. (4), some DoD's are $\pm\infty$ when some of the $[N_j]$'s are zero. We exclude such cases from our treatment, meaning that for all practical purposes, when the concentration of a species j is initially zero, we substitute the zero with a very small value, like $[N_j] = 10^{-10} [N]$.

The mathematical interpretation of Eq. (17) is that the DoD of a reaction is a linear combination of the rows of the stoichiometric matrix, with the $\lambda_{j,\text{off}}$'s as coefficients of the linear combination. Thus, if some columns of the stoichiometric matrix are linearly dependent, then so are the corresponding DoD's.

We also observe that Eq. (17) may be rewritten as the scalar product of the vector \mathbf{A} with the vector

$$\mathbf{v}_\ell = [v_{1\ell} \dots v_{n_s \ell}] \quad (19)$$

whose entries correspond to the ℓ -th column of the matrix $\mathbf{v} = [v_{j\ell}]$ of the stoichiometric coefficients, i.e., we may write

$$\phi_\ell = \sum_{j=1}^{n_s} \lambda_j v_{j\ell} = \langle \mathbf{A} | \mathbf{v}_\ell \rangle \quad (20)$$

where $\langle \mathbf{x} | \mathbf{y} \rangle = \sum_{i=1}^{n_s} x_i y_i$ denotes the scalar product of two vectors $\mathbf{x} = [x_1 \dots x_{n_s}]$ and $\mathbf{y} = [y_1 \dots y_{n_s}]$ in the vector space \mathbb{R}^{n_s} consisting of all ordered n_s -tuples of real numbers.

From Eq. (5) and defining the *overall production density* vector

$$\mathbf{\Omega} = [\dot{\omega}_1 \dots \dot{\omega}_{n_s}] \quad (21)$$

the entropy production density may also be written as

$$\sigma_{\text{chem}} = R \sum_{j=1}^{n_s} \lambda_j \sum_{\ell=1}^{n_r} v_{j\ell} (r_\ell^+ - r_\ell^-) = \langle \mathbf{A} | \mathbf{\Omega} \rangle R \quad (22)$$

In general the reactions in a given DKM are not all independent. Element conservation requires the stoichiometric coefficients to satisfy the following n_{el} balance conditions

$$\sum_{j=1}^{n_s} a_{ij}^{\text{EL}} v_{j\ell} = 0 \quad \text{for } i=1, \dots, n_{\text{el}} \text{ and } \ell=1, \dots, n_r \quad (23)$$

where of course a_{ij}^{EL} represents the number of atoms of type i in a molecule of species j . These conditions guarantee that the chemical production/consumption terms in the species balances equations satisfy the *element conservation constraints*

$$\sum_{j=1}^{n_s} a_{ij}^{\text{EL}} \dot{\omega}_j = 0 \quad \text{for } i=1, \dots, n_{\text{el}} \quad (24)$$

Defining the n_{el} linearly independent vectors

$$\mathbf{a}_i^{\text{EL}} = [a_{i1}^{\text{EL}} \dots a_{in_s}^{\text{EL}}] \quad \text{for } i=1, \dots, n_{\text{el}} \quad (25)$$

the stoichiometric balance conditions (23) become orthogonality conditions

$$\langle \mathbf{a}_i^{\text{EL}} | \mathbf{v}_\ell \rangle = 0 \quad (26)$$

implying that the column space $\text{span}(\{\mathbf{v}_\ell\})$ of the stoichiometric matrix \mathbf{v} , i.e., the linear span of the set of stoichiometric vectors \mathbf{v}_ℓ whose entries are given by its

columns, often called the *reactive subspace*, is orthogonal to the n_{el} -dimensional linear span $\text{coker}(\mathbf{v})$ of the elemental constraint vectors $\{\mathbf{a}_i^{\text{EL}}\}$, often called the *inert subspace*. This also implies that the matrix \mathbf{v} of stoichiometric coefficients has rank $r = n_s - n_{\text{el}}$. The *reactive subspace* and the *inert subspace* are orthogonal complements in the n_s -dimensional real vector space \mathbb{R}^{n_s} , i.e., we may write

$$\mathbb{R}^{n_s} = \text{span}(\{\mathbf{v}_\ell\}) \oplus \text{coker}(\mathbf{v}) \quad (27)$$

meaning that any vector $\mathbf{x} = [x_1 \dots x_n]$ in \mathbb{R}^{n_s} may be decomposed as $\mathbf{x} = \mathbf{x}_{\text{span}(\{\mathbf{v}_\ell\})} + \mathbf{x}_{\text{coker}(\mathbf{v})}$ with $\mathbf{x}_{\text{span}(\{\mathbf{v}_\ell\})}$ in $\text{span}(\{\mathbf{v}_\ell\})$, $\mathbf{x}_{\text{coker}(\mathbf{v})}$ in $\text{coker}(\mathbf{v})$, and of course $\langle \mathbf{x}_{\text{span}(\{\mathbf{v}_\ell\})} | \mathbf{x}_{\text{coker}(\mathbf{v})} \rangle = 0$. Therefore, applying such decomposition to the vector \mathbf{A} we may write

$$\mathbf{A} = \mathbf{A}_{\text{DoD}} + \mathbf{A}_\perp \quad (28)$$

where for shorthand we introduced the notation

$$\mathbf{A}_{\text{DoD}} = \mathbf{A}_{\text{span}(\{\mathbf{v}_\ell\})} \quad \text{and} \quad \mathbf{A}_\perp = \mathbf{A}_{\text{coker}(\mathbf{v})} \quad (29)$$

Clearly, Eqs. (14) and (15) rewrite as

$$\mathbf{A}_{\text{DoD}} = \mathbf{A}_{\text{pure}}(T, p_o) - \mathbf{A}_\perp - \ln(p/p_o) - \ln \mathbf{X} \quad (30)$$

$$\mathbf{A}_{\text{DoD}} = \mathbf{A}_{\text{pure}}(T, p) - \mathbf{A}_\perp - \ln \mathbf{X} \quad (31)$$

We call \mathbf{A}_{DoD} the *overall degree of disequilibrium* vector (ODoD). In general we can write

$$\mathbf{A}_\perp = \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL}} \mathbf{a}_i^{\text{EL}} \quad (32)$$

Since $\langle \mathbf{A}_\perp | \mathbf{v}_\ell \rangle = 0$, we can rewrite Eqs. (20) and (22) as follows

$$\phi_\ell = \sum_{j=1}^{n_s} \lambda_j \nu_{j\ell} = \langle \mathbf{A}_{\text{DoD}} | \mathbf{v}_\ell \rangle \quad \text{for } \ell=1, \dots, n_r \quad (33)$$

$$\sigma_{\text{chem}} = \langle \mathbf{A}_{\text{DoD}} | \mathbf{\Omega} \rangle R \quad (34)$$

Moreover, importantly, we can construct a (non orthogonal) basis for the r -dimensional $\text{span}(\{\mathbf{v}_\ell\})$ by choosing a subset of r linearly independent columns of the stoichiometric matrix identified by the column numbers ℓ_k , for $k = 1, \dots, r$. With respect to this basis we can write

$$\mathbf{A}_{\text{DoD}} = \sum_{k=1}^r \alpha_k \mathbf{v}_{\ell_k} \quad (35)$$

It is also worth noting that the component \mathbf{A}_\perp lies in the n_{el} -dimensional linear span of the elemental constraints and is all that remains of vector \mathbf{A} at complete chemical equilibrium where all the DoD's are zero and, therefore, $\mathbf{A}_{\text{DoD}} = 0$.

We now substitute Eq. (35) into Eq. (33) for $\ell = \ell_{k'}$ to obtain

$$\phi_{k'} = \sum_{k=1}^r \alpha_k \langle \mathbf{v}_{\ell_k} | \mathbf{v}_{\ell_{k'}} \rangle \quad (36)$$

which can be viewed as a linear system of equations that we can solve for the α_k 's because the $r \times r$ matrix $M_{kk'} = \langle \mathbf{v}_{\ell_k} | \mathbf{v}_{\ell_{k'}} \rangle$ is non-singular by virtue of the linear independence of the basis vectors \mathbf{v}_{ℓ_k} . Hence, denoting its inverse by $\mathbf{W} = \mathbf{M}^{-1}$, we can write the solution of the system as

$$\alpha_k = \sum_{k'=1}^r \phi_{k'} W_{k'k} \quad (37)$$

Substituting into Eq. (35), we obtain $\mathbf{A}_{\text{DoD}} = \sum_{k=1}^r \sum_{k'=1}^r \phi_{k'} W_{k'k} \mathbf{v}_{\ell_k} = \sum_{k=1}^r \phi_k \sum_{k'=1}^r W_{kk'} \mathbf{v}_{\ell_{k'}}$ which shows that we can transform to a more convenient (still

non orthogonal) basis for $\text{span}(\{\mathbf{v}_\ell\})$, defined by the transformation

$$\chi_k = \sum_{k'=1}^r W_{kk'} \mathbf{v}_{\ell_{k'}} \quad (38)$$

with respect to which the coordinates of \mathbf{A}_{DoD} are the DoD's of the chosen r linearly independent reactions ℓ_k , for $k = 1, \dots, r$, i.e.,

$$\mathbf{A}_{\text{DoD}} = \sum_{k=1}^r \phi_k \chi_k \quad (39)$$

It is important to note that the basis vectors χ_k can be computed once and for all, for the given DKM, by simple algebraic operations based exclusively on the matrix \mathbf{v} of stoichiometric coefficients. Note also that the same procedure may yield different linearly independent sets of reactions and basis vectors χ_k if the columns of the stoichiometric matrix are sorted in a different order.

Relation (39) is very important for the ASVDADD algorithm of automatic selection of RCCE constraints. It is also important in general for the analysis of results obtained from a DKM simulation because it allows to construct the ODoD vector \mathbf{A}_{DoD} from the values ϕ_k of the DoD's of only a subset of r independent reactions.

In this paper, we consider the unsteady problem of predicting the ignition delay time of a homogeneous gas mixture. Therefore, the results of a DKM simulation will be functions of time t only, i.e., Eq. (39) rewrites as

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t) = \sum_{k=1}^r \phi_k^{\text{DKM}}(t) \chi_k \quad (40)$$

4 RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM APPROXIMATION

The main assumption of the RCCE modeling approximation is that the gas mixture evolves along a low-dimensional manifold in composition space where the associated local equilibrium states of the "surrogate system", i.e., the stable equilibrium state obtained by instantaneously "freezing" all reactions, have the *constrained equilibrium* composition \mathbf{X}^{CE} that minimizes the Gibbs free energy for the instantaneous local values of the temperature T , the pressure p , the element concentrations $[N_i^{\text{EL}}]$, and a set of $n_c (< r)$ rate-controlling constraint densities $c_i([\mathbf{N}])$, defined as linear combinations of the local species concentration via the relations

$$\sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{EL}} [N_j] = [N_i^{\text{EL}}] \quad \text{for } i = 1, \dots, n_{\text{el}} \quad (41)$$

$$\sum_{j=1}^{n_{\text{sp}}} a_{ij}^{\text{CE}} [N_j] = c_i([\mathbf{N}]) \quad \text{for } i = 1, \dots, n_c \quad (42)$$

where the constraint matrix $\mathbf{a}^{\text{CE}} = [a_{ij}^{\text{CE}}]$ plays a crucial role and must be chosen so that Eqs. (42) possibly represent the slowest varying linear combinations of the local concentrations, in principle associated with the main rate-controlling bottlenecks of the underlying DKM at the local conditions. The composition \mathbf{X}^{CE} defined by such constrained minimization is

$$\ln X_j^{\text{CE}} = \lambda_{jj}(T, p) - \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL,CE}} a_{ij}^{\text{EL}} - \sum_{i=1}^{n_c} \gamma_i^{\text{CE}} a_{ij}^{\text{CE}} \quad (43)$$

Introducing as in the previous section the following notation,

$$\mathbf{A}_{\perp}^{\text{CE}} = \sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL,CE}} \mathbf{a}_i^{\text{EL}} \quad (44)$$

$$\mathbf{A}_{\text{DoD}}^{\text{CE}} = \sum_{i=1}^{n_c} \gamma_i^{\text{CE}} \mathbf{a}_i^{\text{CE}} \quad (45)$$

$$\mathbf{a}_i^{\text{CE}} = [\alpha_{i1}^{\text{CE}} \dots \alpha_{in_s}^{\text{CE}}] \quad \text{for } i=1, \dots, n_c \quad (46)$$

$$\ln \mathbf{X}^{\text{CE}} = [\ln X_1^{\text{CE}} \dots \ln X_{n_s}^{\text{CE}}] \quad (47)$$

we may rewrite Eq. (43) in the following form

$$\mathbf{A}_{\text{DoD}}^{\text{CE}} = \mathbf{A}_{\text{pure}}(T, p) - \mathbf{A}_{\perp}^{\text{CE}} - \ln \mathbf{X}^{\text{CE}} \quad (48)$$

suitable for comparison with the ODoD vector resulting from a full DKM simulation, which according to Eq. (31) is

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}} = \mathbf{A}_{\text{pure}}(T, p) - \mathbf{A}_{\perp}^{\text{DKM}} - \ln \mathbf{X}^{\text{DKM}} \quad (49)$$

Subtracting these two equations, if the composition \mathbf{X}^{CE} is a good approximation of \mathbf{X}^{DKM} , we may write the following formal expression for the vector of relative errors

$$\frac{\mathbf{X}^{\text{CE}} - \mathbf{X}^{\text{DKM}}}{\mathbf{X}^{\text{DKM}}} \approx \ln \left(\frac{\mathbf{X}^{\text{CE}}}{\mathbf{X}^{\text{DKM}}} \right) =$$

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}} - \mathbf{A}_{\text{DoD}}^{\text{CE}} + \sum_{i=1}^{n_{\text{el}}} (\gamma_i^{\text{EL,DKM}} - \gamma_i^{\text{EL,CE}}) \mathbf{a}_i^{\text{EL}} \quad (50)$$

where of course we introduced the shorthand notation

$$\ln(\mathbf{X}/\mathbf{X}^{\text{CE}}) = [\ln(X_1^{\text{CE}}/X_1^{\text{DKM}}) \dots \ln(X_{n_s}^{\text{CE}}/X_{n_s}^{\text{DKM}})] \quad (51)$$

$$\frac{\mathbf{X}^{\text{CE}} - \mathbf{X}^{\text{DKM}}}{\mathbf{X}^{\text{DKM}}} = \left[\frac{X_1^{\text{CE}} - X_1^{\text{DKM}}}{X_1^{\text{DKM}}} \dots \frac{X_{n_s}^{\text{CE}} - X_{n_s}^{\text{DKM}}}{X_{n_s}^{\text{DKM}}} \right] \quad (52)$$

Also, for the entropy production density the error is

$$\sigma_{\text{chem}}^{\text{CE}} - \sigma_{\text{chem}}^{\text{DKM}} = \langle \mathbf{A}_{\text{DoD}}^{\text{DKM}} - \mathbf{A}_{\text{DoD}}^{\text{CE}} | \mathbf{\Omega} \rangle R \quad (53)$$

5 SELECTION OF RCCE CONSTRAINTS

The general idea behind the RCCE method [1-14] is that for each set of conditions and a given degree of acceptable approximation there is a threshold time scale which essentially separates the "relatively fast" equilibrating mechanisms from those that slow down and control the spontaneous relaxation towards stable chemical equilibrium. The "relatively slow" mechanisms control the interesting part of the non-equilibrium dynamics in that they effectively identify a low-dimensional manifold in composition space, where, for the chosen level of approximation, the dynamics can be assumed to take place. In general, as shown in [18], time-scale based methods for the selection of constraints do not necessarily identify the most effective set of constraints, whereas it was shown in [12] that the analysis of DoD traces provides important information. Ref. [1] developed the idea into a truly algorithmic method for automatic RCCE-constraint selection based on choosing, for a preset value of n_c , the n_c constraint vectors \mathbf{a}_i^{CE} that minimize a suitably weighted average of the relative error between the ODoD vector time-traces $\mathbf{A}_{\text{DoD}}^{\text{CE}(n_c)}(t)$ and $\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t)$ obtained respectively from the RCCE simulation and the DKM simulation, starting from the same initial conditions.

A weighted average of the relative error may be defined as

$$\epsilon(n_c) = \frac{\int_{t_{\text{initial}}}^{t_{\text{final}}} \left| \mathbf{A}_{\text{DoD}}^{\text{DKM}}(t) - \mathbf{A}_{\text{DoD}}^{\text{CE}(n_c)}(t) \right|^2 w^2(t) dt}{\int_{t_{\text{initial}}}^{t_{\text{final}}} \left| \mathbf{A}_{\text{DoD}}^{\text{DKM}}(t) \right|^2 w^2(t) dt} \quad (54)$$

where $|\Lambda|^2 = \sum_{j=1}^{n_{\text{sp}}} [\Lambda_j]^2$ and the weight function $w^2(t)$ is to be chosen so as to emphasize the important features of the time traces, in particular, where the solution varies rapidly.

A DKM or RCCE simulation requires the numerical integration of a set of (stiff) differential equations for T, p, \mathbf{X} or $T, [N]$ or T, p, \mathbf{A} . Typically, we use a differential equation solver which chooses variable integration time steps so as to meet efficiently the prescribed error tolerances. For the homogeneous ignition problem at hand, the resulting time-discretization grid is typically a non-uniform time sequence, $t_0 \dots t_p \dots t_P$ where the index p labels the P points and P is usually a large integer. The ODoD vector that results from such a DKM simulation is an $n_s \times P$ matrix,

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p) = [\mathbf{A}_{\text{DoD},jp}^{\text{DKM}}] \quad (55)$$

that using Eq. (39) we can write as

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p) = \sum_{k=1}^r \phi_k^{\text{DKM}}(t_p) \mathbf{x}_k \quad (56)$$

Therefore, this $n_s \times P$ matrix has rank $r = n_s - n_{\text{el}}$.

The RCCE method seeks to approximate this matrix with one of smaller rank $n_c < r$

$$\mathbf{A}_{\text{DoD}}^{\text{CE}(n_c)}(t_p) = \sum_{i=1}^{n_c} \gamma_i^{\text{CE}}(t_p) \mathbf{a}_i^{\text{CE}} \quad (57)$$

where the constraint vectors \mathbf{a}_i^{CE} are chosen so as to minimize an error measure such as that defined in Eq. (54).

6 ASVDADD ALGORITHM BASED ON DOD ANALYSIS OF A DKM SIMULATION

The ASVDADD algorithm bases the selection of constraints on the singular value decomposition [19] (SVD) of the $n_s \times P$ matrix $\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p)$ obtained from a preliminary DKM simulation for the problem at hand. The canonical form of the SVD is

$$\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p) = \mathbf{U} \mathbf{\Sigma} \mathbf{V}^T \quad (58)$$

The $r = n_s - n_{\text{el}}$ nonzero singular values σ_j are in decreasing order in the $n_s \times P$ diagonal matrix $\mathbf{\Sigma}$ followed by the zero ones. The first r columns of the $n_s \times n_s$ orthogonal matrix \mathbf{U} identify an orthonormal basis for the r -dimensional co-kernel of $\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p)$.

For a chosen number $n_c < r$ of constraints, let us define the $n_s \times P$ diagonal matrix $\mathbf{\Sigma}^{\text{CE}(n_c)}$ obtained from $\mathbf{\Sigma}$ by setting to zero its diagonal elements with index $j > n_c$. By the Eckart-Young theorem of linear algebra, the $n_s \times P$ matrix

$$\mathbf{A}_{\text{DoD}}^{\text{CE}(n_c)}(t_p) = \mathbf{U} \mathbf{\Sigma}^{\text{CE}(n_c)} \mathbf{V}^T \quad (59)$$

represents the 'best approximation' to $\mathbf{A}_{\text{DoD}}^{\text{DKM}}(t_p)$ that can be achieved by a matrix of rank n_c , in the sense of minimizing the Frobenius measure δ_{Fro} of the approximation defined by

$$\delta_{\text{Fro}}^2(n_c) = \frac{\|A_{\text{DoD}}^{\text{DKM}}(t_p) - A_{\text{DoD}}^{\text{CE}(n_c)}(t_p)\|_{\text{Fro}}^2}{\|A_{\text{DoD}}^{\text{DKM}}(t_p)\|_{\text{Fro}}^2} \quad (60)$$

$$= \frac{\sum_{j=1}^{n_s} \sum_{p=1}^P [A_{\text{DoD}j}^{\text{DKM}}(t_p) - A_{\text{DoD}j}^{\text{CE}(n_c)}(t_p)]^2}{\sum_{j=1}^{n_s} \sum_{p=1}^P [A_{\text{DoD}j}^{\text{DKM}}(t_p)]^2}$$

which turns out to be equal to the ratio

$$\delta_{\text{Fro}}(n_c) = \frac{\sum_{i=n_c+1}^r \sigma_i}{\sum_{i=1}^r \sigma_i} \quad (61)$$

where σ_{n_c+1} is the first neglected singular value.

The ASVDADD algorithm adopts

$$\epsilon_{\text{ASVDADD}}(n_c) = \delta_{\text{Fro}}^2(n_c) \quad (62)$$

This error measure corresponds to accepting in Eq. (54) the weight function $w^2(t)$ that has been implicitly chosen by the differential equation solver we used for the DKM simulation so as to adapt and refine the time discretization grid where the solution changes rapidly.

By construction, the first n_c columns of the $n_s \times n_s$ orthogonal matrix \mathbf{U} identify an orthonormal basis for the n_c -dimensional co-kernel of $A_{\text{DoD}}^{\text{CE}(n_c)}(t_p)$. This means that, if we denote these columns by \mathbf{a}_i^{CE} , we can write

$$A_{\text{DoD}}^{\text{CE}(n_c)}(t_p) = \sum_{i=1}^{n_c} \gamma_i^{\text{CE}}(t_p) \mathbf{a}_i^{\text{CE}} \quad (63)$$

thus achieving the objective of the RCCE modeling approximation, because the first n_c columns of the matrix \mathbf{U} can be taken as the desired n_c 'best' RCCE constraints \mathbf{a}_i^{CE} (in addition to the n_{el} elemental ones).

The great advantage of the ASVDADD procedure is that -- at the expense of a specific but very natural choice for the measure of 'approximation' and hence of 'optimality' of the choice of constraints -- the SVD of $A_{\text{DoD}}^{\text{DKM}}(t_p)$ provides at once the entire spectrum of optimal constraints (the first r columns of \mathbf{U}) in decreasing order of importance. The optimal set of n_c constraint vectors \mathbf{a}_i^{CE} are just the first n_c columns of \mathbf{U} .

7 VALIDATION OF THE ASVDADD METHOD FOR AN IGNITION PROBLEM

The present validation study focuses on the ignition of a homogeneous stoichiometric mixture of methane and air in a constant volume and constant energy setup, for two initial conditions, 900 K and 10 atm, and 1500 K and 1 atm. In Ref. 1 a demonstration of the efficiency and robustness of the ASVDADD algorithm was done for a 29 species/133 reactions C1/H/O sub mechanism [10] of the GRI-Mech 3.0 scheme [21]. Here, instead, to probe the new algorithm in a more complex situation, we retain the full GRI-Mech 3.0 scheme, which considers $n_r = 325$ reactions between $n_s = 53$ species with $n_{\text{el}} = 5$ elements (C,H,O,N,Ar).

From the numerical point of view, considering our limited computational needs, especially the choice of the homogeneous

ignition problem which requires no integration with CFD, we opted for the flexibility that could gain by rewriting the entire set of DKM, ASVDADD and RCCE codes in MatLab so as to use the built-in differential equations solvers. In particular, we used the ode15s for the integration of the stiff DKM and RCCE system of species balance and energy balance equations.

To avoid infinite values of the DoD's, we set an initial composition $N_j(0)$ that is not exactly stoichiometric. We assume 1 mol of CH₄, stoichiometric amounts of O₂, N₂, and Ar (respectively, 2 mol, 7.52 mol, and 0.08 mol), and 10^{-10} mol for each of the other 49 species.

We proceed as follows. We first run a full DKM simulation with these initial amounts and the initial temperature $T(0)$ and pressure $p(0)$ of interest (in this study, either 1500 K and 1 atm or 900 K and 10 atm). Clearly, the volume is fixed by $V = N(0)RT(0)/p(0)$ and so is the energy via the specific heats dependence on temperature. We use the results of the DKM simulation to compute the $n_s \times P$ matrix $A_{\text{DoD}}^{\text{DKM}}(t_p)$ where the non-uniform sequence of P time steps has been chosen by the ode15s solver. We then compute the SVD of this matrix using svd MatLab function which returns the $n_s \times n_s$ orthogonal matrix \mathbf{U} whose columns essentially identify all the ASVDADD constraints to be added to the elemental constraints. Thus, for a chosen value of n_c we take the first n_c columns of the matrix \mathbf{U} as the non-elemental constraints, \mathbf{a}_i^{CE} , additional to the n_{el} elemental ones, \mathbf{a}_i^{EL} . Next, we run the RCCE(C) simulation based on these $C = n_c + n_{\text{el}}$ constraints. Since, as explained for example in [10-13], it is computationally convenient to solve the rate equations for the C constraint potentials $\gamma_i^{\text{EL,CE}}(t)$ and $\gamma_i^{\text{CE}}(t)$ (rather than for the species concentrations), we need to start the computation by establishing initial values $\gamma_i^{\text{EL,CE}}(0)$ and $\gamma_i^{\text{CE}}(0)$ of the constraint potentials that through Eq. (43) approximate well the given initial composition. We do so by imposing Eq. (43) only for a set of C 'major species', i.e., by solving the system of C equations

$$\sum_{i=1}^{n_{\text{el}}} \gamma_i^{\text{EL,CE}}(0) \mathbf{a}_{ij}^{\text{EL}} + \sum_{i=1}^{n_c} \gamma_i^{\text{CE}}(0) \mathbf{a}_{ij}^{\text{CE}} = \lambda_{jj}(T(0), p(0)) - \ln X_j^{\text{CE}}(0) \quad j = 1, \dots, C \quad (64)$$

for the C unknown values $\gamma_i^{\text{EL,CE}}(0)$ and $\gamma_i^{\text{CE}}(0)$, where we empirically selected as major species the first C in a list where they are ranked in decreasing order by their values of the sum

$$\left(\sum_{i=1}^{n_{\text{el}}} a_{ij}^{\text{EL}} + \sum_{i=1}^{n_c} a_{ij}^{\text{CE}} \right) \lambda_{jj}(T(0), p(0)) N_j(0) \quad (65)$$

The values $\gamma_i^{\text{EL,CE}}(0)$ and $\gamma_i^{\text{CE}}(0)$ are also used, again in Eq. (43), to compute the corrected initial mole fractions X_j^{CE} of all the other species and, using $N = p(0)V/RT(0)$, the corrected initial amounts $N'_j(0)$. Finally, we use these corrected initial amounts to run a corrected DKM simulation that we use to compare results with the RCCE(C) simulations.

The plots in Figures 1 compare temperature, pressure and mole-fraction time-traces obtained from the DKM simulation with those obtained, for $T(0) = 1500$ K and $p(0) = 1$ atm, from the RCCE(C) simulations based on $C = n_c + n_{\text{el}}$

constraints. It is noted that with a relatively small number (5 and 8) of non-elemental constraints the RCCE results are in very good agreement with the DKM results, even in capturing fine details such as the overshoot/undershoot in the OH concentration at ignition time shown in one of the insets. To check the robustness of the ASVDADD algorithm, the plots for temperature show RCCE results also for $C = 7$ and 16, showing that to capture well also the temperature overshoot we need 11 non-elemental constraints.

Figure 2 shows similar comparisons for $T(0) = 900$ K and $p(0) = 10$ atm.

For a small sample of reactions, Figures 3 and 4 compare, for the same simulations as in Figures 1 and 2 respectively, the DoD time traces obtained from the DKM simulation with those obtained from the RCCE(C) simulations.

8 CONCLUSIONS

The ASVDADD algorithm for systematic RCCE constraint identification is based on analyzing how the degrees of disequilibrium (DoD) of the chemical reactions behave in a full DKM test simulation. Geometrically, the procedure identifies a

low-dimensional subspace in DoD space from which the actual DoD traces do not depart beyond a fixed distance related to a preset tolerance level.

The effectiveness and robustness of the methodology has already been demonstrated in [1] for several test cases of increasing complexity in the framework of oxy-combustion of hydrogen (8 species, 24 reactions) and methane (29 species, 133 reactions). In the present paper, we provide a demonstration for the even more complex full GRI-Mech 3.0 kinetic scheme (53 species, 325 reactions) for methane/air combustion including nitrogen oxidation.

The excellent performance of the ASVDADD constraints confirm that conclusion in [1] that the new algorithm essentially resolves the difficulties that have prevented the RCCE method from a more widespread use in model order reduction of detailed combustion kinetic models of hydrocarbon fuels.

In future work we will show that the same model order reduction logic can find natural extensions also in the more general field of nonequilibrium thermodynamics, in particular in the general frameworks discussed in [22].

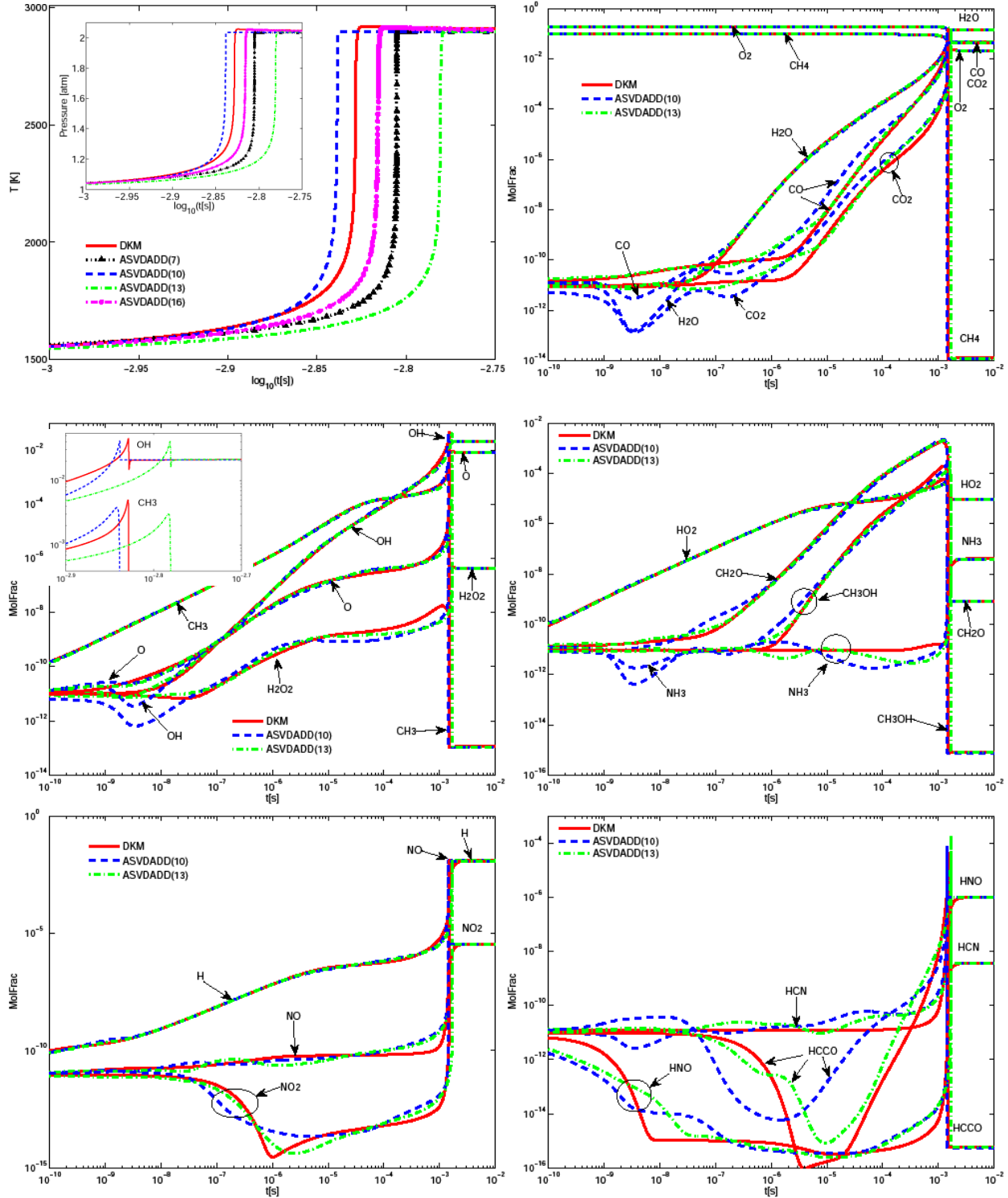


Figure 1. Constant- (E, V) ignition of a homogeneous mixture of methane and air. Initially, the mixture is at 1500 K and 1 atm, with 1 mol of CH_4 , stoichiometric amounts of O_2 , N_2 , and Ar (respectively, 2 mol, 7.52 mol, and 0.08 mol), and very small amounts (between $10^{-12} \div 10^{-10}$ mol) for each of the other 49 species. The plots compare temperature, pressure and mole-fraction time traces obtained from the DKM simulation with those obtained from the RCCE(C) simulations based on $C = n_c + n_{el}$ constraints, with $C = 10$ and 13, of which $n_{el} = 5$ are the element conservation ones (C,H,O,N,Ar) and the remaining $n_c = C - n_{el}$ are those obtained from the ASVDADD algorithm based on the DoD traces produced by the DKM simulation. To check the robustness of the ASVDADD algorithm, the plots for temperature shows RCCE results also for $C = 7$ and 16.

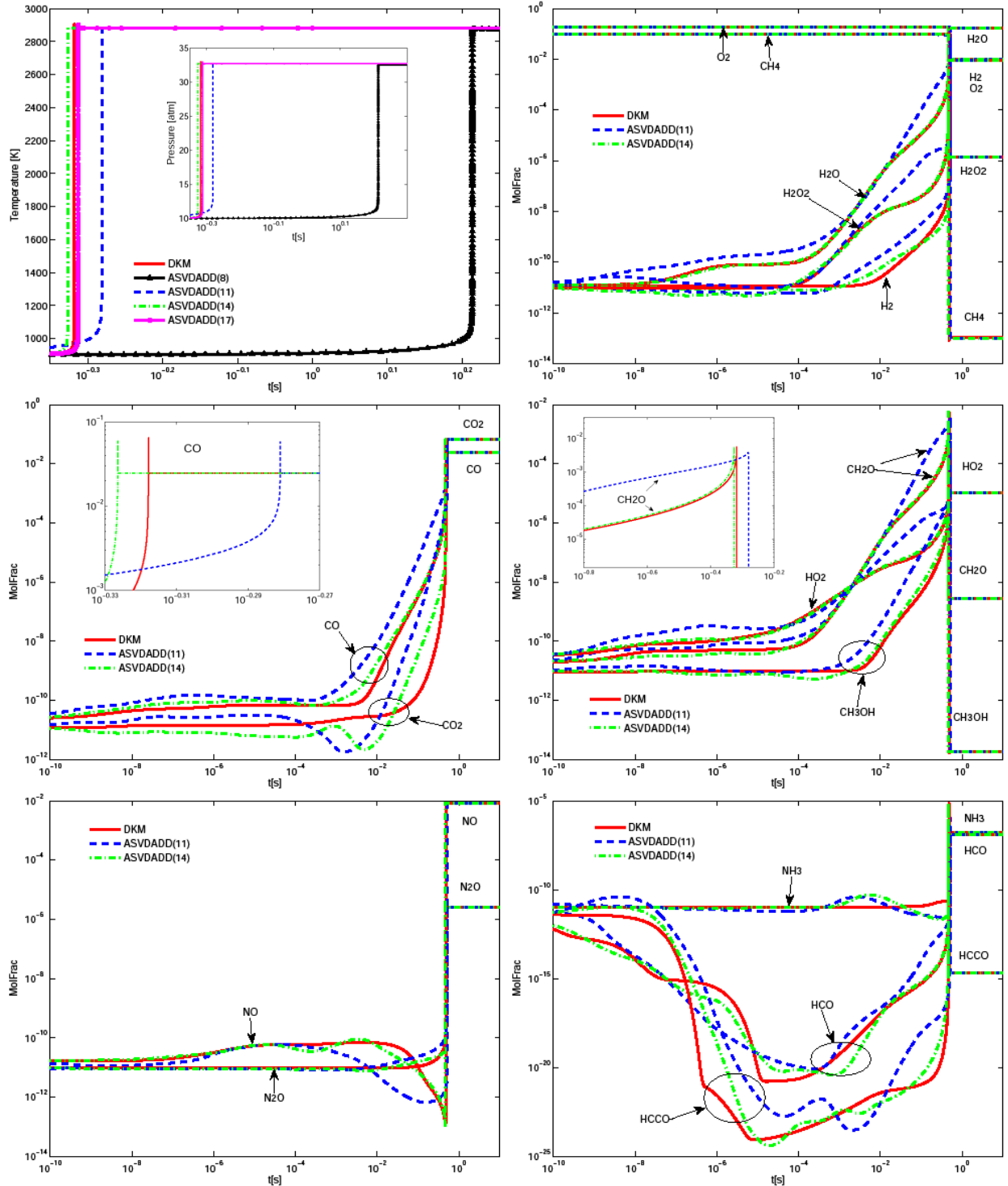


Figure 2. Constant- (E, V) ignition of a homogeneous mixture of methane and air. Initially, the mixture is at 900 K and 10 atm, with 1 mol of CH_4 , stoichiometric amounts of O_2 , N_2 , and Ar (respectively, 2 mol, 7.52 mol, and 0.08 mol), and very small amounts (between $10^{-12} \div 10^{-10}$ mol) for each of the other 49 species. The plots compare temperature, pressure and mole-fraction time traces obtained from the DKM simulation with those obtained from the RCCE(C) simulations based on $C = n_c + n_{el}$ constraints, with $C = 11$ and 14 , of which $n_{el} = 5$ are the element conservation ones (C,H,O,N,Ar) and the remaining $n_c = C - n_{el}$ are those obtained from the ASVDADD algorithm based on the DoD traces produced by the DKM simulation. To check the robustness of the ASVDADD algorithm, the plots for temperature shows RCCE results also for $C = 8$ and 17 .

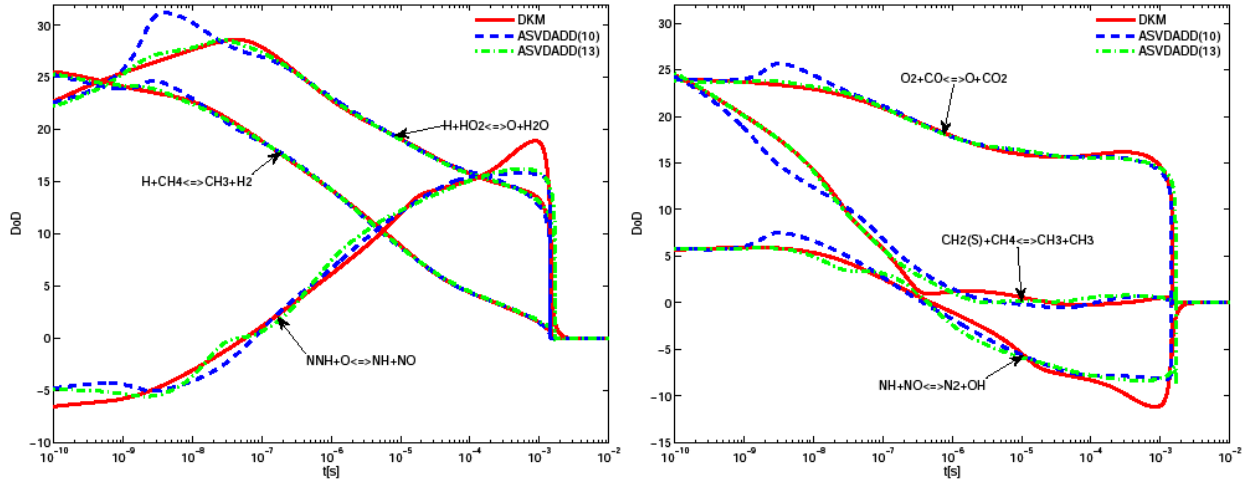


Figure 3. Constant- (E, V) ignition of a homogeneous mixture of methane and air. Initially, the mixture is at 1500 K and 1 atm, with 1 mol of CH_4 , stoichiometric amounts of O_2 , N_2 , and Ar (respectively, 2 mol, 7.52 mol, and 0.08 mol), and very small amounts (between $10^{-12} \div 10^{-10}$ mol) for each of the other 49 species. Same simulations as in Figure 1. The plots compare, for a small sample of reactions, the DoD time traces obtained from the DKM simulation with those obtained from the RCCE(C) simulations based on $C = n_c + n_{el}$ constraints, with $C = 10$ and 13, of which $n_{el} = 5$ are the element conservation ones.

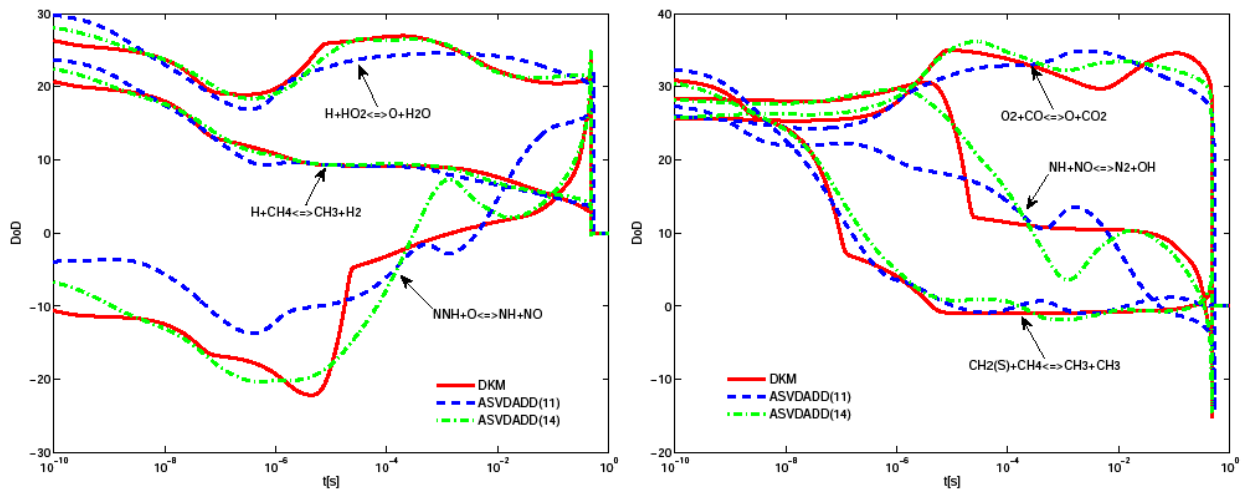


Figure 4. Constant- (E, V) ignition of a homogeneous mixture of methane and air. Initially, the mixture is at 900 K and 10 atm, with 1 mol of CH_4 , stoichiometric amounts of O_2 , N_2 , and Ar (respectively, 2 mol, 7.52 mol, and 0.08 mol), and very small amounts (between $10^{-12} \div 10^{-10}$ mol) for each of the other 49 species. Same simulations as in Figure 2. The plots compare, for a small sample of reactions, the DoD time traces obtained from the DKM simulation with those obtained from the RCCE(C) simulations based on $C = n_c + n_{el}$ constraints, with $C = 11$ and 14, of which $n_{el} = 5$ are the element conservation ones.

REFERENCES

- [1] G.P. Beretta, M. Janbozorgi, and H. Metghalchi, Degree of Disequilibrium Analysis for Automatic Selection of Kinetic Constraints in the Rate-Controlled Constrained-Equilibrium Method, *Combustion and Flame*, in press.
- [2] J.C. Keck, D. Gillespie, Rate-controlled partial-equilibrium method for treating reacting gas mixtures, *Combust. Flame* 17 (1971) 237-241.
- [3] J.C. Keck, Rate-controlled constrained equilibrium method for treating reactions in complex systems, in: R.D. Levine, M. Tribus (Eds.), *The Maximum Entropy Formalism*, MIT Press, Cambridge, MA, 1979, pp. 219-245. Available online: <http://www.jameskeckcollectedworks.org/>
- [4] G.P. Beretta, J.C. Keck, The constrained-equilibrium approach to nonequilibrium dynamics, in: R.A. Gaggioli (Ed.), *Second Law Analysis and Modeling*, ASME Book H0341C-AES, Vol.3, ASME, New York, 1986, pp. 135-139. Available online: <http://www.jameskeckcollectedworks.org/>
- [5] R. Law, M. Metghalchi, J.C. Keck, Rate-controlled constrained equilibrium calculations of ignition delay times in Hydrogen-Oxygen mixtures, *Symp. (Int.) Combust.* 22 (1988) 1705-1713.
- [6] J.C. Keck, Rate-controlled constrained-equilibrium theory of chemical reactions in complex systems, *Prog. Energy Combust. Sci.* 16 (1990) 125-154.
- [7] P. Bishnu, D. Hamiroune, H. Metghalchi, J.C. Keck, Constrained-equilibrium calculations for chemical systems subject to generalized linear constraints using the NASA and STANJAN equilibrium programs, *Combust. Theory Modelling* 1 (1997) 295-312.
- [8] D. Hamiroune, P. Bishnu, H. Metghalchi, J.C. Keck, Rate-controlled constrained-equilibrium method using constraint potentials, *Combust. Theory Modelling* 2 (1998) 81-94.
- [9] V. Yousefian, A rate-controlled constrained-equilibrium thermochemistry algorithm for complex reacting systems, *Combust. Flame* 115 (1998) 66-80.
- [10] M. Janbozorgi, S. Ugarte, H. Metghalchi, J.C. Keck, Combustion modelling of mono-carbon fuels using the rate-controlled constrained-equilibrium method, *Combust. Flame* 156 (2009) 1871-1885.
- [11] G.P. Beretta, J.C. Keck, M. Janbozorgi, H. Metghalchi, The rate-controlled constrained-equilibrium approach to far-from-local-equilibrium thermodynamics, *Entropy* 14 (2012) 92-130.
- [12] M. Janbozorgi, H. Metghalchi, Rate-controlled constrained-equilibrium modeling of H-O reacting nozzle flow, *J. Propul. Power* 28 (2012) 677-684.
- [13] G. Nicolas, M. Janbozorgi, H. Metghalchi, Constrained-equilibrium modeling of Methane oxidation in air, *ASME J. Energy Res. Technol.* 136 (2014) 032205.
- [14] G. Nicolas, H. Metghalchi, Comparison between RCCE and shock tube ignition delay time at low temperatures, *ASME J. Energy Res. Technol.* 137 (2015) 062203.
- [15] E.P. Gyftopoulos, G.P. Beretta, *Thermodynamics. Foundations and Applications.* (First edition, Macmillan, NY, 1991), Dover Publications, Mineola, NY, 2005.
- [16] G.P. Beretta E.P. Gyftopoulos, What is a chemical equilibrium state?, *ASME J. Energy Res. Technol.* 137 (2015) 021008.
- [17] G.P. Beretta, E.P. Gyftopoulos, Thermodynamic derivations of conditions for chemical equilibrium and of Onsager reciprocal relations for chemical reactors, *J. Chem. Phys.* 121 (2004) 2718-2728.
- [18] V. Hiremath, Z. Ren, S.B. Pope, Combined dimension reduction and tabulation strategy using ISAT-RCCE-GALI for the efficient implementation of combustion chemistry, *Combust. Flame* 158 (2011) 2113-2127[19] C.D. Martin, M.A. Porter, The extraordinary SVD, *Am. Math. Monthly* 119 (2012) 838-851.
- [20] S. Wold, K. Esbensen, P. Geladi, Principal component analysis, *Chemom. Intell. Lab. Syst.* 2 (1987) 37-52.
- [21] Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski, and Zhiwei Qin, GRI-Mech 3.0, http://www.me.berkeley.edu/gri_mech/
- [22] G.P. Beretta, Steepest entropy ascent model for far-nonequilibrium thermodynamics: Unified implementation of the maximum entropy production principle, *Phys. Rev. E* 90 (2014) 042113.