JOURNAL OF COMPUTATIONAL PHYSICS **128,** 261–273 (1996)
ARTICLE NO. 0209

On the Construction and Use of Reduced Chemical Kinetic Mechanisms Produced on the Basis of Given Algebraic Relations

D. A. GOUSSIS

Department of Mechanical Engineering, University of Patras, 26110 Rio-Patras, Greece

Received May 8, 1995; revised December 28, 1995

An algorithm proposed by Chen (*Combust. Sci. Technol.* **57,** 89 (1988)) for the construction of reduced chemical kinetic mechanisms is reviewed. It is shown that the algorithm can be formally used only with the steady state approximation. A new algorithm is presented which can accept more general assumptions. However, for the new algorithm to be successful these assumptions must meet a certain condition which is presented. The reduced mechanisms generated by both algorithms do not provide optimum accuracy and stability in numerical simulations. This can be achieved by a specific refinement of these reduced mechanisms according to the CSP method. © 1996 Academic Press, Inc.

1. INTRODUCTION

There is a growing literature on subjects related to the construction of reduced chemical kinetic mechanisms. This need was created by the efficiency and accuracy required in the simulation of combustion phenomena on the basis of large and complex detailed chemical kinetic mechanisms. A conventional reduced mechanism consists of a few global steps involving a small number of chemical species. The reaction rates of the global steps are usually very simple linear combinations of some of the elementary rates. The stoichiometric coefficients of the global steps and the coefficients in their rate's linear combination are constants. This feature is desired in the case of laminar flame simulations (due to the simplicity of the computations) and is required for turbulent flame simulations (due to the additional computations for closure such as presumed or transported pdf's).

A typical example is the reduced mechanism developed for wet CO flames. Starting from a detailed mechanism involving 21 elementary steps (forward and backward directions counted separately), 10 reacting chemical species and 3 elements, Wang, Rogg, and Williams [1] and Wang and Rogg [2] produced and successfully tested the following sequence of 3, 2, and 1 step mechanisms:

3-step mechanism,

$$\begin{aligned} &H_2O + CO \leftrightarrow H_2 + CO_2 && w_{\mathrm{I}} = w_{18f} - w_{18b} \\ &2\,H + M \leftrightarrow H_2 + M && w_{\mathrm{II}} = w_{5f} + w_{15} + w_{16} \\ & && \quad - w_{24f} + w_{24b} \\ &3\,H_2 + O_2 \leftrightarrow 2\,H_2O + 2\,H && w_{\mathrm{III}} = w_{1f} - w_{1b} \\ & && \quad + w_6 + w_9; \end{aligned} \tag{1a}$$

2-step mechanism,

$$\begin{aligned} &H_2O + CO \leftrightarrow H_2 + CO_2 && w_{\mathrm{I}} = w_{18f} - w_{18b} \\ &2\,H_2 + O_2 \leftrightarrow 2\,H_2O && w_{\mathrm{II}} = w_{1f} - w_{1b} \\ & && \quad + w_6 + w_9; \end{aligned} \tag{1b}$$

1-step mechanism,

$$CO + \tfrac{1}{2}O_2 \leftrightarrow CO_2 \quad w_{\mathrm{I}} = w_{18f} - w_{18b}. \tag{1c}$$

From these three mechanisms (which were constructed on the basis of 4, 5, and 6, respectively, steady state approximations for the appropriate species), we can make the following observations. From a total of 10 reacting species in the detailed mechanism, the stoichiometry of the three reduced mechanisms above contain 6, 5, and 3 species, respectively. The global reaction rates of the three mechanisms involve 11, 6, and 2 elementary rates, respectively, out of a total of 21. Finally, the stoichiometric coefficients in the global steps and the coefficients multiplying the elementary rates in the linear relations making up the global rates are constants. Similar remarks are valid for all reduced mechanisms in the literature (e.g., [3]).

A thorough review of the process of constructing a reduced mechanism is presented in Refs. [4, 5]. The starting point is the identification of:

(i) the linear relations among the elementary rates, resulting from steady state or partial equilibrium approximations;

0021-9991/96 $18.00
Copyright © 1996 by Academic Press, Inc.
All rights of reproduction in any form reserved.

(ii) the "steady state" species, the mass fraction of which shall be computed by these relations; and

(iii) the fast elementary reactions.

These identifications can be made in a number of ways (e.g., sensitivity analysis [6–9], rate of production analysis [10, 11], principal component analysis [12], minimizing the Q.S.S.A. error [13], and CSP [14–16]) with various degrees of accuracy. Some of these methods for analyzing chemical kinetics mechanisms are encoded in the public domain code KINALC [17]. The problem is how to use this information in constructing reduced mechanisms.

For the derivation of reduced chemical kinetic mechanisms, it is commonly accepted that "steady state" species and rates of fast elementary reactions should not appear in the stoichiometry of the reduced mechanism and its global rates, respectively. The absence of fast elementary rates is desired since it renders the reduced mechanism free of fast time scales. However, the absence of "steady state" species is not necessary since the problem can be stated in terms of the progress variables (linear combinations of the species mass fraction) the number of which does not depend on the appearance of the radicals in the stoichiometry of the reduced mechanism (equals the number of species in the detailed mechanism minus the number of given algebraic relations among the elementary reaction rates).

Chen [18] developed an algorithm which, given (i) a detailed mechanism, (ii) a number of fast reactions, and (iii) an equal number of "steady state" species, produces a reduced mechanism in the stoichiometry of which the identified "steady state" species are absent. In addition, the identified fast elementary reactions are not involved in the rates of the reduced mechanism. Chen concludes that a reduced mechanism derived in this way can be used with any algebraic relations among the elementary reaction rates for the computation of the "steady state" species mass fractions. The implication is that one might use any steady state or partial equilibrium relation, of course, within the confines imposed by the given fast reactions and "steady state" species. The algorithm developed by Chen was employed successfully in a number of problems [19–21]. The public domain code RedMech [22], which was developed independently, is similar to the Chen algorithm utilizing steady state assumptions only.

In this paper it will be shown that Chen's algorithm can only accommodate algebraic relations among the elementary reaction rates which refer to steady state approximations. For any other approximation (i.e., partial equilibrium), the algorithm is not formally valid. The question is whether an algorithm exists which can handle more general approximations having the form of linear relations among the elementary reaction rates. It will be shown that such an algorithm exists only for a limited range of such relations which must meet certain conditions. The new algorithm produces a reduced mechanism the rates of which do not involve the rates of the fast elementary reactions. However, its stoichiometry involves all species. This is not a problem since, both algorithms (Chen's and the one presented here) produce the same number of progress variables.

Having constructed a reduced mechanism, the question is how to use it in the numerical solution of the governing equations. The conventional method is to treat the reduced mechanism as a detailed one. For example, for the wet CO flame problem one uses the 2-step mechanism (1.b) in the governing equations in exactly the same way as the detailed mechanism. The only difference is that the mass fractions of the species which do not appear in the stoichiometry but are involved in the global rates must be computed by the appropriate steady state approximations [1, 2]. This method has two major sources of errors. The first is related to the fact that only some of the species appear in the stoichiometry of the reduced mechanism. As a result, differences between the detailed and reduced mechanisms arise in the conservation of elements [23]. The second source of error is related to the way the algebraic relations among the elementary reaction rates are used in the procedure of constructing a reduced mechanism. In simple terms, this kind of error can be described as follows. The algebraic relations are linear combinations of reaction rates equaling zero. It will be shown later that these relations can provide accurate predictions for the mass fraction of the appropriate "steady state" species. However, when they are used in order to construct the global steps, one has to replace the zero in the RHS of the algebraic relations by an asymptotic value which is time or space dependent.

The latter modification of the algebraic relations is equivalent to using a reduced mechanism which is not global (as the mechanisms (1a–1c)), but which is time or space dependent. It will be shown that such a, local in character, mechanism can be constructed by the CSP-provided formulas. All that is needed is an initial guess for a reduced mechanism which CSP will refine so that a higher accuracy is obtained. It will be shown that such an initial guess can be provided by either the algorithm developed by Chen [18] or the more general one presented here.

Reduced mechanisms which are time or space dependent can also be constructed with the *intrinsic low dimensional manifold* method [24–27]. It will be shown that these mechanisms are to leading order similar to the ones constructed with the CSP method.

The structure of the manuscript is as follows. First, the physical problem is defined and the corresponding governing equations are stated. Some of the tools used by the CSP method are presented which will be used in the analy-

sis that follows. Chen's algorithm is then presented and its limitations are identified. Subsequently, a new algorithm is developed which relaxes the conditions under which Chen's algorithm is formally valid. The validity of the conventional methodology of using reduced mechanisms is discussed. Finally, a more accurate methodology is presented and its relation to the CSP and the inertial manifold methods is established. The accuracy improvement is illustrated by a simple example.

2. GOVERNING SPECIES EQUATIONS

We consider the numerical simulation of a combustion process on the basis of a detailed mechanism consisting of N species, K elementary reactions, and E elements. The species equation has the form:

$$\frac{\partial \mathbf{y}}{\partial t} = \mathbf{L}(\mathbf{y}, \mathbf{u}, T) + \mathbf{g}(\mathbf{y}, T), \tag{2}$$

where $\mathbf{y}$ is the N-dimensional vector of species mass fractions, $\mathbf{u}$ is the velocity vector, T is the temperature, $\mathbf{L}$ is an N-dimensional spatial differential vector operator (e.g., diffusion and convection), and $\mathbf{g}$ is the N-dimensional source term vector. The source term $\mathbf{g}$ is of the form

$$\mathbf{g} = \mathbf{WSR}, \tag{3}$$

where $\mathbf{W}$ is a diagonal $N \times N$ matrix with the species molecular weights as entries, $\mathbf{S}$ is a $N \times K$ matrix with constant coefficients, and $\mathbf{R}$ is a K-dimensional vector. The N elements of the columns $\mathbf{S}_i$ $(i = 1, K)$ of the $\mathbf{S}$ matrix correspond to the N stoichiometric coefficients of the ith elementary step in the detailed chemical kinetic mechanism and the K elements R^i $(i = 1, K)$ of the $\mathbf{R}$ vector correspond to the K elementary reaction rates:

$$\mathbf{S} = [\mathbf{S}_1, \mathbf{S}_2, ..., \mathbf{S}_K], \quad \mathbf{S}_i = \begin{pmatrix} S_i^1 \\ S_i^2 \\ \vdots \\ S_i^N \end{pmatrix}, \quad \mathbf{R} = \begin{pmatrix} R^1 \\ R^2 \\ \vdots \\ R^K \end{pmatrix}. \tag{4}$$

With these definitions, the source term $\mathbf{g}$ becomes

$$\mathbf{g} = \mathbf{WS}_1 R^1 + \mathbf{WS}_2 R^2 + \cdots + \mathbf{WS}_K R^K. \tag{5}$$

Note that, since the vectors $\mathbf{S}_i$ are N-dimensional, only $N - E$ of them are linearly independent due to the conservation of elements in the elementary steps. The representation (5) of $\mathbf{g}$ is physically meaningful, since it displays clearly all the processes (reactions) involved. However, this representation is not that meaningful if a reduced mechanism must be constructed. The appropriate form of $\mathbf{g}$ can be provided by the CSP method which is outlined next.

3. CSP FORMULATION OF THE CHEMICAL SOURCE TERM

The CSP methodology [14–16] is based on the appropriate split of the species mass fraction space in two subdomains. The first (fast) subdomain produces the mathematical formulation of all physical assumptions (steady state and partial equilibrium) required for the construction of a reduced mechanism. The second (slow) subdomain produces the required data (stoichiometry and reaction rates) of the reduced mechanism. The split of the species mass fraction space is defined by a specific set of basis vectors. The development of the algorithm for identifying this base can be found elsewhere [14–16, 24]. Here only a brief outline is presented on what such a basis can accomplish and on how it can be produced.

It is assumed that the N-dimensional space of species mass fraction is spanned by a set of N linearly independent N-dimensional *column* vectors $\mathbf{a}_i$:

$$\mathbf{a} = [\mathbf{a}_1, \mathbf{a}_2, ..., \mathbf{a}_N]. \tag{6}$$

The corresponding orthonormal (inverse) set of basis vectors consists of N N-dimensional *row* vectors $\mathbf{b}^i$:

$$\mathbf{b} = \begin{pmatrix} \mathbf{b}^1 \\ \mathbf{b}^2 \\ \vdots \\ \mathbf{b}^N \end{pmatrix}, \tag{7}$$

where

$$\mathbf{b}^i \cdot \mathbf{a}_j = \delta_j^i \quad \text{or} \quad \mathbf{ab} = \mathbf{ba} = \mathbf{I} \tag{8}$$

and $\mathbf{I}$ is the $N \times N$ unit matrix. From the definitions (3)–(8), the vector $\mathbf{g}$ can be expanded in terms of the vectors $\mathbf{a}_i$ as

$$\begin{aligned} \mathbf{g} = \mathbf{abg} &= \mathbf{a}_1(\mathbf{b}^1\mathbf{WS}) \cdot \mathbf{R} + \mathbf{a}_2(\mathbf{b}^2\mathbf{WS}) \cdot \mathbf{R} \\ &\quad + \cdots + \mathbf{a}_N(\mathbf{b}^N\mathbf{WS}) \cdot \mathbf{R} && (9a) \\ &= \mathbf{a}_1(\mathbf{B}^1 \cdot \mathbf{R}) + \mathbf{a}_2(\mathbf{B}^2 \cdot \mathbf{R}) \\ &\quad + \cdots + \mathbf{a}_N(\mathbf{B}^N \cdot \mathbf{R}) && (9b) \\ &= \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2 + \cdots + \mathbf{a}_N f^N, && (9c) \end{aligned}$$

where the $\mathbf{B}^i$'s are N ($i = 1, N$) K-dimensional row vectors and the f^i's are N ($i = 1, N$) scalars:

$$\mathbf{B}^i = \mathbf{b}^i\mathbf{WS} = [\mathbf{b}^i \cdot \mathbf{WS}_1, \mathbf{b}^i \cdot \mathbf{WS}_2, ..., \mathbf{b}^i \cdot \mathbf{WS}_K] = [B_1^i, B_2^i, ..., B_K^i] \tag{10}$$

$$f^i = \mathbf{b}^i \cdot \mathbf{WSR} = \mathbf{B}^i \cdot \mathbf{R} = B_1^i R^1 + B_2^i R^2 + \cdots + B_K^i R^K. \tag{11}$$

Comparing the two expressions (5) and (9c) for the source term **g,** we can make the following observations:

(a) the vectors $\mathbf{a}_i$ ($i = 1, N$) are the stoichiometric vectors of a nonphysical chemical kinetic mechanism comprising N elementary steps, and

(b) the scalars f^i ($i = 1, N$) are the corresponding elementary reaction rates. As Eq. (11) indicates, the nonphysical reaction rates f^i are formed by a linear combination of the K elementary rates R^i of the original kinetic mechanism.

The fact that the two expressions (5) and (9c) for the source term **g** are identical, indicates that *the physical mechanism* (comprising N species and K elementary steps) *and the nonphysical one* (comprising N species and N steps) *are equivalent.*

Let us assume that, given the basis vectors (6), there exist M ($M < N$) linearly independent relations among the elementary reaction rates:

$$B_1^i R^1 + B_2^i R^2 + \cdots + B_K^i R^K \approx 0, \quad i = 1, M. \tag{12}$$

This suggests that there exists a $(N-M)$-step mechanism which can be identified as follows. Substituting the algebraic relations (12) in the expression for **g** (9c) yields

$$\mathbf{g} \approx \mathbf{a}_{M+1} f^{M+1} + \mathbf{a}_{M+2} f^{M+2} + \cdots + \mathbf{a}_N f^N. \tag{13}$$

We conclude that the $N-M$ vectors $\mathbf{a}_i$ and the $N-M$ scalars f^i ($i = M+1, N$) are the stoichiometric vectors and reaction rates, respectively, of the $(N-M)$-step mechanism.

It is clear that for the construction of the reduced mechanism all that is required are the basis vectors $\mathbf{a}_i$ and the number M. The first M vectors,

$$[\mathbf{a}_1, \mathbf{a}_2, ..., \mathbf{a}_M], \tag{14a}$$

describe the fast subdomain in the species space, while the remaining $N-M$ vectors,

$$[\mathbf{a}_{M+1}, \mathbf{a}_{M+2}, ..., \mathbf{a}_N], \tag{14b}$$

describe the slow subdomain. As it is shown elsewhere [14–16], the basis vectors (14a) describe the subdomain in which the fast time scales in the problem have a direct influence. The relations (12) are the result of this influence expressing the fact that these time scales have exhausted themselves. Furthermore, these relations indicate that the trajectory in the state space moves in a $(N-M)$-dimensional manifold. Finally, Eq. (13) indicates that the motion of the trajectory on this manifold can be accurately described by the $(N-M)$-step mechanism.

According to the CSP theory [14–16], the appropriate sets of vectors **a** and **b** (6), (7) are provided by the following procedure. First, two arbitrary N-dimensional sets of orthonormal vectors are chosen and are partitioned as

$$\mathbf{a}_r^o = [\mathbf{a}_1^o, \mathbf{a}_2^o, ..., \mathbf{a}_M^o], \tag{15a}$$

$$\mathbf{a}_s^o = [\mathbf{a}_{M+1}^o, \mathbf{a}_{M+2}^o, ..., \mathbf{a}_N^o], \tag{15b}$$

and

$$\mathbf{b}_o^r = \begin{pmatrix} \mathbf{b}_o^1 \\ \mathbf{b}_o^2 \\ \vdots \\ \mathbf{b}_o^M \end{pmatrix}, \quad \mathbf{b}_o^s = \begin{pmatrix} \mathbf{b}_o^{M+1} \\ \mathbf{b}_o^{M+2} \\ \vdots \\ \mathbf{b}_o^N \end{pmatrix}. \tag{16b}$$

The desired sets of orthonormal basis vectors are produced by the sequence of operations,

$$\mathbf{a}_r = \mathbf{J}\mathbf{a}_r^o \tau, \qquad \mathbf{b}^r = \tau_o \mathbf{b}_o^r \mathbf{J}, \tag{17b}$$

$$\mathbf{a}_s = [I - \mathbf{a}_r^o \mathbf{b}^r]\mathbf{a}_s^o, \qquad \mathbf{b}^s = \mathbf{b}_o^s [I - \mathbf{a}_r \mathbf{b}^r], \tag{18b}$$

where

$$\tau_o = (\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}, \qquad \tau = (\mathbf{b}^r \mathbf{J} \mathbf{a}_r^o)^{-1}, \tag{19b}$$

and **J** is the gradient of **g**. This transformation (the physical interpretation of which shall be presented in Section 6) for the basis vectors provides leading order accuracy. Higher accuracy can be provided by more complicated calculations [28]. On the basis of the vectors (17a)(17b) and (18a)(18b), the species equation (2) becomes

$$\frac{\partial \mathbf{y}}{\partial t} = \mathbf{a}_r \mathbf{h}^r + \mathbf{a}_s \mathbf{h}^s, \tag{20a}$$

where

$$\mathbf{h}^r = \mathbf{b}^r[\mathbf{L} + \mathbf{g}], \quad \mathbf{h}^s = \mathbf{b}^s[\mathbf{L} + \mathbf{g}]. \tag{20b}$$

The M elements h^i ($i = 1, M$) of $\mathbf{h}^r$ and the $N-M$ elements h^i ($i = M+1, N$) of $\mathbf{h}^s$ are of the form:

$$h^i = \mathbf{b}^i \cdot [\mathbf{L} + \mathbf{g}] = \mathbf{b}^i \cdot \mathbf{L} + B_1^i R^1 + B_2^i R^2 + \cdots + B_K^i R^K. \tag{21}$$

Assuming that the M components in $\mathbf{h}^r$ are negligible,

$$\mathbf{h}^r \approx 0, \tag{22}$$

Eq. (20a) becomes

$$\frac{\partial \mathbf{y}}{\partial t} \approx \mathbf{a}_s \mathbf{h}^s \tag{23}$$

or

$$\frac{\partial \mathbf{y}}{\partial t} \approx \mathbf{PL} + \mathbf{a}_s \mathbf{f}^s, \tag{24}$$

where

$$\mathbf{P} = \mathbf{a}_s \mathbf{b}^s = \mathbf{I} - \mathbf{a}_r \mathbf{b}^r, \quad \mathbf{f}^s = \mathbf{b}^s \mathbf{g}. \tag{25}$$

Furthermore, assuming that the projection of the spatial operator $\mathbf{L}$ to the $\mathbf{b}^r$ has negligible contribution in the cancelations occurring in Eqs. (22), they reduce to

$$B_1^i R^1 + B_2^i R^2 + \cdots + B_K^i R^K \approx 0 \tag{26}$$

which were identified before (see Eq. (12)) as the steady state and partial equilibrium relations. The M equations (26) must be solved for the M species mass fraction indicated by the "radical pointer" $\mathbf{a}_r \mathbf{b}^r$ [15, 16]. The remaining $N-M$ species mass fraction are computed by the corresponding components of the differential equations (24).

The assumption that the operator $\mathbf{L}$ has negligible projection in the first subspace might mislead in replacing the projection matrix $\mathbf{P}$ multiplying the spatial operator $\mathbf{L}$ in Eq. (24) with the unit matrix $\mathbf{I}$:

$$\frac{\partial \mathbf{y}}{\partial t} \approx \mathbf{L} + \mathbf{a}_s \mathbf{f}^s. \tag{27}$$

This simplification might not be correct since negligible terms in Eqs. (22) can be important in Eq. (24). This problem, i.e., the correct representation of the spatial operator, shall not be examined here. A preliminary discussion on this subject can be found elsewhere [15, 29]. Here we shall concentrate on the determination of the right vectors $\mathbf{a}_i$ and $\mathbf{b}^i$ so that the most appropriate way of replacing the detailed chemical kinetic mechanism with a reduced one is achieved. For that purpose, we assume that M relations in the form of Eqs. (26) are given and that a reduced mechanism must be constructed in order to be used in Eq. (24) or (27).

4. CHEN'S ALGORITHM

The algorithm for the construction of reduced mechanisms developed by Chen [18], can be simply described as follows. It is assumed that in the $\mathbf{y}$ vector, the first M elements correspond to the M "steady state" species. It is further assumed that in the matrix $\mathbf{S}$, the first M columns (stoichiometric vectors) correspond to the M fastest reactions in the mechanism. As a result we define

$$\mathbf{S} = [\mathbf{S}_M, \mathbf{S}_{K-M}], \quad \mathbf{R} = \begin{pmatrix} \mathbf{R}^M \\ \mathbf{R}^{K-M} \end{pmatrix}, \tag{28}$$

where $\mathbf{S}_M$ and $\mathbf{S}_{K-M}$ are $N \times M$ and $N \times (K-M)$ matrices and $\mathbf{R}^M$ and $\mathbf{R}^{K-M}$ are M and $(K-M)$-dimensional column vectors. In addition, we define the partitions

$$\mathbf{WS}_M = \begin{pmatrix} \mathbf{U} \\ \mathbf{V} \end{pmatrix}, \quad \mathbf{WS}_{K-M} = \begin{pmatrix} \mathbf{Z} \\ \mathbf{X} \end{pmatrix}, \tag{29}$$

where $\mathbf{U}$ and $\mathbf{V}$ are $M \times M$ and $(N-M) \times M$ matrices and $\mathbf{Z}$ and $\mathbf{X}$ are $M \times (M-M)$ and $(N-M) \times (K-M)$ matrices. It is assumed that the M column vectors in $\mathbf{S}_M$ are linearly independent and that $\mathbf{U}$ is invertible. Chen's algorithm can be seen as a specific split of the species mass fraction space in two subdomains. This partition is defined by the following set of orthonormal basis vectors:

$$\mathbf{a}_r = \begin{pmatrix} \mathbf{U} \\ \mathbf{V} \end{pmatrix}, \qquad \mathbf{a}_s = \begin{pmatrix} \mathbf{0} \\ \mathbf{I} \end{pmatrix} \tag{30}$$

$$\mathbf{b}^r = [\mathbf{U}^{-1}, \mathbf{0}], \quad \mathbf{b}^s = [-\mathbf{VU}^{-1}, \mathbf{I}], \tag{31}$$

where the matrices $\mathbf{a}_r$ and $\mathbf{a}_s$ consist of M and $N-M$ column vectors, respectively, $\mathbf{b}^r$ and $\mathbf{b}^s$ consist of M and $N-M$ row vectors, respectively; $\mathbf{0}$ is a $M \times (N-M)$ zero matrix and $\mathbf{I}$ is a $(N-M) \times (N-M)$ unit matrix. According to these vectors, the source term $\mathbf{g}$ can be cast in the form:

$$\mathbf{g} = \begin{pmatrix} \mathbf{U} \\ \mathbf{V} \end{pmatrix} [\mathbf{R}^M + \mathbf{U}^{-1}\mathbf{ZR}^{K-M}] + \begin{pmatrix} \mathbf{0} \\ \mathbf{X} - \mathbf{VU}^{-1}\mathbf{Z} \end{pmatrix} [\mathbf{R}^{K-M}]. \tag{32}$$

On the basis of this equation we can make the following observations. Since $N < K$, the columns of the

$(N-M)\times(K-M)$ matrix $\mathbf{X} - \mathbf{V}\mathbf{U}^{-1}\mathbf{Z}$ span, at most, a $(N-M)$-dimensional space. Therefore, we can define

$$\mathbf{X} - \mathbf{V}\mathbf{U}^{-1}\mathbf{Z} = \mathbf{C}\mathbf{Y}, \tag{33}$$

where $\mathbf{C}$ is a $(N-M)\times(N-M)$ matrix with linearly independent columns and $\mathbf{Y}$ is a $(N-M)\times(K-M)$ matrix. It follows that Eq. (32) becomes

$$\mathbf{g} = \begin{pmatrix}\mathbf{U}\\ \mathbf{V}\end{pmatrix}[\mathbf{R}^M + \mathbf{U}^{-1}\mathbf{Z}\mathbf{R}^{K-M}] + \begin{pmatrix}\mathbf{0}\\ \mathbf{C}\end{pmatrix}[\mathbf{Y}\mathbf{R}^{K-M}]. \tag{34}$$

If we set

$$\mathbf{R}^M + \mathbf{U}^{-1}\mathbf{Z}\mathbf{R}^{K-M} \approx 0 \tag{35}$$

Eq. (34) yields

$$\mathbf{g} \approx \begin{pmatrix}\mathbf{0}\\ \mathbf{C}\end{pmatrix}[\mathbf{Y}\mathbf{R}^{K-M}]. \tag{36}$$

From Eqs. (35), (36) we can notice the following. The M algebraic relations among the K elementary reaction rates (35) represent the steady state assumption for the M first species in the vector of the unknowns $\mathbf{y}$. In addition, Eq. (36) provides the reduced mechanism. The $N-M$ columns of $\mathbf{C}$ are the stoichiometric vectors (involving the last $N-M$ species of $\mathbf{y}$; see also Eq. (11) of [18]) and the $N-M$ components of $\mathbf{Y}\mathbf{R}^{K-M}$ are the corresponding reaction rates.

Obviously, for the success of the algorithm the M species which are in steady state and the M linearly independent fastest reactions must be identified. When M steady state assumptions hold and when the above two identifications can be made, Chen's algorithm produces an $(N-M)$-step mechanism which does not involve:

(i) the M "steady state" species in its stoichiometry, and

(ii) the M fastest elementary reaction rates in its global rates.

From Eq. (35), it is clear that in the case where steady state assumptions for some of the species coexist with quasi-equilibrium assumptions for some of the elementary steps, Chen's algorithm is not formally applicable. In the section that follows, a more general algorithm shall be presented which, under certain conditions, can take into consideration both types of assumptions.

5. A MORE GENERAL ALGORITHM

We use the partition (28) of the matrix $\mathbf{S}$ and the vector $\mathbf{R}$. We still assume that the M stoichiometric vectors in $\mathbf{S}_M$ are linearly independent and belong to the fastest elementary reactions. Let us further assume that the following relations among the elementary reaction rates are valid,

$$\mathbf{Q}_M\mathbf{R}^M + \mathbf{Q}_{K-M}\mathbf{R}^{K-M} \approx \mathbf{0}, \tag{37}$$

where $\mathbf{Q}_M$ is a $M\times M$ matrix (invertible) and $\mathbf{Q}_{K-M}$ is a $M\times(K-M)$ matrix. Both $\mathbf{Q}_M$ and $\mathbf{Q}_{K-M}$ are assumed to be constants. We wish to produce a $(N-M)$-step mechanism on the basis of these algebraic relations. We further wish the rates in $\mathbf{R}^M$ not to appear in the reduced mechanism. For that purpose, we write

$$\begin{aligned}\mathbf{g} &= \mathbf{W}\mathbf{S}_M\mathbf{R}^M + \mathbf{W}\mathbf{S}_{K-M}\mathbf{R}^{K-M}\\ &= \mathbf{W}\mathbf{S}_M\mathbf{Q}_M^{-1}[\mathbf{Q}_M\mathbf{R}^M + \mathbf{Q}_{K-M}\mathbf{R}^{K-M}]\\ &\quad + [\mathbf{W}\mathbf{S}_{K-M} - \mathbf{W}\mathbf{S}_M\mathbf{Q}_M^{-1}\mathbf{Q}_{K-M}]\mathbf{R}^{K-M}.\end{aligned} \tag{38}$$

Let us define a set of basis vector $\mathbf{a}$ as

$$\mathbf{a} = [\mathbf{a}_r, \mathbf{a}_s] \tag{39a}$$

where

$$\mathbf{a}_r = \mathbf{W}\mathbf{S}_M\mathbf{Q}_M^{-1} \tag{39b}$$

and $\mathbf{a}_r$ and $\mathbf{a}_s$ are $N\times M$ and $N\times(N-M)$ matrices. The inverse basis vector is defined by

$$\mathbf{b} = \begin{pmatrix}\mathbf{b}^r\\ \mathbf{b}^s\end{pmatrix}, \quad \mathbf{b}\mathbf{a} = \mathbf{a}\mathbf{b} = \mathbf{I}, \tag{40b}$$

where $\mathbf{b}^r$ and $\mathbf{b}^s$ are $M\times N$ and $(N-M)\times N$ matrices. Therefore, if the relation holds:

$$\mathbf{W}\mathbf{S}_{K-M} - \mathbf{W}\mathbf{S}_M\mathbf{Q}_M^{-1}\mathbf{Q}_{K-M} = \mathbf{a}_s\mathbf{H}_{K-M} \tag{41a}$$

or

$$\mathbf{W}\mathbf{S}_{K-M} = \mathbf{a}_r\mathbf{Q}_{K-M} + \mathbf{a}_s\mathbf{H}_{K-M}, \tag{41b}$$

holds, where $\mathbf{H}_{K-M}$ is a $(N-M)\times(K-M)$ matrix, the expression for $\mathbf{g}$, (38), along with the algebraic relations (37), yields

$$\mathbf{g} \approx \mathbf{a}_s[\mathbf{H}_{K-M}\mathbf{R}^{K-M}]. \tag{42}$$

Clearly, this simplified expression for $\mathbf{g}$ represents a $(N-M)$-step mechanism; the $N-M$ columns of $\mathbf{a}_s$ are the stoichiometric vectors; and the $N-M$ components of the vector $\mathbf{H}_{K-M}\mathbf{R}^{K-M}$ are the corresponding reaction rates.

For the described algorithm to be valid, the relation

(41a) or (41b) must hold. Using the orthogonality condition (40b), it is easy to show that this condition is equivalent to

$$\mathbf{b}^r\mathbf{W}\mathbf{S}_{K-M} = \mathbf{Q}_{K-M} \tag{43a}$$

and

$$\mathbf{b}^s\mathbf{W}\mathbf{S}_{K-M} = \mathbf{H}_{K-M}; \tag{43b}$$

i.e., the projection of the vectors in $\mathbf{WS}_{K-M}$ in the subspace defined by $\mathbf{b}^r$ must equal the vectors in $\mathbf{Q}_{K-M}$ and the projection of the same vectors in the complementary subspace defined by $\mathbf{b}^s$ must equal the vectors in $\mathbf{H}_{K-M}$.

Furthermore, from the definition (39b) it follows that

$$\mathbf{b}^r\mathbf{W}\mathbf{S}_M = \mathbf{Q}_M. \tag{44}$$

In compact form, Eqs. (43a) and (44) yield

$$\mathbf{b}^r[\mathbf{WS}_M, \mathbf{WS}_{K-M}] = [\mathbf{Q}_M, \mathbf{Q}_{K-M}] \tag{45a}$$

or

$$\mathbf{b}^r\mathbf{WS} = \mathbf{Q}, \tag{45b}$$

where $\mathbf{Q}$ is a $(M\times K)$-dimensional matrix. Given the two matrices $\mathbf{S}$ and $\mathbf{Q}$, the reduced mechanism (42) can be constructed only if there exist a $\mathbf{b}^r$ such that the relation (45b) is satisfied; i.e., the M rows in $\mathbf{Q}$ must be linear combinations of the N rows in $\mathbf{WS}$. A physical interpretation of this condition can be obtained by postmultiplying Eq. (45b) by the vector of elementary reaction rates $\mathbf{R}$:

$$\mathbf{b}^r\mathbf{WSR} = \mathbf{QR} \tag{46a}$$

or

$$\mathbf{b}^r\mathbf{g} = \mathbf{QR}. \tag{46b}$$

We see that the algebraic relations among the elementary rates (37) must be linear combinations of the elements of the source vector $\mathbf{g}$.

Given the vectors $\mathbf{a}_r$ (39b) and having available a $\mathbf{b}^r$ which satisfies the condition (45b), the computation of $\mathbf{a}_s$ and $\mathbf{b}^s$ is a simple procedure. $\mathbf{H}_{K-M}$ can be computed from Eq. (43b). Since the matrices $\mathbf{W}$ and $\mathbf{S}$ are constants and since the matrix $\mathbf{Q}$ is assumed to be constant, it follows that the vectors $\mathbf{a}_r$, $\mathbf{a}_s$, $\mathbf{b}^r$, and $\mathbf{b}^s$ are also constants.

Given the matrix $\mathbf{S}$, the vectors in $\mathbf{b}^r$ do not exist for an arbitrary matrix $\mathbf{Q}$. In the case where the algebraic relations (37) denote steady state approximations, Eq. (45b) is always satisfied and the algorithm developed in this section reduces to the one developed by Chen. In fact, for this case Eq. (46b) indicates that the row vectors in $\mathbf{b}^r$ have zero elements except one which equals unity and corresponds to the element in $\mathbf{y}$ assumed in steady state. Of course, there are other cases where the algebraic relations (37) are not related only to steady state approximations but the matrix $\mathbf{Q}$ has the desired structure. In such a case, Chen's algorithm fails from formally producing a reduced mechanism and one has to use the algorithm developed in this section. The conclusion is that the $(N-M)$-step mechanism indicated by Eq. (42) cannot always be obtained for arbitrary relations among the elementary rates (37). Only algebraic relations which can satisfy the condition (45b) can produce the $(N-M)$-step mechanism (42). It is easy to see that this condition is a consequence of the requirement that the rates $\mathbf{R}^M$ of the M fastest elementary reactions must not appear in the expressions for the rates of the $N-M$ steps.

6. THE PROPER USE OF THE REDUCED MECHANISM

Let us assume that, given a set of M algebraic relations among the rates of elementary steps in the form (37), a $(N-M)$-step reduced mechanism was produced from Eq. (42). It is implied that the algebraic relations satisfy the condition (45b). Let us denote the corresponding basis vector sets by $\mathbf{a}_r^o$, $\mathbf{a}_s^o$, $\mathbf{b}_o^r$, and $\mathbf{b}_o^s$. The $N-M$ column vectors in $\mathbf{a}_s^o$ are the stoichiometric vectors of the reduced mechanism and the $N-M$ elements of $\mathbf{b}_o^s\mathbf{WS}_{K-M}\mathbf{R}^{K-M}$ are the corresponding rates. The straightforward method of using this mechanism is to simply substitute it in the species equation (24) or (27). This is done as follows: Considering Eq. (2) in the form (20a) we obtain

$$\frac{\partial \mathbf{y}}{\partial t} = \mathbf{a}_r^o\mathbf{h}_o^r + \mathbf{a}_s^o\mathbf{h}_o^s \tag{47a}$$

$$= \mathbf{a}_r^o\mathbf{b}_o^r[\mathbf{L} + \mathbf{WSR}] + \mathbf{a}_s^o\mathbf{b}_o^s[\mathbf{L} + \mathbf{WSR}] \tag{47b}$$

$$= \mathbf{a}_r^o[\mathbf{b}_o^r\mathbf{L} + \mathbf{QR}] + \mathbf{a}_s^o[\mathbf{b}_o^s\mathbf{L} + \mathbf{b}_o^s\mathbf{WS}_{K-M}\mathbf{R}^{K-M}], \tag{47c}$$

where use of Eqs. (39a), (39b), (40a), (40b), and (45b) was made. Assuming that the algebraic relations (37) hold and that the projection of the spatial operator $\mathbf{L}$ in $\mathbf{b}_o^r$ is negligible, i.e.,

$$\mathbf{h}_o^r = \mathbf{b}_o^r(\mathbf{L} + \mathbf{WSR}) \approx \mathbf{0}, \tag{48}$$

Eq. (47c) yields

$$\begin{aligned}\frac{\partial \mathbf{y}}{\partial t} &\approx \mathbf{a}_s^o\mathbf{h}_o^s = \mathbf{a}_s^o\mathbf{b}_o^s[\mathbf{L} + \mathbf{WSR}] \\ &= \mathbf{P}_o[\mathbf{L} + \mathbf{WS}_{K-M}\mathbf{R}^{K-M}].\end{aligned} \tag{49}$$

The question now is whether the solution of Eq. (49) is compatible with that obtained from the original equation (2), given the algebraic relations (37). To explore this issue

we proceed as follows. Upon differentiation of the algebraic relations (37) with time, we obtain

$$\mathbf{0} \approx \mathbf{b}_o^r \mathbf{J} \frac{\partial \mathbf{y}}{\partial t} = \mathbf{b}_o^r \mathbf{J}[\mathbf{a}_r^o \mathbf{h}_o^r + \mathbf{a}_s^o \mathbf{h}_o^s]. \tag{50}$$

Solving for $\mathbf{h}_o^r$,

$$\mathbf{h}_o^r \approx -(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o)\mathbf{h}_o^s, \tag{51}$$

and substituting in the original equation (47a), we obtain

$$\frac{\partial \mathbf{y}}{\partial t} \approx [\mathbf{a}_s^o - \mathbf{a}_r^o(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o)]\mathbf{h}_o^s \tag{52a}$$

$$\approx [\mathbf{I} - \mathbf{a}_r^o(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}\mathbf{b}_o^r \mathbf{J}]\mathbf{a}_s^o \mathbf{h}_o^s. \tag{52b}$$

Furthermore, from Eq. (51) we obtain

$$[\mathbf{b}_o^r + (\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o)\mathbf{b}_o^s](\mathbf{L} + \mathbf{g}) \approx \mathbf{0}. \tag{53}$$

With the definitions,

$$\mathbf{b}^r = \mathbf{b}_o^r + (\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o)\mathbf{b}_o^s = (\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}\mathbf{b}_o^r \mathbf{J} \tag{54a}$$

$$\mathbf{a}_s = [\mathbf{I} - \mathbf{a}_r^o(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}\mathbf{b}_o^r \mathbf{J}]\mathbf{a}_s^o = [\mathbf{I} - \mathbf{a}_r^o \mathbf{b}^r]\mathbf{a}_s^o, \tag{54b}$$

Eqs. (52a), (52b), and (53) become

$$\frac{\partial \mathbf{y}}{\partial t} \approx \mathbf{a}_s \mathbf{h}_o^s \tag{55}$$

$$\mathbf{b}^r(\mathbf{L} + \mathbf{WSR}) \approx \mathbf{0}. \tag{56}$$

Notice that the two vector sets $(\mathbf{a}_r^o, \mathbf{a}_s)$ and $(\mathbf{b}^r, \mathbf{b}_o^s)$ are still orthonormal. At this point, the following important observations can be made:

(i) Equations (55) and (56) are different from Eqs. (48) and (49). They become identical only in the limiting case:

$$(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o) = \mathbf{0}. \tag{57}$$

(ii) Although the vectors $\mathbf{b}_o^r$ and $\mathbf{a}_s^o$ are constants, the vectors $\mathbf{b}^r$ and $\mathbf{a}_s$ are $\mathbf{y}$-dependent. They are constants only in the limiting case (57), becoming identical to $\mathbf{b}_o^r$ and $\mathbf{a}_s^o$.

(iii) The transformation (54a), (54b), are exactly the same as the CSP formulas (17b), (18a).

The manipulations that lead to Eqs. (55) and (56) indicate that the algebraic relations (37) and the negligible projection of the spatial operator $\mathbf{L}$ in $\mathbf{b}_o^r$ should not be used directly in the original equations as stated by Eq. (48), i.e., by setting $\mathbf{h}_o^r$ equal to zero. Instead, $\mathbf{h}_o^r$ must be substituted by its asymptotic expression which, according to Eqs. (54a) and (56), is

$$\mathbf{h}_o^r \approx -(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_r^o)^{-1}(\mathbf{b}_o^r \mathbf{J} \mathbf{a}_s^o)\mathbf{h}_o^s. \tag{58}$$

In physical terms, this substitution achieves the following: Although the split of the RHS of the original species equation, as expressed by Eq. (47a), might be physically meaningful, it is not the optimal one in terms of computational accuracy. The function $\mathbf{h}_o^r$ which was assumed to be fast enough to reach partial equilibrium is not purely fast. As Eq. (58) indicates, it contains a slow component which must be taken into account. It is exactly this slow component which makes the difference in the two systems of Eqs. (48), (49), and (55), (56).

A similar transformation exists for the treatment of the fast component in the function $\mathbf{h}_o^s$ [21]. This fast component is transferred to $\mathbf{h}_o^r$ by the CSP transformations (17a) and (18b):

$$\mathbf{a}_r = \mathbf{J}\mathbf{a}_r^o(\mathbf{b}^r \mathbf{J} \mathbf{a}_r^o)^{-1}, \quad \mathbf{b}^s = \mathbf{b}_o^s[\mathbf{I} - \mathbf{a}_r \mathbf{b}^r]. \tag{59a) (59b}$$

It is easy to show that with these transformations the simplified problem (55) and (56) becomes

$$\frac{\partial \mathbf{y}}{\partial t} \approx \mathbf{a}_s \mathbf{h}^s = \mathbf{a}_s \mathbf{b}^s \mathbf{L} + \mathbf{a}_s \mathbf{b}^s \mathbf{WSR} \tag{60}$$

$$\mathbf{b}^r(\mathbf{L} + \mathbf{WSR}) \approx \mathbf{0}. \tag{61}$$

Assuming that the projection of $\mathbf{L}$ in $\mathbf{b}^r$ has a negligible contribution, the algebraic relations (61), accompanying the reduced mechanism (60), become

$$\mathbf{b}^r \mathbf{WSR} \approx \mathbf{0}. \tag{62}$$

These relations are of the form of the assumed ones (37) or (46a), (46b), but are not similar, since the vectors $\mathbf{b}^r$ are not constant but $\mathbf{y}$-dependent. From the second term in the RHS of Eq. (60) we can produce a $(N-M)$-step mechanism as follows. The $N-M$ vectors in $\mathbf{a}_s$ are the stoichiometric vectors and the $N-M$ components in $\mathbf{b}^s\mathbf{WSR}$ are the corresponding global reaction rates. Note that in this reduced mechanism, there is no guarantee that the rates of the identified M fast elementary reactions are absent from the global rates. Also, note that the stoichiometry involves, in general, all N species.

On the basis of the $(N-M)$-step mechanism, the N unknowns in the vector $\mathbf{y}$ are determined from the M algebraic relations (62) (which are used for the computation of the M "steady state" species mass fraction) and $N-M$ components of Eqs. (60) (which are used for the computation of the remaining $N-M$ species mass fraction). There are two basic procedures of handling such a system of

algebraic and differential equations. According to the first procedure, the scalar M and the two sets of basis vectors $\mathbf{a}_i$ and $\mathbf{b}^i$ ($i = 1, N$) are computed at the same time as the numerical solution advances in time and space. The second procedure consists of computing M and the vectors $\mathbf{a}_i$ and $\mathbf{b}^i$ ($i = 1, N$) for a sufficiently wide range of all possible states of $\mathbf{y}$, solve the algebraic relations (62), tabulate the results along with the two sets of basis vectors, and then use them as the $N-M$ components of Eqs. (60), are integrated in time and space. The second approach forms the basis of the *intrinsic low dimensional manifolds method* developed by Maas and Pope which was shown to provide very accurate results [24–27]. So far, this method has been used with fixed M and using the left and right eigenvectors of $\mathbf{J}$ as the two sets of basis vectors (note that if the left and right eigenvectors of $\mathbf{J}$ are selected for the vectors in $\mathbf{a}^o$ and $\mathbf{b}_o$, respectively, Eqs. (54a), (54b), and (59a), (59b) are automatically satisfied). The problem with this method is that it requires a large memory allocation in order to store the related look-up tables. This drawback of the method can be significantly eased with parameterization [30]. However, the problem remains especially if M is allowed to vary in time or space.

7. EXAMPLE

In Sections 4, 5, and 6 three different algorithms were developed for the construction of reduced mechanisms, given a set of algebraic relations among the elementary reaction rates. The accuracy of these algorithms shall be studied with regard to a simple problem.

Consider a hypothetical detailed kinetic mechanism involving three species (X, Y, and Z) and consisting of the three hypothetical reversible elementary reactions:

$$X = Y + Y \tag{63a}$$

$$X + Y = Z \tag{63b}$$

$$Y + Z = X. \tag{63c}$$

For simplicity, a homogeneous mixture ($\mathbf{L} = \mathbf{0}$) is assumed. Under conditions of constant temperature and pressure, the reaction process is governed by the system of equations:

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 \\ 2 \\ 0 \end{pmatrix} R^1 + \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix} R^2 + \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix} R^3, \tag{64}$$

where the elementary rates are

$$R^1 = k_{1f}x - k_{1b}y^2,$$

$$R^2 = k_{2f}xy - k_{2b}z,$$

$$R^3 = k_{3f}yz - k_{3b}x;$$

x, y, and z are the concentrations of the three species and k_{if} and k_{ib} are the forward and backward rate constants of reactions (63a)–(63c). It is assumed that the species molecular weights equal one ($\mathbf{W} = \mathbf{I}$). The vectors $\mathbf{S}_i$ ($i = 1, 3$) on the RHS of Eq. (64) are the stoichiometric vectors of the three elementary reactions (63a)–(63c).

It is desired to construct a 2-step reduced mechanism, given that the forward and backward directions of reaction (63a) are in partial equilibrium. It is also given that the forward and backward directions of reaction (63a) are the fastest and should not appear in the reduced mechanism. According to the definitions in the previous paragraph, we have

$$\mathbf{S} = \begin{pmatrix} -1 & -1 & 1 \\ 2 & -1 & -1 \\ 0 & 1 & -1 \end{pmatrix}, \quad \mathbf{S}_M = \begin{pmatrix} -1 \\ 2 \\ 0 \end{pmatrix}, \quad \mathbf{S}_{K-M} = \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}; \tag{65}$$

$$\mathbf{R} = \begin{pmatrix} R^1 \\ R^2 \\ R^3 \end{pmatrix}, \qquad \mathbf{R}_M = (R^1), \qquad \mathbf{R}_{K-M} = \begin{pmatrix} R^2 \\ R^3 \end{pmatrix}; \tag{66}$$

$$\mathbf{Q} = (1 \quad 0 \quad 0), \qquad \mathbf{Q}_M = (1), \qquad \mathbf{Q}_{K-M} = (0 \quad 0). \tag{67}$$

Assuming that X is the radical, Chen's algorithm produces the following sets of vectors $\mathbf{a}_r$, $\mathbf{a}_s$, $\mathbf{b}^r$, and $\mathbf{b}^s$:

$$\mathbf{a}_r = \begin{pmatrix} -1 \\ 2 \\ 0 \end{pmatrix}, \qquad \mathbf{a}_s = \begin{pmatrix} 0 & 0 \\ 1 & 0 \\ 0 & 1 \end{pmatrix}; \tag{68}$$

$$\mathbf{b}^r = (-1 \quad 0 \quad 0), \quad \mathbf{b}^s = \begin{pmatrix} 2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{69}$$

on the basis of which, the original equation is simplified to

$$\frac{d}{dt}\begin{pmatrix} y \\ z \end{pmatrix} = \begin{pmatrix} -3 \\ 1 \end{pmatrix} R^2 + \begin{pmatrix} 1 \\ -1 \end{pmatrix} R^3. \tag{70}$$

Notice that this equation is obtained from the original equation (64) after replacing R^1 in the differential equations for the species Y and Z from the steady state relation for the species X:

$$R^1 = -R^2 + R^3. \tag{71a}$$

According to Chen [18], Eq. (70) must not be accompanied by the above steady state equation but by the partial equilibrium relation:

$$R^1 = 0. \tag{71b}$$

A different result is produced by the more general algorithm presented in Section 5. It can be easily shown that, for the problem considered here, the condition (45b) is satisfied. The corresponding sets of vectors $\mathbf{a}_r$, $\mathbf{a}_s$, $\mathbf{b}^r$, and $\mathbf{b}^s$ are

$$\mathbf{a}_r = \begin{pmatrix} -1 \\ 2 \\ 0 \end{pmatrix}, \qquad \mathbf{a}_s = \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}; \tag{72}$$

$$\mathbf{b}^r = (-1 \quad 0 \quad -1), \quad \mathbf{b}^s = -\frac{1}{2}\begin{pmatrix} 2 & 1 & 1 \\ 2 & 1 & 3 \end{pmatrix}. \tag{73}$$

On the basis of these vectors, Eqs. (48) and (49) yield

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix} R^2 + \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix} R^3 \tag{74}$$

$$R^1 = 0. \tag{75}$$

Equations (74) are obtained in a straightforward fashion from the original equation (64) after setting $R^1 = 0$. In Eq. (74) only two components are linearly independent. Therefore, assuming that X is the "steady state" species, we solve for x from the algebraic relation (75) and y and z are computed from the corresponding components of Eq. (74).

The suggested method of handling the reduced mechanism in Section 6 produces a different set of equations. Using as initial vector sets those in (68), (69) or (72), (73), the resulting sets $\mathbf{a}_r$, $\mathbf{a}_s$, $\mathbf{b}^r$, and $\mathbf{b}^s$ are

$$\mathbf{a}_r = \frac{1}{1+4\kappa y}\begin{pmatrix} -1 \\ 2 \\ 0 \end{pmatrix}, \quad \mathbf{a}_s = \frac{1}{1+4\kappa y}\begin{pmatrix} 6\kappa y & -2\kappa y \\ 3 & -1 \\ -1-4\kappa y & 1+4\kappa y \end{pmatrix}; \tag{76}$$

$$\mathbf{b}^r = (-1 \quad 2\kappa y \quad 0), \quad \mathbf{b}^s = \frac{1}{2}\begin{pmatrix} 2 & 1 & 1 \\ 2 & 1 & 3 \end{pmatrix}, \tag{77}$$

where $\kappa = k_{1b}/k_{1f}$. On the basis of these vectors, Eqs. (60) and (61) yield

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{1}{1+4\kappa y}\begin{pmatrix} -6\kappa y \\ -3 \\ 1+4\kappa y \end{pmatrix} R^2 + \frac{1}{1+4\kappa y}\begin{pmatrix} 2\kappa y \\ 1 \\ -1-4\kappa y \end{pmatrix} R^3 \tag{78}$$

$$(1+4\kappa y)R^1 + (1-2\kappa y)R^2 - (1+2\kappa y)R^3 = 0. \tag{79}$$

Similarly to the previous case, in Eq. (78) only two components are linearly independent. Therefore, assuming that X is the "steady state" species (this is also indicated by the "radical pointer" [15, 16]), we solve for x from the algebraic relation (79) and y and z are computed from the corresponding components of Eq. (78).

In physical terms the three 2-step reduced models developed here correspond to the following global reactions:

Chen Algorithm (70),

$$3Y = Z, \quad w_{\mathrm{I}} = R^2, \tag{80a}$$

$$Z = Y, \quad w_{\mathrm{II}} = R^3, \tag{80b}$$

$$R^1 = 0. \tag{80c}$$

General Algorithm (*74*),

$$X + Y = Z, \quad w_{\mathrm{I}} = R^2, \tag{81a}$$

$$Y + Z = X, \quad w_{\mathrm{II}} = R^3, \tag{81b}$$

$$R^1 = 0 \tag{81c}$$

CSP Algorithm (*78*),

$$\frac{6\kappa y}{1+4\kappa y}X + \frac{3}{1+4\kappa y}Y = Z, \quad w_{\mathrm{I}} = R^2, \tag{82a}$$

$$Z = \frac{2}{1+4\kappa y}X + \frac{1}{1+4\kappa y}Y, \quad w_{\mathrm{II}} = R^3, \tag{82b}$$

$$(1+4\kappa y)R^1 + (1-2\kappa y)R^2 - (1+2\kappa y)R^3 = 0. \tag{82c}$$

In order to test the accuracy of these three reduced mechanisms we solved the appropriate equations for each one. Specifically, for the mechanism (80a)–(80c) we solve the differential equations (70), substituting for x from the algebraic relation (71b). For the mechanism (81a)–(81c) we solve the differential equations for y and z (74), substituting for x from the algebraic relation (75). Finally, for the mechanism (82a)–(82c) we solve the differential equations for y and z (78), substituting for x from the algebraic relation (79). The numerical solution of the differential equations was obtained by the Gear multistep method and the algebraic relations were solved analytically. The following parameters and initial conditions were used:

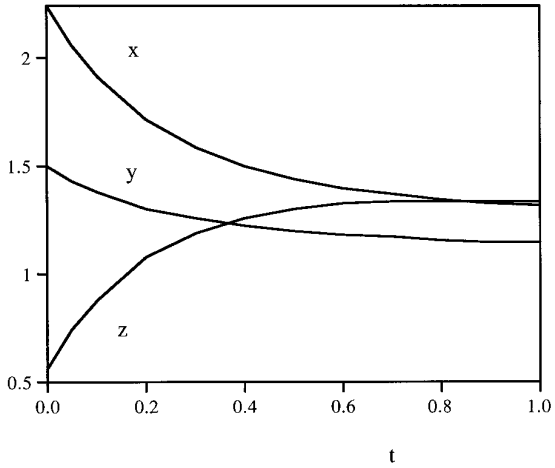

FIG. 1. The numerical solution of the full equations (64).

$$k_{1f} = k_{1b} = 10^3, \quad k_{2f} = k_{2b} = k_{3f} = k_{3b} = 1, \tag{83}$$

$$x(0) = 2.2500, \quad y(0) = 1.5000, \quad z(0) = 0.5625. \tag{84}$$

The values of the parameters (83) guarantee that elementary reaction (63a) is fast and that reactions (63b) (63c) are slow, as assumed. The initial conditions (84) guarantee that reaction (63a) is in equilibrium and that all three algebraic relations (80c), (81c), and (82c) are satisfied at $t = 0$. The solution of the full equations (64) is presented in Fig. 1. It is shown that the three unknowns x, y, and z exhibit a smooth behavior. In Fig. 2 the relative errors of the three approximate solutions are displayed. It is shown that the Chen algorithm produces an error of $O(0.1)$ while the more general algorithm is shown to be little more accurate. The CSP algorithm is shown to be the most accurate, producing a much smaller error. The displayed accuracy of the three reduced models can be explained as follows.

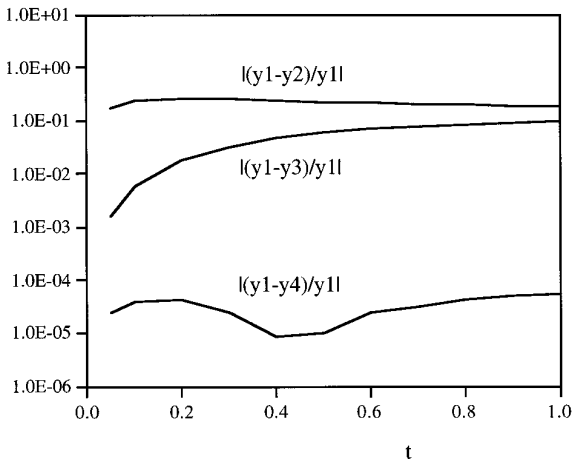

FIG. 2. The relative error for y computed by the three reduced mechanisms. Similar results are obtained for x and z: $y1$, the numerical solution on the basis of the full equations (68); $y2$, the numerical solution on the basis of the approximate equations (70), (71b); $y3$, the numerical solution on the basis of the approximate equations (74), (75); $y4$, the numerical solution on the basis of the approximate equations (78), (79).

In the three models, the unknown x is determined by the algebraic relations (80c), (81c), and (82c). Both, (80c) and (81c) yield

$$x = \frac{k_{1b}}{k_{1f}} y^2 \tag{85a}$$

while (82c) yields

$$x = \frac{k_{1b}}{k_{1f}} y^2 - \frac{1}{k_{1f}} \left(\frac{(1 - 2\kappa y)}{(1 + 4\kappa y)} R^2 + \frac{(1 + 2\kappa y)}{(1 + 4\kappa y)} R^3 \right). \tag{85b}$$

Since $k_{1f} = k_{1b} = 10^3$, the two expressions for x above differ by a term of $O(10^{-3})$. Therefore, the errors displayed in Fig. 2 are not related to the errors of approximating x but are due to the approximations involved in computing y and z. In the three reduced models, these two unknowns are computed from the differential equations (70), (74), and (78). According to the Chen algorithm, Eq. (70) is obtained from the full equations (64) after substituting the reaction rate R^1 from the steady state approximation (71a). According to the more general algorithm, Eq. (74) is obtained after setting equal to zero the reaction rate R^1 in the full equations due to the partial equilibrium approximation (75). Finally, according to the CSP algorithm, Eq. (78) is obtained after substituting the reaction rate R^1 in the full equations (64) from the approximation (79). As is demonstrated in Fig. 3, these three substitutions for R^1 are not equivalent. It is shown that the best approximation to R^1 is provided by the CSP relation (79). Both the steady state and partial equilibrium relations, (71a) and (75), provide much worse approximations. Therefore, the differences in accuracy of the computed approximate solutions shown in Fig. 2 are mainly due to the differences in approximating the rate of the fastest reaction R^1.

8. CONCLUSIONS

It was shown that the algorithm developed by Chen for the construction of reduced mechanisms is formally valid only when the accompanying algebraic relations among the elementary reaction rates are associated with steady state assumptions. An extension of this algorithm was presented which can accommodate more general algebraic relations. However, such an algorithm works only when the algebraic relations are linear combinations of the different components of the source term **g**. On the basis of given algebraic

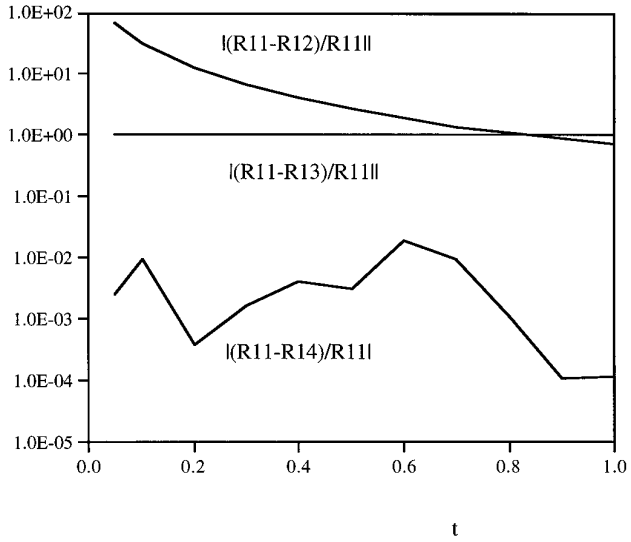

FIG. 3. The accuracy in approximating the rate R1: R11, the rate computed by the exact expression (68); R12, the rate computed by the steady state approximation (71a); R13, the rate computed by the equilibrium approximation (75); R14, the rate computed by the CSP approximation (79).

relations, a third algorithm was developed which was shown to be similar to that developed by the CSP method.

Using a simple example, it was shown that the algorithm developed by Chen and the more general algorithm presented here produce reduced mechanisms the accuracy of which is low. However, the mechanism produced by the CSP method was shown to be much more accurate. It is true that the first two mechanisms are more appealing since their implementation for flame simulations is very simple. This is a consequence of the fact that their stoichiometry and the coefficients multiplying the elementary rates in the expressions of the global rates and algebraic relations are fixed numbers. On the other hand, the mechanism produced by the CSP method is more difficult to handle since both the stoichiometry and the coefficients are time (or space) dependent.

For the case of a turbulent flame simulation, use of a mechanism produced by CSP is not a trivial matter due to the additional closure computations required. However, for the case of a laminar flame simulation, use of such a mechanism is straightforward. Of course, the expected higher accuracy will be obtained at the expense of additional numerical work for the computation of the two sets of basis vectors.

In a case where it is desired to use a reduced chemical kinetic mechanism produced by CSP, a conventional mechanism (such as a mechanism produced by the first two algorithms) can be of significant value. More precisely, it can provide the initial guess (i.e., $\mathbf{a}_r^o$, $\mathbf{a}_s^o$, $\mathbf{b}_o^r$, and $\mathbf{b}_o^s$) for the CSP formulas (17a), (17b), and (18a), (18b). Furthermore, in the case where the detailed mechanism is relatively small, it can provide analytical expressions for the CSP mechanism (i.e., vectors $\mathbf{a}_i$, $\mathbf{b}^i$ in analytic form) which can speed up the computations by a great extend. These issues shall be examined in a later manuscript for a real chemical kinetics problem.

REFERENCES

1. B. Rogg and F. A. Williams, "Structures of Wet CO Flames with Full and Reduced Kinetics Mechanisms," in *22nd Symposium (Intl) on Combustion* (The Combustion Institute, Pittsburgh, 1988), p. 1441.
2. W. Wang and B. Rogg, *Combust. Flame* **94,** 271 (1993).
3. G. Paczko, P. M. Lefdal, and N. Peters, "Reduced Reaction Schemes for Methane, Methanol and Propane Flames," in *21st Symposium (Intl) on Combustion, The Combustion Institute, Pittsburgh, 1986,* p. 739.
4. N. Peters, "Systematic Reduction of Flames Kinetics: Principles and Details," in *Fluid Dynamical Aspects of Combustion Theory,* edited by M. Onofri and A. Tesei (Longman, Harlow/New York, 1990), p. 232.
5. N. Peters, "Numerical and Asymptotic Analysis of Systematically Reduced Reaction Schemes for Hydrocarbon Flames," in *Lecture Notes in Physics,* Vol. 241, edited by Glowinski *et al.* (Springer-Verlag, Berlin/New York, 1985), p. 90.
6. H. Rabitz, M. Kramer, and D. Dacol, *Annu. Rev. Phys. Chem.* **34,** 419 (1983).
7. J. W. Tilden, V. Costanza, G. J. McRae, and J. H. Seinfeld, "Sensitivity Analysis in Chemically Reacting Systems," in *Modelling of Chemical Reaction Systems,* edited by K. H. Ebert *et al.* (Springer-Verlag, New York/Berlin, 1981), p. 69.
8. T. Turanyi, *J. Math. Chem.* **5,** 203 (1990).
9. L. M. T. Somers and L. P. H. De Goey, "Analysis of a Systematic Reduction Technique," in *25th Symposium (Intl) on Combustion* (The Combustion Institute, Pittsburgh, 1994), p. 957.
10. J. Warnatz, *Ber. Bunsenges. Phys. Chem.* **87,** 1008 (1983).
11. J. Warnatz, "Resolution of Gas Phase and Surface Combustion Chemistry into Elementary Reactions," in *24th Symposium (Intl) on Combustion* (The Combustion Institute, Pittsburgh, 1992), p. 553.
12. S. Vajda, P. Valko, and T. Turanyi, *Intl. J. Chem. Kinetics* **17,** 55 (1985).
13. T. Turanyi, A. S. Tomlin, and M. J. Pilling, *J. Phys. Chem.* **97,** 163 (1992).
14. D. A. Goussis and S. H. Lam, "A Study of Homogeneous Methanol Oxidation Kinetics Using CSP," in *24th Symposium (Intl) on Combustion* (The Combustion Institute, Pittsburgh, 1992), p. 113.
15. S. H. Lam, *Combust. Sci. Technol.* **89,** 375 (1993).
16. S. H. Lam and D. A. Goussis, *Intl. J. Chem. Kinetics* **26,** 461 (1994).
17. T. Turanyi, Public Domain Code KINALC, http://chem.leeds.ac.uk/Combustion/Combustion.html, 1995.
18. J. Y. Chen, *Combust. Sci. Technol.* **57,** 89 (1988).
19. J. Y. Chen and R. W. Dibble, "Application of Reduced Chemical Mechanisms for Prediction of Turbulent Nonpremixed Methane Jet Flames," in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames,* edited by M. Smooke, Lecture Notes, (Springer-Verlag, New York/Berlin, 1991), Chap. 9.
20. J. Y. Chen, *Combust. Sci. Technol.* **78,** 127 (1991).
21. K. Y. Lee, M. H. Yang, and I. K. Puri, *Combust. Flame* **92,** 419 (1993).

22. J. Goettgens, P. Terhoeven, and R. Korff, RedMech, public domain code at techmech.ITM.RWTH-Aachen.DE,RWTH.Aachen (1992).

23. F. Mauss, N. Peters, B. Rogg, and F. A. Williams, "Reduced Kinetic Mechanisms for Premixed Hydrogen Flames," in *Reduced Kinetic Mechanisms for Applications in Combustion Systems,* edited by N. Peters and B. Rogg (Springer-Verlag, New York/Berlin, 1993), p. 29.

24. U. Maas and S. B. Pope, *Combust. Flame* **88,** 239 (1992).

25. U. Maas and S. B. Pope, "Implementation of Simplified Chemical Kinetics Based on Intrinsic Low Dimensional Manifolds," in *24th Symposium* (*Intl*) *on Combustion* (The Combustion Institute, Pittsburgh, 1992), p. 103.

26. D. Schmidt, U. Maas, and J. Warnatz, "Simplifying Chemical Kinetics for the Simulation of Hypersonic Flows Using Intrinsic Low Dimensional Manifolds," in *Proceedings 5th Int. Symposium on CFD, Sendaï, Japan, 1993.*

27. U. Maas and S. B. Pope, "Laminar Flame Calculations Using Simplified Chemical Kinetics Based on Intrinsic Low Dimensional Manifolds," in *25th Symposium* (*Intl*) *on Combustion* (The Combustion Institute, Pittsburgh, 1994), p. 1349.

28. S. H. Lam and D. A. Goussis, "Conventional Asymptotics and Computational Singular Perturbation for Simplified Kinetics Modelling," in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane–Air Flames,* edited by M. Smooke, Lecture Notes, (Springer-Verlag, New York/Berlin, 1991), Chap. 10.

29. S. H. Lam, MAE report, Princeton University, 1993 (unpublished).

30. T. Turanyi, *Comput. Chem.* **18,** 45 (1994).